A.B.Abdulhayev

Namangan davlat texnika universiteti doktoranti

O.K.Ergashov

Namangan davlat texnika universiteti, Kimyo fanlari doktori, professor

A.A.Nodirov

Namangan davlat pedagogika instuti PhD, dotsent v.b.

D.M.Sattarova

Namangan davlat pedagogika instuti PhD, dotsent

CAA (M-34) RUSUMIDAGI SEOLITDA VODOROD SULFID ADSORBSIYASINING IZOTERMASI, DIFFERENSIAL ISSIQLIGI, ENTROPIYASI VA ISSIQLIK MUVOZANAT VAQTI

Anotatsiya. *Bugungi kunda jahonda adsorbsiya jarayonlari uchun mikro-, mezo- va makrog‘ovakli seolitlar sintez qilish texnologiyasini yaratish, jumladan 5A rusumidagi seolitlarni sintez qilishga mos keluvchi kimyoviy reagentlarni, jumladan mahalliy xom ashyolarni tanlash, sintezlash, mikro-, mezo- va makrog‘ovakli seolitlarda turli fizkimyoviy tabiatdagi, ya’ni qutbli va qutbsiz molekulalar adsorbsiyasini tadqiq etish orqali seolit kristall tuzilishi, faol markazlarining miqdori, joylashishi, tabiati va kuchini, hamda ion-molekulyar komplekslarini shakllanishini aniqlash, mikrog‘ovaklar kationlar migratsiyasini o‘rganish, bu seolitlarda sorbsion jarayonlari to‘liq molekulyar mexanizmlarini aniqlash kabi ilmiy yechimlarni asoslash lozim5A rusumidagi seolitlarda turli fizkimyoviy tabiatdagi molekulalar adsorbsiyasining izotermalari, differensial entalpiyalari, entropiya o‘zgarishi, issiqlik muvozanati vaqti xususiyatlarini va adsorbsiya mexanizmini aniqlashdan iborat*

Kalit so`zlar. *neft, 5A rusumidagi seolitlar, Ca^{2+} va Na^{+} kation, NH_3, H_2S, C_2H_6 molekulalari adsorbsiyasining izotermalari, issiqlik muvozanati vaqti va asosiy termodinamik tavsiflari (ΔH, ΔG va ΔS),*

А.Б. Абдулхаев

Докторант Наманганского инженерно-технологического университет

О.К. Эргашов

Доктор химических наук, профессор, Наманганский инженерно-технологический университет

А.А. Нодиров

PhD, исполняющий обязанности доцента, Наманганский государственный педагогический институт

Д.М.Саттарова

PhD, доцента, Наманганский государственный педагогический институт

ИЗОТЕРМА АДСОРБЦИИ СЕРОВОДОРОДА, ДИФФЕРЕНЦИАЛЬНАЯ ЭНТАЛЬПИЯ, ЭНТРОПИЯ И ВРЕМЯ ТЕПЛОВОГО РАВНОВЕСИЯ НА ЦЕОЛИТЕ ТИПА CaA (M-34)

Аннотация. *В настоящее время разработка технологий синтеза микропористых, мезопористых и макропористых цеолитов для процессов адсорбции имеет большое значение в мировой науке. В частности, необходимо определение подходящих химических реагентов, включая местное сырье, для синтеза цеолитов типа 5A. Изучение адсорбции молекул различной физико-химической природы (полярных и неполярных) на таких цеолитах позволяет определить кристаллическую структуру, количество, расположение, природу и силу активных центров, а также механизмы образования ионно-молекулярных комплексов. Кроме того, исследуется миграция катионов в микропорах и устанавливаются молекулярные механизмы сорбционных процессов. В данной работе определены изотерма адсорбции молекул сероводорода (H_2S) на цеолитах типа 5A, их дифференциальная энтальпия, изменение энтропии, время достижения теплового равновесия и механизм адсорбции.*

Ключевые слова: *нефть, цеолиты типа 5A, катионы Ca^{2+} и Na^{+}, изотермы адсорбции молекул NH_3, H_2S и C_2H_6, время теплового равновесия, основные термодинамические параметры (ΔH, ΔG и ΔS)*

