

Isotherms of differential heat and entropy adsorption of carbonyl sulfide in zeolite NaX when cleaning gases

Oybek Ergashev*, and Olimjon Nuridinov

Namangan Engineering-Technological Institute, Namangan, Uzbekistan

Abstract. The task of this research cycle was to measure adsorption isotherms (a) in the temperature range from 273 to 373 K, based on isotherms measured at different temperatures, to calculate isosteric heats (Q_d) and entropies (ΔS_d) of adsorption in order to select an effective adsorbent for purifying natural gas and oil products from sulfur-containing compounds. This article presents the results of studies of the isotherms of COS adsorption on NaX, carried out at four temperatures: 273, 298, 303, and 373 K, and the corresponding thermodynamic functions of adsorption in NaX zeolite.

1 Introduction

When cleaning gases containing hydrogen sulfide and carbon dioxide, the complication is the reaction between these components with the formation of poorly absorbed carbon sulfide, which negatively affects the total sulfur content in the gas. Carbon sulfide is a highly toxic compound that drastically worsens the ecological situation, and when interacting with water drops, it turns back into hydrogen sulfide, which causes intense corrosion of gas pipelines and equipment.

2 Materials and methods

Centers of strong adsorption in NaX zeolite are Na^+ cations in position S_{III} , with which carbon sulfide forms monomeric $(\text{COS})/\text{Na}^+$ complexes. Reversible adsorption proceeds on S_{II} cations, with which carbon sulfide forms monomeric complexes. In type A zeolites, calcium cations prefer the S_{I} position. [1].

The study was carried out on a universal high-vacuum volumetric installation, which makes it possible to dose the adsorbate both by gas-volume and volume-liquid methods, with an accuracy of 0.1% [2]. The samples were preliminarily subjected to thermal vacuum treatment at 623 K.

* Corresponding author: abrorov1975@mail.ru

3 Results and discussion

COS adsorption isotherms on zeolites are satisfactorily and completely described by the two-term TMVF equations [3-5]. Figure 1 shows adsorption isotherms of COS with NaX zeolite at different temperatures (273, 298, 303, and 373 K).

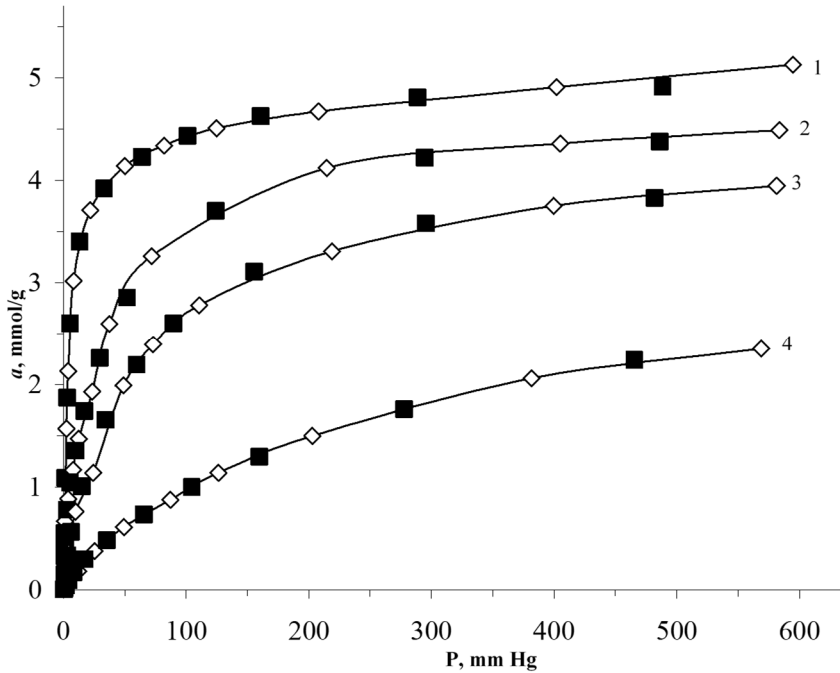


Fig. 1. Adsorption isotherms of COS vapors in NaX zeolite: Black dots - calculated using TMVF. 1- 273 K; 2- 298 K; 3-303 K; 4-373 K.

