

# Investigation of isotherms of differential heat-entropy adsorption of carbonyl sulfide in CaA zeolite during gas purification

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**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 ( $\Delta S_d$ ) 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 CaA, carried out at four temperatures: 273, 298, 303, and 373 K, and the corresponding thermodynamic functions of adsorption in CaA 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 absorbing carbonyl sulfide, which negatively affects the total sulfur content in the gas. Carbonyl 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. 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 ( $\Delta S_d$ ) of adsorption in order to select an effective adsorbent for purifying natural gas and oil products from sulfur-containing compounds.

The article presents the results of studying the isotherms of COS adsorption in CaA zeolite at four temperatures: 273, 298, 303 and 373 K and differential isosteric heats and entropies of adsorption.

## 2 Materials and methods

In type A zeolite, not all cations occupy the same positions in the lattice. There are 2 types of cation localization sites -  $S_I$  sites - in the center of six-membered oxygen rings and  $S_{II}$  sites, which are statistically distributed near the eight-membered oxygen rings of a large cavity. The investigated sample was subjected to ion exchange of calcium for sodium and consists

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mainly of  $\text{Ca}^{2+}$  ions. In type A zeolites, calcium cations prefer the  $S_1$  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 [3].

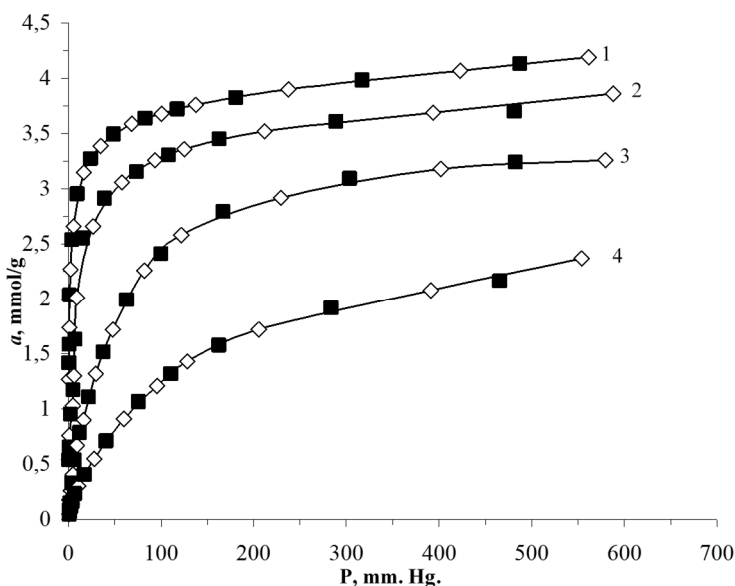
### 3 Results and discussion

Figure 1 shows the adsorption isotherms of COS in CaA at different temperatures (273, 298, 303 and 373K). COS adsorption isotherms on zeolites are satisfactorily described by the two- and three-term TMVF (the theory of micropore volumetric filling) equations [4, 5]. Below are the equations of isotherms measured at different temperatures. COS - CaA:

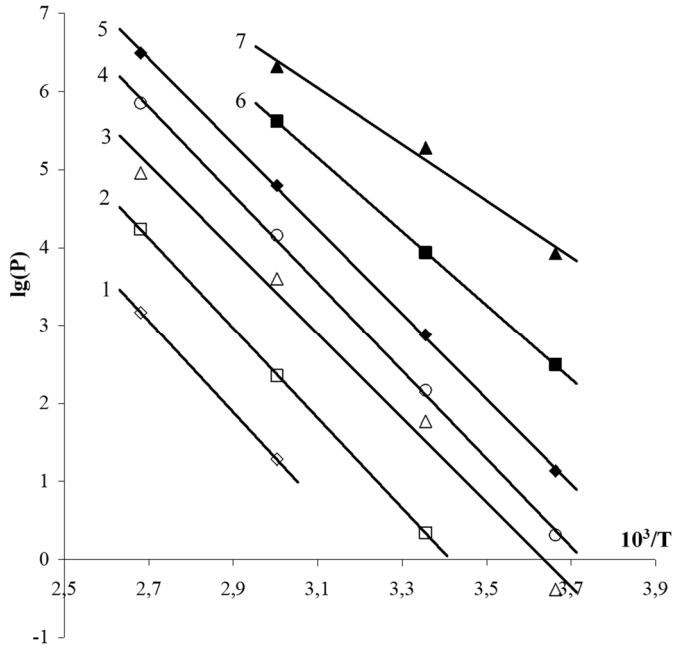
$$\begin{aligned} 273 \quad a &= 2,95 \exp[-(A/23,96)^7] + 0,97 \exp[-(A/13,71)^4] + 0,67 \exp[-(A/5,98)^3] \\ 298 \quad a &= 1,09 \exp[-(A/25,23)^{12}] + 1,62 \exp[-(A/18,27)^{20}] + 1,08 \exp[-(A/12,81)^5] \\ 303 \quad a &= 2,14 \exp[-(A/19,05)^4] + 1,31 \exp[-(A/15,17)^7] \\ 373 \quad a &= 1,53 \exp[-(A/18,18)^3] + 1,21 \exp[-(A/15,8)^6] \end{aligned}$$