A.B. Abdulhayev
Doctoral Student, Namangan University of Engineering and Technology
O.K. Ergashov
Doctor of Chemical Sciences, Professor, Namangan University of Engineering and Technology
A.A. Nodirov
PhD, Acting Associate Professor, Namangan State Pedagogical Institute
D.M.Sattarova
PhD, Associate Professor, Namangan State Pedagogical Institute

ADSORPTION ISOTHERM, DIFFERENTIAL ENTHALPY, ENTROPY, AND THERMAL EQUILIBRIUM TIME OF HYDROGEN SULFIDE ON ZEOLITE OF CaA (M-34) TYPE

Abstract. *Currently, the development of technologies for synthesizing micro-, meso-, and macroporous zeolites for adsorption processes is of global importance. In particular, it is necessary to identify appropriate chemical reagents, including local raw materials, for synthesizing type 5A zeolites. Studying the adsorption of various physicochemical types of molecules (polar and nonpolar) on such zeolites allows for the determination of the crystal structure, quantity, location, nature, and strength of active sites, as well as the formation of ion-molecular complexes. Furthermore, it provides insights into the migration of cations in micropores and the complete molecular mechanisms of sorption processes. This study focuses on determining the adsorption isotherm of hydrogen sulfide (H_2S) on 5A zeolites, along with its differential enthalpy, entropy change, thermal equilibrium time, and adsorption mechanism.*

Keywords: *petroleum, type 5A zeolites, Ca^{2+} and Na^{+} cations, adsorption isotherms of NH_3, H_2S, and C_2H_6 molecules, thermal equilibrium time, main thermodynamic parameters (ΔH, ΔG, and ΔS).*

In the global production of environmentally friendly fuels from oil, petroleum products, and natural gas, the presence of additional harmful compounds

in the raw materials negatively affects product quality and technological processes. When producing fuels that meet Euro standards and drying natural gases, purification from nitrogen- and sulfur-containing compounds is crucial. This process is carried out using 5A-type zeolites. Therefore, synthesizing highly adsorptive microporous adsorbents, studying them, and achieving scientific and practical innovations based on the obtained results are of significant importance.[1]

M.M. Dubinin (Russia) was one of the first to study the water adsorption isotherms on A-type zeolites using microcalorimetric methods. G. Martra, S. Coluccia, and others (Italy) investigated ammonia and benzene adsorption on NaX and NaY zeolites using IR spectroscopy. Jian Jiao, Wei Wang, and colleagues (China) studied the mechanism of ammonia adsorption on Y-type zeolites using NMR spectroscopy. Anett Kondor, András Dallos, Huimin Zheng, Liang Zhao, and others studied the adsorption isotherms of mono- and diaromatic compounds on faujasites using gas-liquid chromatography[2].

In Uzbekistan, researchers such as A.A. Agzamkhodjayev, S.S. Khamrayev, S.Z. Mo‘minov, I.D. Eshmetov, D.S. Salikhanova, and Sh.A. Kuldasheva have investigated the adsorption of various molecules on Angren coal and clay minerals. H.I. Akbarov and A.Yu. Yarkulov have studied adsorption on polymer-silica hybrid nanocomposites using vacuum magben devices. Under the scientific school founded by Doctor of Chemical Sciences, Professor G.U. Rakhmatkariev at the Institute of General and Inorganic Chemistry, Uzbekistan Academy of Sciences, his team (O.K. Ergashev, F.G. Rakhmatkarieva, E.B. Abdurakhmonov, D.J. Jumayeva, Y.Yu. Yakubov, H.N. Bakhronov, G‘.A. Doliev, T.D. Abdulkhayev, and others) have conducted extensive research using high-vacuum adsorption microcalorimetric systems to fully characterize the main thermodynamic parameters and adsorption mechanisms of ammonia, water, carbon dioxide, aromatic hydrocarbons, methanol, ethanol, hydrogen sulfide, n-pentane, n-hexane, and other adsorbates on various adsorbents including MFI, A, X, Y, and LSX zeolites, clay minerals, aerosil, muscovite, rutile, etc.[3,4,5]

For Ca^{2+} and Na^{+} ion-exchanged 5A zeolites, the adsorption isotherms, equilibrium heat times, and key thermodynamic parameters (ΔN, ΔG, and ΔS) for NH_3, H_2S, COS, C_2H_6, and CH_3SH molecules have been determined. These adsorption isotherms have been recharacterized using the Three-Term Langmuir (TTL) equation, and the mechanisms have been justified using the three-term mathematical model of TTL[6].