The corresponding equations for isotherms measured at different temperatures are given below:

COS - NaX:

$$273 \quad a = 3,98 \exp[-(A/19,41)^7] + 1,03 \exp[-(A/10,66)^4]$$

$$293 \quad a = 1,62 \exp[-(A/21,5)^6] + 2,9 \exp[-(A/14,0)^5]$$

$$303 \quad a = 2,06 \exp[-(A/19,31)^4] + 2,146 \exp[-(A/15,01)^5]$$

$$373 \quad a = 0,3 \exp[-(A/22,95)^7] + 4,23 \exp[-(A/12,92)^3]$$

For comparison carried out the isosteric heats of adsorption of carbonyl sulfide in CaA are constant in the initial region (~43 kJ/mol), then they begin to increase and pass a maximum at 2 mmol/g, then sharply decrease in the direction of the abscissa (Figure 2). When extrapolated to zero fillings, the Q_d curve cuts off 43 kJ/mol on the y-axis, which corresponds to the heat of adsorption of carbonyl sulfide on Ca^{2+} cations in the S_1 position of the zeolite lattice. Ca^{2+} cations are more preferred adsorption sites than monovalent cations Na^+ [6].

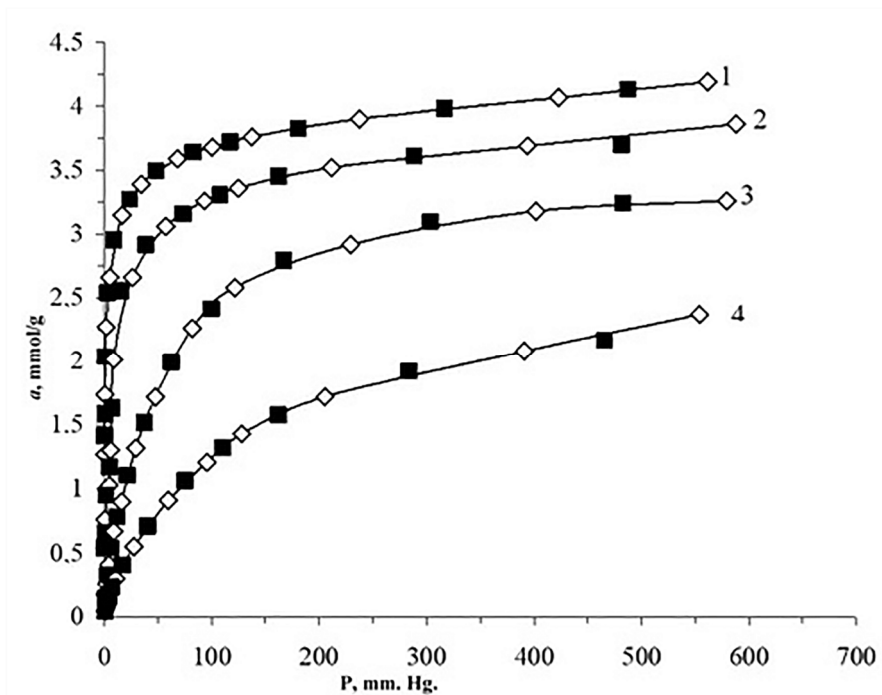


Fig. 2. Adsorption isotherms of COS vapors in zeolite CaA: Black dots - calculated using TMVF. 1- 273 K; 2- 298 K; 3-333 K; 4-373 K.

On the basis of adsorption isotherms studied at different temperatures (273, 298, 303 and 373 K), isosteres were calculated - dependences of equilibrium pressures on temperature at constant values of adsorption (Figure 3). [7-10]. Isosteres in the $\ln P - T^{-1}$ coordinates are linear, their slope to the temperature axis changes with an increase in the filling of the adsorbent surface (Figure 4). The curve of isosteric heats of adsorption of COS on NaX in the region of small fillings sharply decreases from the heat of adsorption exceeding 48 kJ/mol. To 34 kJ/mol at $a \approx 1.5$ mmol/g, after passing the minimum, it increases sharply, then passes a maximum of 39 kJ/mol and drops to 34.5 kJ/mol at 4 mmol/g. A total of 4 mmol/g COS is adsorbed, which is 6.7 in terms of the number of COS molecules per unit cell.

The unit cell of NaX zeolite contains 86 Na⁺ cations. In terms of 1/8 ey - 10.7 Na⁺. The cations are distributed as follows: 4 each in SII and SI' in the large and small cavities, the remaining 2.7 in the large cavity in the SIII position [11-14]. The most preferred adsorption sites are cations in the open position SIII. The area with a high heat of adsorption on the Q_d curve (0 - 1.55 mmol/g or 2.7 COS/e.c.) we attribute to adsorption on these centers, since the number of adsorbed COS molecules is very close to the number of these centers. Further, the heats of adsorption increase, pass through a maximum and decrease, reaching 4 mmol/g or 6.7 COS/e.c. If we subtract 2.7 from the total number of COS molecules, then 4 COS/e.c. remains, i.e. as many as there are Na⁺ cations in the SII and SI' positions. Given that carbonyl sulfide molecules do not penetrate into sodalite cavities for steric reasons, and therefore cannot interact with cations in the SI' position, it can be argued that they interact with cations in the SII position. An increase in heat with filling points to the superposition of the adsorbate-adsorbate interaction energy on the total adsorption energy. In total, 6.7 molecules of carbonyl sulfide are adsorbed in the supercavities [15-17].

