ENTROPY OF HYDROGEN SULFIDE ADSORPTION IN ACTIVATED SORBENT

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Abstract: *In this work, the results of adsorption microcalorimetric studies are presented, aimed at determining the main energetic characteristics of hydrogen sulfide (H_2S) adsorption on an activated carbon sorbent derived from hybrid* Paulownia tomentosa *wood. The differential values of the molar adsorption entropy were calculated, and a stepwise character of its variation was revealed. The average value of the molar integral adsorption entropy was found to be 7 $J \cdot mol^{-1} \cdot K^{-1}$, which indicates an enhanced mobility of H_2S molecules compared to the liquid phase and, consequently, a weak restriction of their movement within the sorbent pores.*

Keywords: *Hydrogen sulfide, adsorption, adsorption microcalorimetry, activated carbon,* Paulownia Tomentosa, *adsorption entropy.*

INTRODUCTION

Activated carbons (ACs) derived from wood represent a class of highly porous adsorptive materials with a developed specific surface area and rich surface chemistry, produced from renewable lignocellulosic raw materials. According to the IUPAC definition, activated carbon is a porous carbonaceous material obtained from a carbonized precursor by treatment with gases or chemical reagents before or after carbonization, which enhances its adsorption properties. Such materials predominantly adsorb small molecules effectively and are widely applied for purification of liquids and gases [1].

A typical production scheme includes carbonization/pyrolysis of wood at 400–700 °C under an inert atmosphere, resulting in the formation of primary microporosity, followed by activation, either physical or chemical. In physical activation, steam or CO_2 at 750–950 °C is used to enlarge and open pores; in chemical activation, reagents such as H_3PO_4 or KOH (less commonly $ZnCl_2$ and others) enable the development of microporosity or mesoporosity and functionalized surfaces at lower temperatures [2–8].

Phosphoric acid activation (H_3PO_4) induces dehydration, esterification, and partial cross-linking reactions in the lignocellulosic matrix, which ensures high yields (often >50%), the formation of predominantly mesoporous structures, and the incorporation of phosphorus-containing groups on the surface. For wood precursors, at optimal

"precursor:acid" ratios and temperatures of 400–600 °C, specific surface areas up to ~2000 m^2/g and higher can be achieved, as demonstrated both for model lignins and real lignocellulosic wastes [6–7].

The pore hierarchy (micro–meso–macro) defines the balance between capacity and mass transfer: micropores contribute the main share to equilibrium adsorption and selectivity, mesopores accelerate diffusion to active sites, and macropores act as transport "highways." Surface chemistry (carboxyl, phenolic, lactone, phosphate groups) dictates interaction mechanisms: ion exchange/complexation for heavy metals, π–π donor–acceptor interactions for aromatic organics, and acid–base interactions for H_2S/volatile organic compounds, etc. [2, 6–8, 9].

Wood-based ACs are applied in drinking and wastewater treatment—reduction of COD (chemical oxygen demand)/BOD (biological oxygen demand), decolorization, and removal of micropollutants; in gas purification—capture of H_2S in biogas, removal of SO_2/VOCs and odors; in the food industry—syrup decolorization; in catalysis—as supports; in energy—supercapacitors and battery systems; and in medicine and sanitation—as filtering materials. Modern reviews emphasize both the versatility of ACs and the need for fine tuning of pore texture and surface chemistry for specific targets [10-12]. To extend the service life of ACs, thermal or chemical regeneration is applied; in gas purification from H_2S, thermal regeneration of granular AC (GAC) allows maintaining performance over multiple cycles, although the chosen regime depends on the nature of loaded species (elemental sulfur, sulfides/sulfates) and the risk of chemical burnout. In aqueous systems, the solubility of adsorbates and the stability of functional groups are critical. Reviews on regeneration and operation in water and gas treatment systems summarize regimes and limitations [10-12].

RESEARCH METHODS

In this study, a universal high-vacuum adsorption apparatus equipped with a Tian–Calvet type differential microcalorimeter (DAC-1-1A) was used. This system is distinguished by its high accuracy and stability. The calorimeter provides access to the thermokinetic characteristics of the processes occurring in the studied adsorption systems, which is of great importance for elucidating the mechanism of adsorption. The adsorption–calorimetric method applied in this work allows for highly accurate determination of molar thermodynamic properties and offers detailed insights into the mechanisms of adsorption processes taking place in adsorbents.

RESULTS AND DISCUSSION

This article presents the results of a study on the change in adsorption entropy and the adsorption mechanism of hydrogen sulfide on an activated carbon adsorbent derived from the bark of Paulownia tomentosa at a temperature of 303 K [3-5].

The dependence of the molar differential entropy change (ΔS_a) of hydrogen sulfide molecule adsorption on an activated carbon adsorbent derived from the bark of Paulownia tomentosa on adsorption saturation is shown in Figure 1 (the entropy of liquid hydrogen sulfide was taken as zero). The adsorption entropy was calculated using the Gibbs–Helmholtz equation:

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

where λ is the heat of condensation, and ΔH and ΔG are the changes in adsorption enthalpy and free energy, respectively, when transitioning from the standard state to the adsorbed state.