On the basis of adsorption isotherms obtained at different temperatures (273, 298, 303, and 373 K), isosteres were calculated, i.e., lines of dependence of equilibrium pressures on temperature at constant values of adsorption. Isosteres in coordinates  $\lg P - T^{-1}$  are linear, their slope to the temperature axis changes with increasing filling of the adsorbent surface (Figure 2). The isosteric heats of adsorption were calculated from the slope of the isosteres (Figure 3). From these heats and the dependence of the maximum work of adsorption on the amount of adsorbed carbonyl sulfide, the molar entropy of adsorption was calculated (Figure 4).

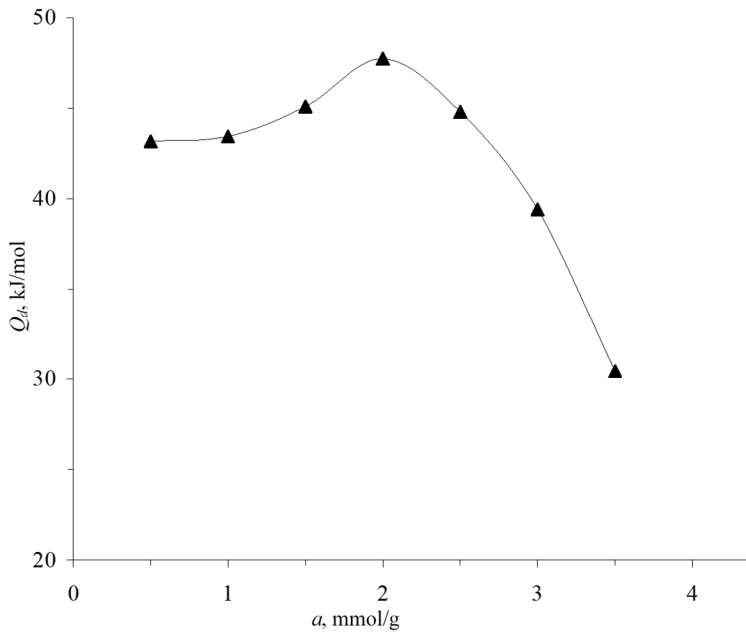
The isosteric heats of adsorption of carbonyl sulfide in CaA are constant in the initial region ( $\sim 43$  kJ/mol), then they begin to increase and pass a maximum at 2 mmol/g, then sharply decrease in the direction of the abscissa axis (Figure 3). When extrapolated to zero fillings, the  $Q_d$  curve cuts off 43 kJ/mol on the y-axis, which corresponds to the heat of adsorption of carbonyl sulfide on  $\text{Ca}^{2+}$  cations in the  $S_1$  position of the zeolite lattice.  $\text{Ca}^{2+}$  cations are more preferred adsorption sites than monovalent cations  $\text{Na}^+$  [6-9].



