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## DYNAMIC ADSORPTION OF THIOPHENES, THIOLS AND SULPHIDES FROM *n*-HEPTANE SOLUTIONS ON MOLECULAR SIEVE 13X

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### SUMMARY

The adsorption of selected sulphur compounds from *n*-heptane solution on molecular sieve 13X was investigated under dynamic conditions, mainly at concentrations of the order of 0.032–1 mg/ml of sulphur. Some thiophenes, sulphides and thiols likely to occur in the 50–150° gasoline cut from crude oil were submitted to adsorption. The influence of benzene on the adsorption of selected sulphur compounds was also investigated. The sulphur compounds adsorbed on molecular sieve 13X were desorbed to *n*-heptane or isooctane using a hydrochloric–hydrofluoric acid mixture to determine the degree of concentration.

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### INTRODUCTION

Studies of the adsorption of sulphur compounds on different adsorbents not only provide theoretical data but also offer practical advantages, as this technique can be employed for concentrating sulphur compounds in various petroleum fractions, and thus for separating them from excess of hydrocarbons. The fact that suitable concentrates are obtained in this way facilitates analysis and decreases the detection limit. Moreover, smaller samples of the initial material can be used during analysis. Utilization of such adsorbents as silica gel<sup>1–3</sup>, aluminium oxide<sup>4–9</sup> and active carbon<sup>10</sup>, however, does not provide satisfactory results.

The better knowledge of the structure and properties of molecular sieves has drawn attention to the possibility of utilizing them for the adsorption of sulphur compounds. Owing to their specific crystalline structure<sup>11</sup>, molecular sieves achieve a noticeably higher adsorption potential and, consequently, a much greater sorption capability at low adsorbate concentrations than do the adsorbents mentioned earlier.

The literature on the adsorption of sulphur compounds from solutions on molecular sieves is sparse. The adsorption of thiophene and *n*-heptane on molecular sieve 5A was studied by Kiselev *et al.*<sup>12</sup>, and the adsorption of these compounds on zeolites was studied by Eltekov and Semenova<sup>13</sup>, who extended their investigations to silica gel and aluminium oxide. Eltekov *et al.*<sup>14</sup> also studied the adsorption of thiophene from solutions on variously prepared X-type molecular sieves. Salyukov *et al.*<sup>15</sup> investigated the adsorbability of a benzene–thiophene mixture, while Novikova

and Eltekov<sup>16</sup> utilized porous faujasite crystals to study the adsorption of thiophene from solutions. The adsorption of thiols and sulphides from solutions in decalin was studied by Grazev and Rachlevskaja<sup>17,18</sup>. However, as the adsorption of sulphur compounds from different systems was investigated, these studies cannot be used for comparison. Also, most of these studies were conducted under static conditions, while for the concentration of sulphur compounds from petroleum fractions a dynamic adsorption process is generally preferred.

In the present work, molecular sieve 13X was employed under dynamic conditions to investigate the adsorption of some thiophenes, sulphides and thiols likely to occur in the 50–150° gasoline cut from crude oil.

## EXPERIMENTAL

### *Adsorption and its control*

The adsorption was conducted by the frontal technique from standard solutions of selected sulphur compounds. These solutions were prepared by dissolving the sulphur compounds mentioned below in sulphur-free *n*-heptane or in an *n*-heptane–benzene mixture. The standard solutions were passed at room temperature

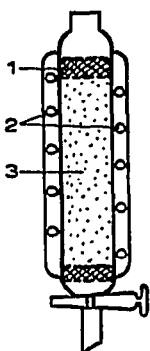


Fig. 1. Adsorption tube. 1 = Glass-wool; 2 = electric furnace; 3 = molecular sieve 13X.

through a glass column (Fig. 1) of dimensions 22 × 0.5 cm, filled with activated molecular sieve 13X (0.5 g) at the rate of 1 ml/min.

