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Note

Sorption properties of some modified molecular sieves 13X towards thiophene and benzene

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The gas chromatographic (GC) separation of thiophene from benzene, especially when thiophene is present as a trace or minor impurity is a difficult task[1,2]. Equally difficult is the selective removal of thiophene from gasoline[3,4], which normally has a substantial content of benzene and substituted benzenes. These difficulties result from the similarities in physical constants, geometric and electronic structures of the thiophene and benzene molecules. For these reasons, efforts are still made to evaluate more selective sorbents for the separation of these compounds[5–7].

In this work, we have evaluated some modified sieves 13X for their adsorption properties in the preconcentration of thiophene from samples containing benzene and for analytical separation of these compounds.

EXPERIMENTAL

All new forms of sieves were prepared from molecular sieve 13X (100–200 mesh) (POCH, Gliwice, Poland). For ion-exchange purposes aqueous solutions of $Ni(NO_3)_2$, $AgNO_3$ and NH_4NO_3 (each 0.5 *M*) were used. Thiophene (Fluka, Buchs, Switzerland) and sulphur-free benzene (Chemistry of Coke Works, Chorzów, Poland) were analytical reagent-grade.

Preparation of exchanged and decationized sieves

Nickel(II)- and silver(I)-containing sieves were prepared from molecular sieve 13X (Na^+) by ion exchange with 0.5 *M* nickel nitrate or silver nitrate solutions. The ion-exchange process was preceded by hydrolysis of and acidification of the sieve with 0.5 *M* hydrochloric acid to pH = 6.2. An exact amount of a solution containing the cation to be exchanged was then added to a known weight of sieve. The exchange was performed for 4 h at 70–80°C with continuous stirring. The decationized sieve was also prepared from the sodium form by exchange with ammonium ions in the same manner, followed by decomposition of the ammonium form by heating at 400°C for 4 h with a continuous flow of argon.

All exchanged forms were dried and activated at 400°C for 5 h before use. Their characteristics are listed in Table I.

Chromatographic conditions

All studies of the adsorptive properties were carried out on a Fractovap 2200

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TABLE I

CHARACTERISTICS OF THE SIEVES USED

Sieve	*Fraction (mesh)*	*Amount packed in a 150 × 3 mm I.D. column (mg)*	*% of Na^+ exchanged*
NaX	100–200	130	–
HNaX	100–200	110	45
NiNaX	100–200	120	50
AgNaX	100–200	120	50

TABLE II

RETENTION VOLUMES, V_R (dm^3/g), OF THIOPHENE AND BENZENE ON VARIOUS SIEVES

Carrier gas (argon) flow-rate: 60 cm^3/min.

Temperature (°C)	*NaX*		*HNaX*		*NiNaX*		*AgNaX*	
	Thiophene	*Benzene*	*Thiophene*	*Benzene*	*Thiophene*	*Benzene*	*Thiophene*	*Benzene*
170	5.2	9.1	2.2	4.2	3.7	8.4	3.1	3.4
150	6.3	12.0	3.8	7.4	7.1	18.0	5.6	5.8
130	7.9	15.6	6.9	13.7	14.6	41.7	10.5	10.5
Calculated volumes								
20	44.9	147.2	821.4	1848.5	4307.4	32 231.6	1715.3	1207.9

Model gas chromatograph (Carlo Erba, Italy) equipped with a flame ionization detector and a Speedomax recorder. The sieves were packed into 15 cm × 3 mm glass columns. The carrier gas was argon at a flow-rate of 60 cm^3/min.

Evaluation procedure

The performance of the sieves was evaluated by comparison of their retention properties towards thiophene and benzene. The retention volumes of thiophene and benzene on unsubstituted molecular sieve, NaX, and on nickel-, silver- and hydrogen-containing sieves were determined by elution gas chromatography at 130–170°C. Three injections were made in each case and average values of V_R were calculated.

TABLE III

PARAMETERS OF THE REGRESSION CURVES $\log V_R = a + b \cdot \frac{1}{T}$

Parameter	*NaX*		*HNaX*		*NiNaX*		*AgNaX*	
	Thiophene	*Benzene*	*Thiophene*	*Benzene*	*Thiophene*	*Benzene*	*Thiophene*	*Benzene*
a	−1.116	−1.394	−4.672	−4.537	−5.414	−6.076	−4.849	−4.455
b	811.6	1044.3	2224.2	2287.7	2652.5	3102.8	2369.6	2209.6
r	0.9995	0.9982	0.9957	0.9999	0.9985	0.9998	0.9930	0.9975
r^2	0.9997	0.9991	0.9978	0.9999	0.9992	0.9998	0.9965	0.9987

The retention volumes at the preconcentration temperature, 20°C, were calculated by extrapolation of the relationship

$$\log V_R = a + b \cdot \frac{1}{T}$$

where V_R = retention volume per gram of adsorbent, T = column temperature (K) and a and b = constants. The values of V_R were not corrected for the gas hold-up volume because of the small amount of sieves used and the long retention times of thiophene and benzene.