The isotherm shows a linear variation corresponding to the number of calcium cations (a secondary active site) in the zeolite, around ~1.91 mmol/g, indicating that hydrogen sulfide molecules begin to adsorb on Ca^{2+} ions. At LnP/Ps = –3.58 (corresponding to relative pressure P/Ps = 0.0278 or R = 582 mm Hg) and adsorption of 5.75 mmol/g, a $1H_2S:Ca^{2+}$ monomer ion-molecular complex is formed. In general, the adsorbate/adsorbent forms a $5H_2S$:Me complex, and the adsorption process of hydrogen sulfide on CaA (M-34) zeolite ends at ~6.6 mmol/g.

The hydrogen sulfide adsorption isotherm on CaA (M-34) zeolite is described by the three-term TTL equation:

$$a=1.62\exp[-(29.17A)7]+2.4\exp[-(18.57A)5]+5.43\exp[-(9.43A)3]$$

Here, aaa is the adsorption value (mmol/g), and A=RTln(Ps/P)A = RT\ ln(P_s/P)A=RTln(Ps/P), representing the Gibbs energy or the work required to transfer the gas into the equilibrium phase (kJ/mol). The sum of the first and second terms of Equation (1) accounts for 61% of the adsorption.

Figure 1 demonstrates that the calculated TTL values match the experimental adsorption amount of 6.6 mmol/g. The first two terms of the equation describe the adsorption of H_2S on the sodium cation sites of the zeolite. The amount of adsorption in the formation of $4H_2S{:}Na^+$ and $1NH_3{:}Ca^{2+}$ complexes is 5.75 mmol/g.

Because the adsorption process follows an exponential law, the third term of Equation (1) does not influence the process at low saturation pressures (LnP/Ps = –5.9, P/Ps = 0.027, R = 49 mm Hg). Initially, H_2S adsorbs on Ca^{2+} sites, then on the second coordination sphere (cation-free regions), driven by Van der Waals interactions.

The first term accounts for adsorption up to 1.3 mmol/g; the second and third terms do not influence the initial adsorption region. The second term starts to contribute from Ln(P/Ps) = –9.5, and the third from Ln(P/Ps) = –5.9. Each term describes the formation of specific adsorbate/adsorbent complexes. The zeolite contains 1.91 mmol/g of Ca^{2+} and 0.96 mmol/g of Na^+. The coefficients of each term in Equation (1) are integer multiples of these cation amounts.

The adsorption mechanism derived from the micropore volume saturation theory is consistent with the experimental mechanism. Up to 90 mm Hg, 58% of the total adsorption corresponds to H_2S binding to sodium cations.

Figure 1 presents the calculated isotherms based on each term of the TTL equation and their sum. The theoretical values match the experimental isotherm up to 6.54 mmol/g. The first two terms represent H_2S adsorption on Na^+ active sites. The values calculated with the first and second terms match the experimental data up to LnP/Ps = –5.3 (P/Ps = 0.0054 or P = 96 mm Hg) and 4 mmol/g adsorption.

However, the second and third terms show zero adsorption up to P/Ps = 7.44×10^{-5}. This confirms that adsorption initially occurs only at the primary active site. As relative pressure increases, values calculated by the first term deviate from the experimental data beyond LnP/Ps = –9.5 (P = 1.34 mm Hg, 1.62 mmol/g), indicating that adsorption at the primary site is complete. Beyond this, the second term becomes active, indicating H_2S adsorption at the second active site.