The control of the adsorption process consisted in analysing successive portions of the effluent from the adsorption column. The volume of these portions varied from 0.1 to 1 ml, depending on the concentration of the solution passed through the sieve. Analysis was conducted by the reaction gas chromatography technique in a system similar to that described by Staszewski *et al.*<sup>19</sup>, using a Giede GCHF 18.3 gas chromatograph. The pre-column, acting as a micro-reactor, was filled with active Raney nickel (VEB, Berlin, Laborchemie Apolda, G.D.R.) supported on glass beads. The Raney nickel was prepared by the modified method of Granatelli<sup>20</sup> cited by Reed<sup>21</sup>. The use of reaction gas chromatography resulted in a decrease in the detection limit for the different sulphur compounds, and facilitated their chromatographic isolation from the solvent. (Hydrogenolysis on Raney nickel had the effect that hydrocarbons corresponding to sulphur compounds were analysed instead of the latter.)

*Chromatographic conditions*

A steel column, 200 × 0.5 cm, filled with 20% squalane on Sterchamol (60–80 mesh), was used with argon as carrier gas at a flow-rate of 50 ml/min, with a flame ionization detector, a thermostat maintained at 80° and a micro-reactor at 180°.

*Activation of molecular sieve 13X*

Activation of the molecular sieve and adsorption were conducted in the same column. The glass column was placed in an electric furnace with a regulated temperature and the sieve was heated for 4 h at 350°, maintaining a steady flow of nitrogen that had previously been de-oiled and dried. The scheme of the activating system is shown in Fig. 2.

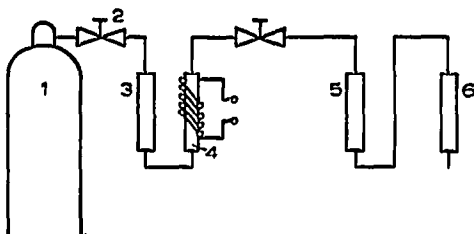


Fig. 2. Apparatus for activation of molecular sieve 13X. 1 = Argon reservoir; 2 = reducing valve; 3 = filter packed with molecular sieve 5A; 4 = filter packed with activated copper; 5 = flow meter; 6 = adsorption tube packed with molecular sieve 13X.

The sieve was cooled to room temperature after activation without interrupting the nitrogen flow. The sieve was used immediately after activation.

*Reagents and standard solutions*

The study was carried out using molecular sieve 13X, 100–200 mesh (Serva, Heidelberg, G.F.R.). The following sulphur compounds (all pure) were investigated: thiophene, *n*-butanethiol and 2-methyl-1-propanethiol (Fluka, Buchs, Switzerland); 2-methylthiophene (Koch-Light, Colnbrook, Great Britain); 2-ethylthiophene (Aldrich, Milwaukee, Wisc., U.S.A.); and dimethyl, dipropyl and ethyl propyl sulphides (synthesized in this Institute). Standard solutions were prepared using *n*-heptane (VEB Berlin, Laborchemie Apolda, G.D.R.), freed from possibly present sulphur compounds by shaking with Raney nickel, and then distilled, and sulphur-free benzene (Chemistry of Coke Works, Chorzów, Poland). The standard solutions of sulphur compounds in *n*-heptane were prepared directly prior to the adsorption process by dissolving known amounts of the various compounds in a determined amount of *n*-heptane.

*Estimation of the adsorptive capacity of molecular sieve 13X*

The amount of substance adsorbed per unit mass of the molecular sieve was calculated by the equation<sup>22</sup>

$$x_2^v = v' \cdot c_2 \quad (1)$$

where

$x_2^v$  = the amount of the substance adsorbed per unit mass of the adsorbent (1 g), called the excess adsorption;

$v'$  = the breakthrough volume corresponding to the breakthrough point on the curve of the concentration of the substance as a function of the effluent volume;

$c_2$  = the initial concentration of the constituent adsorbed.

In calculating  $x_2^v$  for various concentrations of a given sulphur compound, the excess adsorption isotherm was plotted. Both the excess adsorption and the course of the excess isotherm are a measure of the adsorptive capacity of the molecular sieve with regard to the various sulphur compounds.

#### *Desorption of sulphur compounds*

The liberation of sulphur compounds from molecular sieve 13X to *n*-heptane or isooctane was carried out by destruction of the molecular sieve with a hydrochloric-hydrofluoric acid mixture by the method described by Staszewski<sup>23</sup>.