The molar differential entropy of hydrogen sulfide adsorption on the activated carbon adsorbent from Paulownia tomentosa bark can be divided into four regions. Regions 1, 2, and 4 lie above the entropy value of liquid hydrogen sulfide, while Region 3 corresponds to an average entropy value equal to zero.

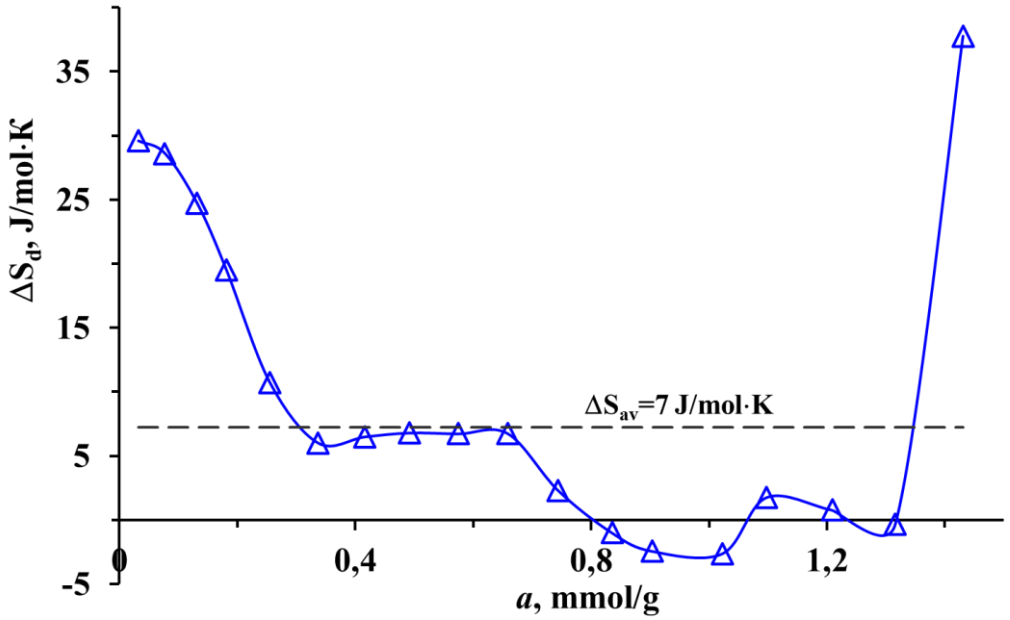

Fig.1. Molar differential entropy of hydrogen sulfide adsorption on an activated carbon adsorbent derived from Paulownia tomentosa. The horizontal dashed line represents the average molar integral entropy.

In the initial region, the entropy change is equal to 30 J/mol·K. This value indicates that the mobility of the initially adsorbed hydrogen sulfide molecules in the pores is not sufficiently restricted, i.e., the adsorbate–adsorbent interaction is relatively weak. It is well known that adsorption in the pores or on the surface of carbon adsorbents occurs mainly through physical sorption. The unrestricted mobility of hydrogen sulfide molecules in the initial adsorption region reflects the absence of cationic active centers in carbon adsorbents that could form ion–molecular complexes. Therefore, the change in sorption entropy lies above the entropy value of liquid hydrogen sulfide at the experimental temperature (303 K).

As the sorption pores gradually fill, entropy begins to decrease sharply and reaches 6 J/mol·K at an adsorption amount of 0.34 mmol/g. Up to 0.66 mmol/g, entropy increases slightly to 6.8 J/mol·K. At ~1 mmol/g of adsorption, entropy smoothly decreases to -2.62 J/mol·K. During further adsorption of hydrogen sulfide molecules, the entropy changes in a wave-like manner and reaches zero at 1.33 mmol/g of adsorption.

The dependence of entropy change on adsorption at ~0.35 mmol/g indicates that the number of active centers in the activated carbon adsorbent is ~0.35 mmol/g. Thus, in the

activated carbon adsorbent derived from the bark of Paulownia tomentosa, hydrogen sulfide molecules form a $4H_2S$/adsorbent complex.

The average value of the molar differential entropy of hydrogen sulfide adsorption on the activated carbon adsorbent derived from the bark of Paulownia tomentosa is 7 J/mol·K, which lies above the entropy of liquid hydrogen sulfide molecules at the experimental temperature. This demonstrates that the mobility of hydrogen sulfide molecules remains largely unrestricted.

Conclusion. It was established that the variation of molar differential adsorption entropy exhibits a stepwise behavior depending on the number of active centers of the activated carbon adsorbent. The number of active centers in the pores of this adsorbent with respect to hydrogen sulfide molecules was determined to be ~0.35 mmol/g.

Overall, the hydrogen sulfide molecules form $4H_2S$/adsorbent complexes within the pores of the activated carbon derived from Paulownia tomentosa bark.

At the experimental pressure (588 torr), the average entropy change was found to be 7 J/mol·K. This indicates that the mobility of hydrogen sulfide molecules within the activated carbon adsorbent derived from Paulownia tomentosa bark remains largely unrestricted.

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