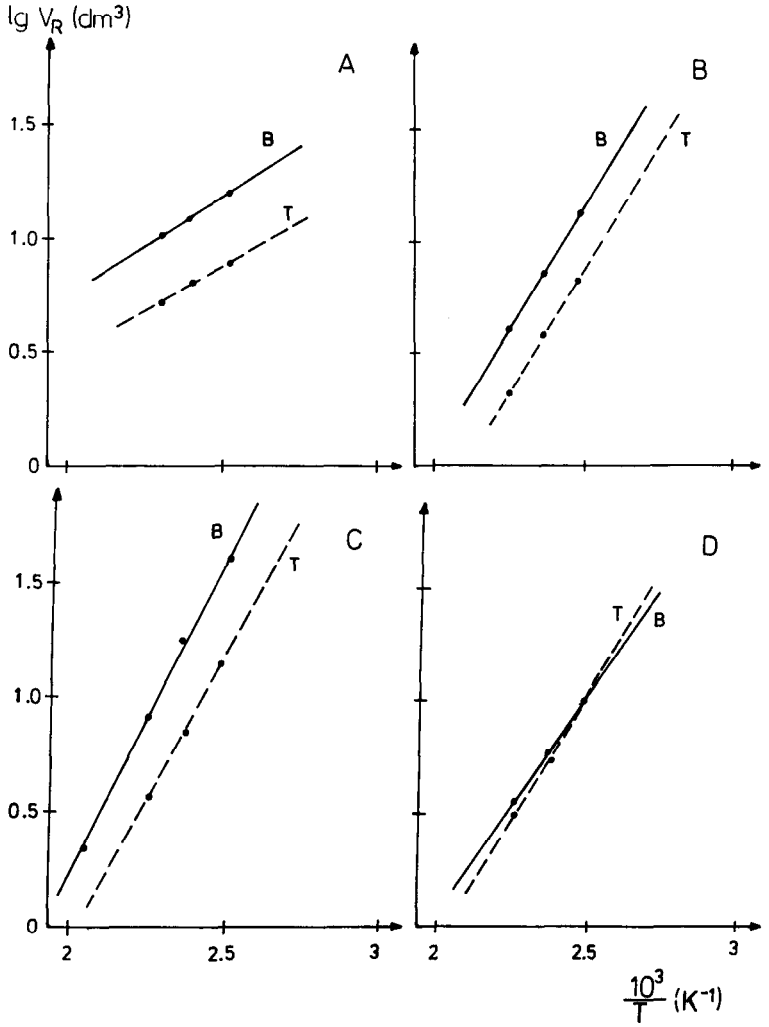

Fig. 1. The dependence of the retention volumes of thiophene (T) and benzene (B) on temperature. A, Molecular sieve 13X; B, hydrogen-containing; C, nickel-containing; D, silver-containing sieve.

RESULTS AND DISCUSSION

The retention volumes of thiophene and benzene on all forms of sieves at three temperatures in the range 130–170°C and extrapolated values for 20°C are presented in Table II. In Table III the parameters of the regression curve $\log V_R = a + b(1/T)$ are collected. Because each curve is based only on three points, the regression constants as well as the V_R data at 20°C can be used only as rough estimates.

The data in Table II reveal the substantial differences in sorption properties of the modified sieves in comparison with the unsubstituted sieve, NaX. The changes in retention volumes with temperature are larger on the modified forms than on NaX (Fig. 1). On the silver form a considerable change in the relative retention of thiophene and benzene in comparison to NaX is observed. This sieve is the best sorbent for preconcentration purposes because at temperatures below 130°C thiophene is more strongly retained than benzene; the relative retention of thiophene and benzene changes from 0.91 at 170°C to 1.42 at 20°C. It should enable the preconcentration and isolation of thiopohene at room temperature from samples containing benzene. Preliminary experiments have confirmed this. From an analytical point of view, the most useful relative retention was observed on the nickel-containing sieve. On this sieve the lowest relative retention (0.44) at 170°C was observed. This would enable the separation and determination of thiophene in benzene on a column of the nickel-containing sieve using a flame ionization detector.

A paper on this new method has recently been published[8].

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