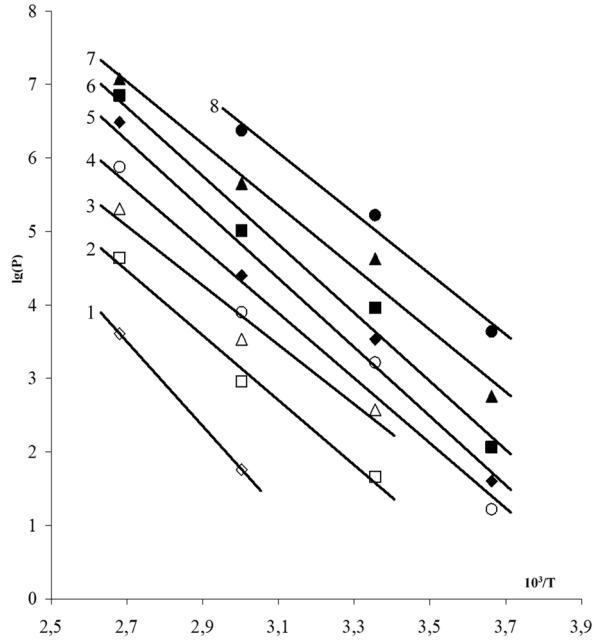


Fig. 3. COS adsorption isotherms in NaX zeolite, corresponding to giving different amounts of adsorbed substance (mmol/g): 1-0.5; 2-1.0; 3-1.5; 4-2.0; 5-2.5; 6-3.0; 7-3.5; 8-4.0.

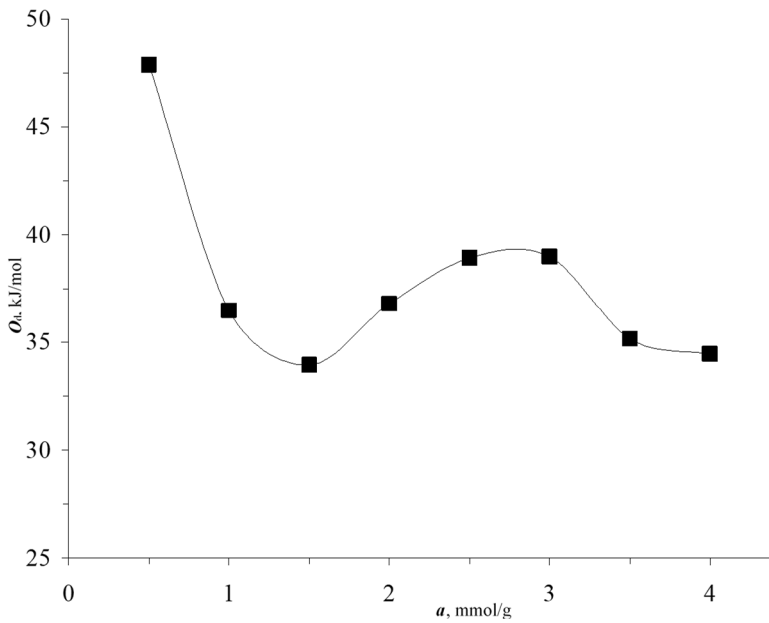


Fig. 4. Differential isosteric heats of adsorption COS in NaX zeolite.

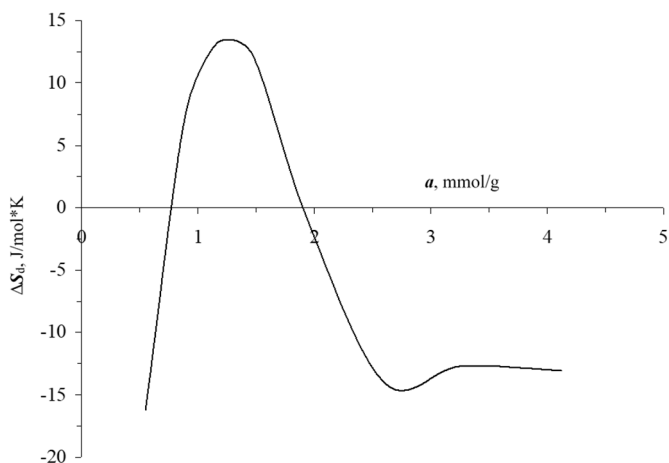


Fig. 5. Differential entropy of COS adsorption in NaX zeolite at 298 K. The entropy of liquid COS is taken as zero.