As the pressure increases, values calculated by the second term reach 2.4 mmol/g at LnP/Ps = –3. The logarithmic isotherm based on the sum of the first two terms corresponds to 3.8 mmol/g, matching the experimental data. This corresponds to tetramer complex formation ($4H_2S{:}Na^+$) with sodium. Once the second term reaches saturation, the third term becomes active, showing adsorption at the third active site at LnP/Ps = –5.9 (P = 49 mm Hg). The total isotherm calculated from Equation (1) matches the experimental data up to 6.6 mmol/g.

This matches previously determined values for complex formation: 3.84 mmol/g ($4H_2S{:}Na^+$) and 5.75 mmol/g ($1H_2S{:}Ca^{2+}$).

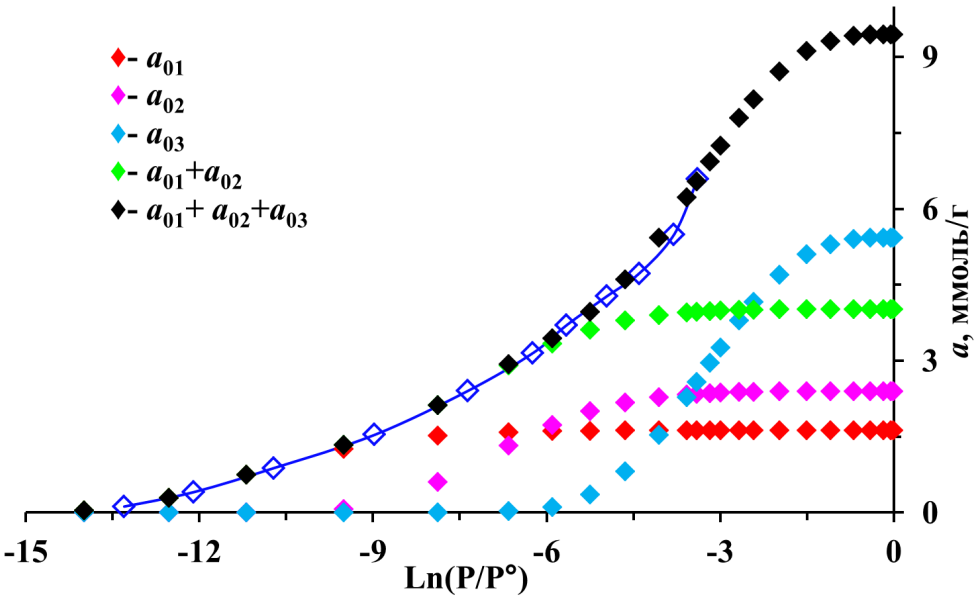

Figure 1. General Equation of TTL

In Figure 1, the logarithmic-coordinate isotherm of hydrogen sulfide adsorption up to its saturation pressure at the experimental temperature (303 K) is presented, based on the general TTL (Three-Term Langmuir) equation and its reformulated version (Equation 1). The experiment was conducted within the measurement range of the device (from 10^{-5} to 600 mm Hg), and Gibbs energy was calculated based on these values. Using this data, the adsorption and energetic coefficients of the TTL model were determined. From Equation 1, the total adsorption capacity of hydrogen sulfide at its saturation pressure and at 303 K was found to be 9.45 mmol/g. The adsorption amount calculated using the first and second terms of the equation is approximately 4 mmol/g, which confirms that hydrogen sulfide molecules form a tetramer complex with sodium cations[6,7].

Figure 2 shows the experimentally obtained values of the isotherm for hydrogen sulfide adsorption on CaA (M-34) zeolite, in relation to relative pressure (P/P_s), as well as the calculated isotherm values for each term of the TTL equation up to a relative pressure of 0.035. The isotherm corresponds to Type I of the Brunauer classification, indicating that hydrogen sulfide molecules are adsorbed exclusively in the micropores of the zeolite.