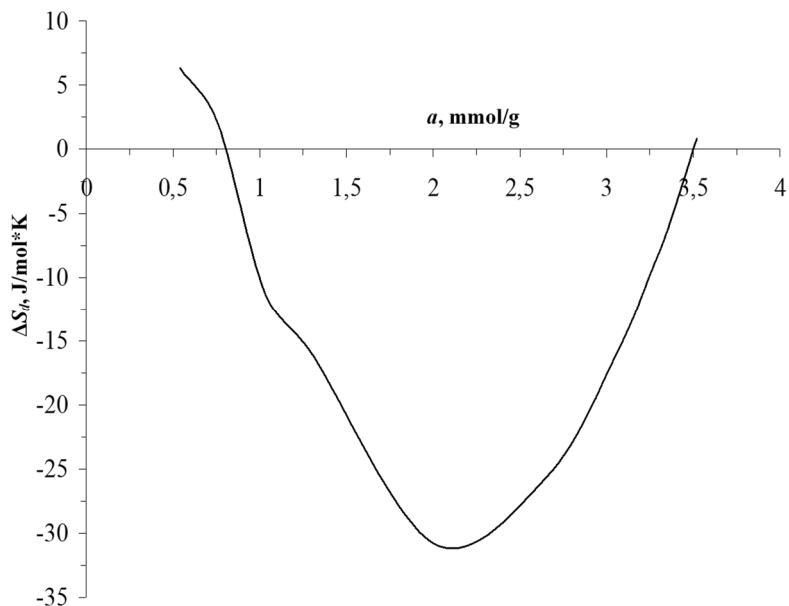
**Fig. 1.** Adsorption isotherms of COS vapors in zeolite CaA: Black dots - calculated using TOZM. 1- 273 K; 2- 298 K; 3-303 K; 4-373 K.



**Fig. 2.** COS adsorption isotherms in CaA zeolite corresponding to 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.

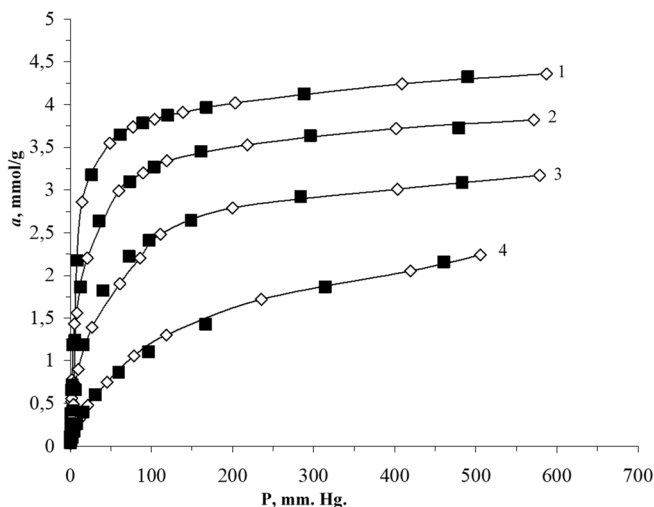


**Fig. 3.** Differential isosteric heats of COS adsorption in CaA zeolite.



**Fig. 4.** Differential adsorption entropies of COS in zeolite CaA at 298 K. The entropy of liquid COS is taken as zero.

Na<sup>+</sup>. Next, a correlation was made between adsorption and the number of energetically different centers. CaA contains 2.97 mmol/g calcium, which corresponds to 5 Ca<sup>2+</sup> cations per unit cell. On the  $Q_d$  curve, this amount corresponds to a section where the curve is constant, then passes through a maximum and decreases to 39.4 kJ/mol. Further, adsorption occurs on half (0.59 mmol/g or 1 Na<sup>+</sup> cation /e.i.) of all Na<sup>+</sup> cations with a heat below 39 kJ/mol. Thus, the adsorption of carbonyl sulfide in CaA zeolite occurs on all 5 Ca<sup>2+</sup> cations in the SI position and on 1 of the 2 Na<sup>+</sup> cations in the same position. The unit cell of CaA zeolite contains 6 COS molecules [10-12].