### RESULTS AND DISCUSSION

The solvent utilized for sulphur compounds was *n*-heptane because the results to be obtained were to serve as basis for predicting the possibility of concentrating those compounds from the 50–150° gasoline cut whose properties could be represented by *n*-heptane. As this fraction also contains some aromatic hydrocarbons, the influence of benzene on adsorption was also investigated. The concentrations of sulphur compounds in standard solutions were selected to be within the range of the amounts of these compounds expected in the 50–150° fraction, *i.e.*, 0.001–0.1% of sulphur calculated for one compound (this giving approximately 0.01–1 mg/ml of sulphur).

The beginning of the course of the adsorption isotherms obtained for three sulphur compounds with similar molecular weights (thiophene, diethyl sulphide and *n*-butanethiol) within the 0–1 mg/ml of sulphur concentration range shows the molecular sieve to have a relatively high adsorptive capacity with regard to low concentrations of these compounds (Fig. 3). This result is essential in the concentration process from highly diluted solutions. Fig. 3 shows that within the concentration range up to 1 mg/ml of sulphur, the sulphide is more strongly adsorbed than the thiol or thiophene. The adsorption of thiophene within the 0.6–1 mg/ml of sulphur concentration range is similar to that of the thiol, and surpasses it at higher concentration ranges. This is evident from the further section of the isotherm for these compounds up to a concentration of 30 mg/ml of sulphur (Fig. 4).

The above order of adsorptivity of sulphur compounds is essentially in accord with that observed on silica gel<sup>1,2</sup>. This is probably due to the chemical similarity of the surfaces of these adsorbents (hydroxyl groups on the surface of silica gel and cationic surface of the molecular sieve micropores). One of the factors responsible for this order may be electrophilicity. As the molecular sieve is an electrophilic adsorbent, it will adsorb more strongly sulphides that have free electrons than thiophenes, which are proton acceptors. It seems that this is not the only factor that influences adsorptivity; an important role is also played by the size of the molecules adsorbed.

Our investigations have shown that the limiting adsorption on the sieve, *i.e.*, the overall amounts defined by extrapolation (Fig. 5) of sulphur compounds filling

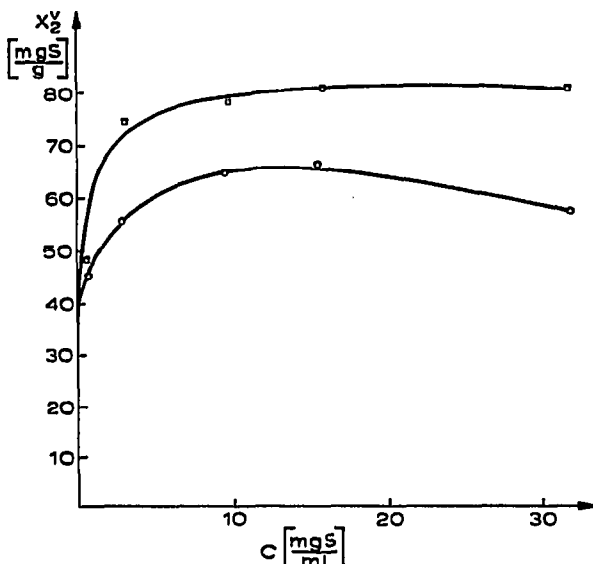
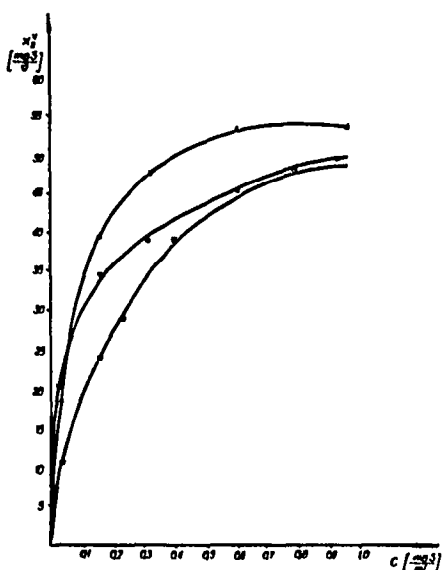


Fig. 3. Initial course of excess adsorption isotherms.  $\Delta$ , Diethyl sulphide;  $\circ$ , *n*-butanethiol;  $\square$ , thiophene.