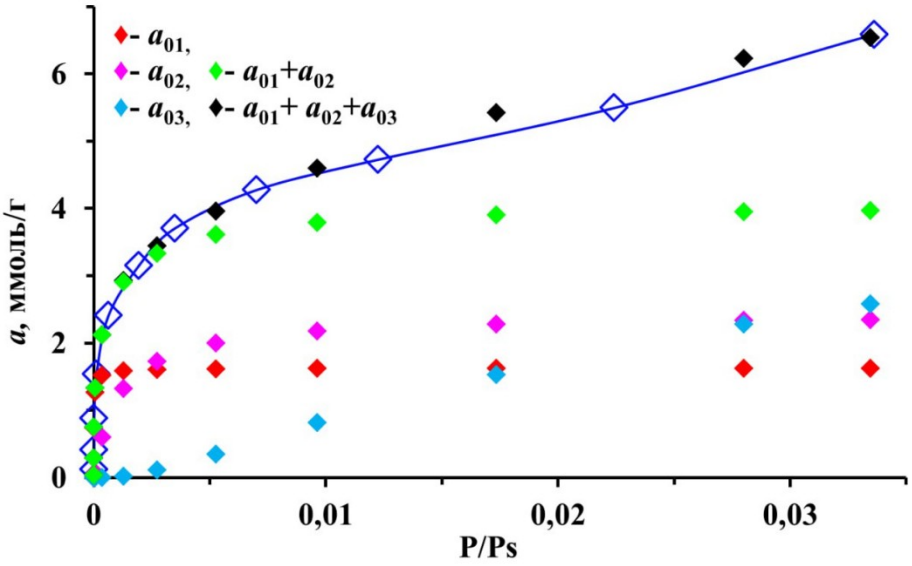

Figure 2. Isotherm of Hydrogen Sulfide Adsorption on CaA (M-34) Zeolite at 303 K in P/Ps Coordinates.

♢ – Experimental isotherm values, ♦, ♦, ♦, ♦, ♦ – Values calculated based on the TTL equation.

The sorption mechanism inferred from the isotherm graph in P/Ps coordinates is confirmed by differential adsorption enthalpy, entropy change, and the isotherm's behavior in logarithmic coordinates of relative pressure (Figure 2). The isotherm values calculated from Equation 1 correspond to the formation of ion-molecular adsorbate/adsorbent complexes of hydrogen sulfide molecules with sodium and calcium cations in the zeolite matrix. In particular, a sharp upward rise in the isotherm is observed up to an adsorption of 3.9 mmol/g at P/Ps = 0.00527, where a bend in the isotherm appears. From this point, the equilibrium pressure increases rapidly.

These values also correspond to the adsorption capacity required for the formation of tetrameric ion-molecular complexes of $4H_2S:Na^+$ in the zeolite matrix. The isotherm calculated from the TTL equation coincides with the experimental isotherm up to an adsorption of approximately 6.5 mmol/g. This suggests that the adsorption capacity includes tetramer complexes ($4H_2S:Na^+$) and monomer complexes ($1H_2S:Ca^{2+}$) with sodium and calcium cations, respectively, at an adsorption level of 5.75 mmol/g. Therefore, hydrogen sulfide molecules are adsorbed in the non-cationic part of the zeolite at about 0.85 mmol/g[8].

Figure 2 shows the isotherm of hydrogen sulfide up to a relative pressure of P/Ps = 0.035 at the experimental temperature (303 K), recalculated using Equation 1 of the general TTL equation.

Based on both the experimental and theoretical values, the adsorption mechanism of hydrogen sulfide molecules on CaA (M-22) and CaA (M-34) zeolites was identified, including the nature, quantity, and strength of the active sorption sites toward hydrogen sulfide. The stepwise changes in adsorption isotherm, heat equilibrium time, and key thermodynamic parameters were found to

depend on the amount of sodium and calcium cations in the zeolite composition. It was established that on CaA (M-22) zeolite, hydrogen sulfide molecules form trimer complexes ($3H_2S:Na^+$) with sodium cations and monomer complexes ($1H_2S:Ca^{2+}$) with calcium cations, leading to the overall formation of a $4H_2S$:CaA (M-22) complex. In addition, about 0.78 mmol/g of hydrogen sulfide molecules were found to adsorb in the second coordination sphere of the zeolite.

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