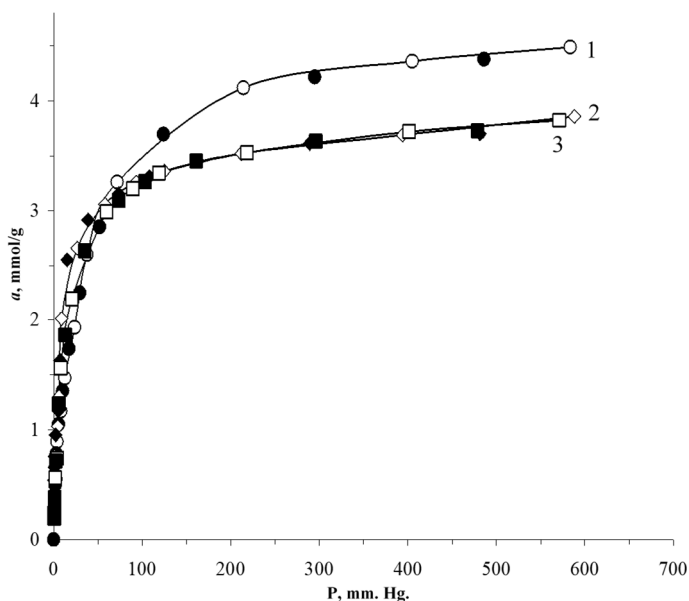
**Fig. 5.** COS adsorption isotherms in NaCaA zeolite. Black dots - calculated using TMVF. 1-273 K; 2-298 K; 3-333 K; 4-373 K.

The entropy diagram (Figure 4), plotted from the entropy of liquid carbonyl sulfide, is generally in the negative region. The curve passes a deep minimum ( $-31 \text{ J/mol}\cdot\text{K}$ ) at  $a = 2 \text{ mmol/g}$ , then grows sharply, crossing the zero level corresponding to the entropy of liquid carbon sulphide. Low negative entropy values indicate that the mobility of carbonyl sulfide molecules in the CaA zeolite matrix is strongly inhibited.

To compare the characteristics, the studied zeolite sample was subjected to partial exchange for  $\text{Na}^+$  ions. The content of calcium and sodium cations is approximately the same. In general, both calcium and sodium cations are tetrahedral arranged in the  $S_1$  position [13].

Adsorption isotherms of carbonyl sulfide in NaCaA at temperatures of 273, 293, 303, and 373 K are shown in Figure 5.

The isotherms of carbonyl sulfide adsorption on CaA, CaNaA and NaX zeolites at 298 K are presented. All of them are r-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).



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

As it can be seen from the above results, the adsorption capacity of CaA and NaCaA is approximately the same. Both of them are noticeably inferior in adsorption capacity to NaX zeolite with respect to carbonyl sulfide, especially in the area of small fillings.

The heat of adsorption at low fillings is the same for both CaA and NaCaA, since in both cases adsorption proceeds on calcium cations. In general, the heat of COS adsorption in CaA is noticeably higher than in NaCaA. This is caused by the superimposition of the adsorption interaction adsorbate-adsorbate on the general background of the heat of adsorption. In the case of NaCaA, we see the opposite effect at higher fillings. This difference in the energy of adsorption is due to the fact that a high concentration of  $\text{Ca}^{2+}$  cations allows them to be located closer to each other and, therefore, conditions are created for the association of COS molecules with each other. In the case of NaCaA, calcium cations are located tetrahedrally in the supercavity, therefore the association between them is difficult, and polarized

complexes of carbonyl sulfide with the cation lead to mutual repulsion, which leads to a drop in the heat of adsorption.

## 4 Conclusion

The adsorption capacity of CaA with respect to COS is 14% lower than in type X zeolites.

The adsorption capacity of NaCaA in terms of COS is ~14% lower than in type X zeolites.

Adsorption centers in CaA zeolite are  $\text{Ca}^{2+}$  and  $\text{Na}^+$  cations in the  $S_{II}$  position, with which carbonyl sulfide molecules form monomeric complexes  $(\text{COS})/\text{Ca}^{2+}$  and  $(\text{COS})/\text{Na}^+$ . The unit cell contains 6 molecules of carbonyl sulfide, of which 5 are localized on  $\text{Ca}^{2+}$  and 1- on  $\text{Na}^+$ .

Zeolites CaA and NaCaA should be used for purification of natural gas from trace amounts of carbonyl sulfide. At higher gas concentrations, it is necessary to use CaA, which strongly adsorbs carbonyl sulfide in a wide range of fillings of the sorption space.

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