Fig. 4. Further course of excess adsorption isotherms.  $\square$ , Thiophene;  $\circ$ , *n*-butanethiol.

the pores of the sieve for thiophene, *n*-butanethiol, and dipropyl sulphide are 89.9, 75.9 and 57.4 mg/ml of sulphur, respectively.

The adsorptive capacity decreases for each group of compounds with increase in molecular size. As shown in Table I, 2-methylthiophene is adsorbed less strongly than thiophene, but more strongly than 2-ethylthiophene. The example of sulphides shows (Fig. 6), however, that this dependence can undergo changes. As the adsorption curve of ethyl propyl sulphide does not run between the adsorption curves of diethyl and dipropyl sulphides, as it should, some other factors must be involved, and the greatest role seems to be played by molecular size and configuration, which result in different packings in the pores of the molecular sieve. This can be exemplified by comparing the adsorption of two mercaptans that have the same molecular weights

TABLE I

COMPARISON OF ADSORPTION OF THIOPHENE, 2-METHYLTHIOPHENE AND 2-ETHYLTHIOPHENE

Compound	Concentration (mg/ml of sulphur)			
	0.032		0.32	
	$v'$ (ml/g)	$x_2'$ (mg/g of sulphur)	$v'$ (ml/g)	$x_2'$ (mg/g of sulphur)
Thiophene	322	10.3	84.2	26.9
2-Methylthiophene	153.7	4.9	58.6	18.8
2-Ethylthiophene	146.4	4.7	51.2	16.4

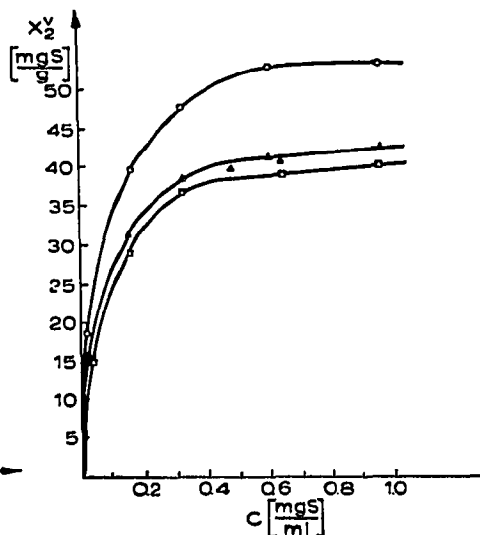
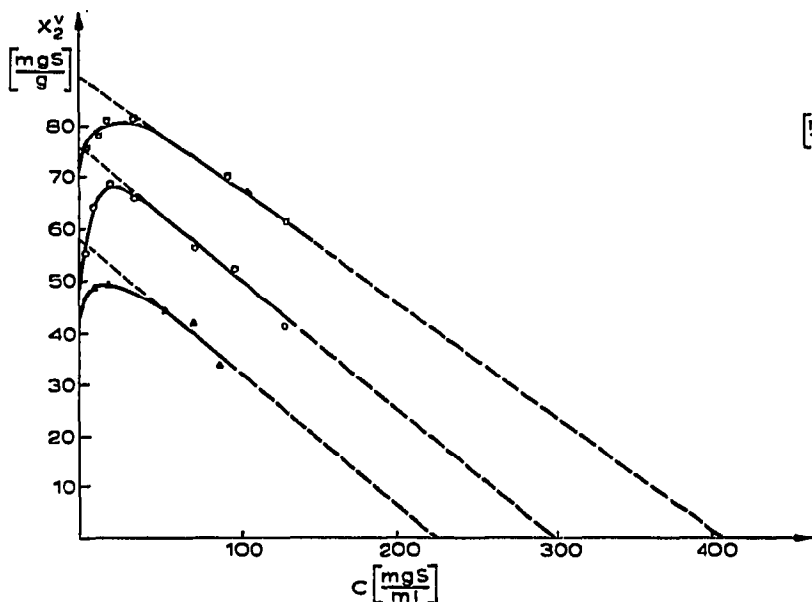


Fig. 5. Overall excess adsorption isotherms.  $\square$ , Thiophene;  $\circ$ , *n*-butanethiol;  $\triangle$ , dipropyl sulphide.

Fig. 6. Initial course of excess adsorption isotherms.  $\circ$ , Diethyl sulphide;  $\triangle$ , dipropyl sulphide;  $\square$ , ethyl *n*-propyl sulphide.

but different molecular structures. The adsorption of isobutanethiol is markedly lower than that of *n*-butanethiol (Table II).