The molar differential entropy of COS adsorption in NaX (Figure 5) was calculated from the given heats and free energy of adsorption. The entropy of adsorption is plotted against the entropy of liquid carbonyl sulfide. Entropy starts from negative values (-16 J/mol*K) increases, crosses the zero line, then passes through a maximum (+14 J/mol*K), decreases again, crosses the zero line passes through a minimum (-14 J/mol* K), then slightly increases and stabilizes at -12.8 J/mol*K. Carbon sulfide adsorbed on the cation in position SIII has a certain degree of freedom, which causes an increase in entropy. When adsorbed on Na⁺ cations, the adsorbate associates with preadsorbed COS molecules, which leads to a decrease in entropy towards negative values. In general, the mobility of carbonyl sulfide molecules is lower than that of the liquid adsorbate.

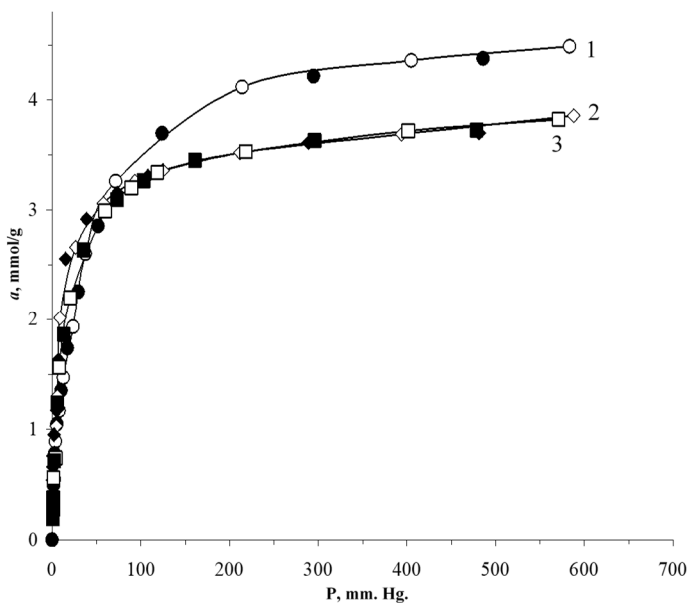


Fig. 6. Adsorption isotherms of COS in zeolites at 298 K: 1 - NaX; 2 - CaA; 3 - NaCaA.

The isotherms of carbon sulfide adsorption on NaX, CaA, and CaNaA zeolites at 298 K are presented. All of them are I-shaped and are characterized by a sharp rise with a slight change in equilibrium pressure. A noticeable excess of the sorption capacity of the NaX zeolite over zeolites of the CaA and NaCaA types is associated with their structural features. open and openwork (Figure 6).

The NaX zeolite structure holds ~0.63 mmol/g more carbon sulphide than CaA and NaCaA when the cavities are saturated with adsorbate. Calcium cations present in zeolites A greatly increase their ability to strongly adsorb carbon sulfide, adsorb sodium somewhat weaker.

4 Conclusion

The adsorption capacity of NaX with respect to COS is, on average, 14% higher than in type A zeolites.

Centers of strong adsorption in NaX zeolite are Na⁺ cations in position S_{III}, with which carbon sulfide forms monomeric (COS)/Na⁺ complexes. Reversible adsorption proceeds on S_{II} cations, with which carbon sulfide forms monomeric complexes. During the adsorption of carbon sulfide, a collective adsorbate-adsorbate interaction is observed, leading to an increase in the heat of adsorption. One eighth of the unit cell of NaX contains 6.7 molecules of carbon sulfide, of which 2.7 are localized on Na⁺ in position S_{III} and 4 - on Na⁺ in position S_{II}.

The mobility of carbon sulphide molecules in the zeolite matrix is inhibited. The time of establishment of adsorption equilibrium at low fillings is slowed down (up to ~2 hours), and at high fillings the process is accelerated, and the equilibrium is established in ~30 minutes.

At higher gas concentrations, it is necessary to use CaA, which strongly adsorbs carbon sulfide in a wide range of fillings of the sorption space. NaX should be used in cases where it is necessary to purify the gas not only from hydrogen sulfide, but also from larger (up to 0.8 nm in diameter) molecules.

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