The results show that molecular sieve 13X is suitable for the adsorptive concentration and isolation of sulphur compounds from saturated hydrocarbons. The initial adsorption isotherms already mentioned for thiophene, *n*-butanethiol and diethyl sulphide show the possibility of using molecular sieve 13X for this purpose.

Fig. 1 shows that at 0.032 mg/ml of sulphur (approximately 0.003% of sulphur) concentrations of these compounds, 1 g of the molecular sieve adsorbs about 10 mg of thiophene sulphur, about 20 mg of sulphide sulphur and about 20 mg of mercaptan sulphur. The concentrations of these compounds achieved after total desorption of these amounts to 5 ml of isooctane are 2, 4 and 4 mg/ml of sulphur, respectively, *i.e.*, about 60–120 times higher than in the initial solutions.

Compounds of different classes but of similar molecular size would, however, be difficult to separate, as their adsorption differs only slightly. The influence of benzene on the adsorption of sulphur compounds is shown in Table III. These results were obtained by studying adsorption from solutions in *n*-heptane containing 5 and 10% (v/v) of benzene. It can be seen from Table III that benzene decreases the breakthrough volume (and consequently the amount of substance adsorbed) for the various compounds. It is worth mentioning that this decrease is lowest for sulphide (about two-fold at a concentration of 0.032 mg/ml of sulphur and three-fold at 0.32 mg/ml of sulphur) and highest for thiophene (about 30- and 10-fold, respectively). For *n*-butanethiol and thiophene, the decrease diminishes with increasing concentration of the sulphur compound, while there is hardly any change for sulphide. An increase

TABLE II

COMPARISON OF ADSORPTION OF *n*-BUTANETHIOL AND 2-METHYL-1-PROPANE-THIOL

Compound	Concentration (mg/ml of sulphur)			
	0.032		0.32	
	$v'$ (ml/g)	$x_2^0$ (mg/g of sulphur)	$v'$ (ml/g)	$x_2^0$ (mg/g of sulphur)
<i>n</i> -Butanethiol	627	20.1	122.5	39.2
2-Methyl-1-propanethiol	453.9	14.5	103.6	33.1

in the benzene concentration, however, always decreases the breakthrough volume. Because of this, the applicability of molecular sieves for the concentration of some sulphur compound groups in some benzene fractions is unfortunately limited, as these always contain certain amounts of aromatic hydrocarbons. This does not mean, however, that molecular sieves cannot be used for concentrating sulphides when the breakthrough volume is only slightly decreased in the presence of benzene. Concentrates of these compounds can be obtained by passing the given fraction through the molecular sieve and repeating the operation if washing the column with benzene to remove other classes of sulphur compounds is necessary.

## CONCLUSIONS

Molecular sieve 13X can be used successfully for concentrating sulphides, thiols and thiophenes from alkane solvents. Sulphur compounds can be concentrated

TABLE III

EFFECT OF BENZENE ON BREAKTHROUGH VOLUME

Compound	Concentration (mg/ml of sulphur)	Addition of benzene (% v/v)	Breakthrough volume (ml/g)
Thiophene	0.032	—	322
	0.032	5	10.9
	0.032	10	3.7
	0.32	—	84.2
	0.32	5	9.7
	0.32	10	2.4
Diethyl sulphide	0.032	—	578
	0.032	5	244
	0.032	10	175.7
	0.32	—	148
	0.32	5	42.7
	0.32	10	31.7
<i>n</i> -Butanethiol	0.032	—	627
	0.032	5	109.8
	0.032	10	76.4
	0.32	—	122.5
	0.32	5	35.6
	0.32	10	23.9

as much as 100 times in comparison with the concentration of the initial solution. The concentration can still be increased by increasing the weight of the molecular sieve. The sulphur compounds are so strongly retained by the sieve that even gas can be passed through it after adsorption, to remove the adsorbed hydrocarbons, and to obtain solely sulphur compound concentrates. Some difficulties arise, however, when aromatic hydrocarbons are present, but even then a certain concentration of some classes of compounds can be achieved, although lower than is possible in absence of aromatic hydrocarbons.

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