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Lead selenide as a polar adsorbent for gas chromatography

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ABSTRACT

The properties of lead selenide (PbSe), a crystalline adsorbent with a simple cubic lattice, were investigated by means of gas chromatography. The retention volumes V_g (per gram of adsorbent), the relative retention volumes V_{rel} (with respect to *n*-alkane), Kováts retention indices and differential initial heats of adsorption with a close-to-zero filling of the surface for different classes of compounds were determined on PbSe. The presence of π-bonds in aromatic compounds, a free electron pair on the oxygen atom in the esters and hydroxyl groups in the alcohols is shown to make considerable contributions to adsorption on PbSe. The characteristics of adsorption on PbSe were compared with those on adsorbents and liquid stationary phases of different polarity. It is shown that PbSe can be classified as a medium-polarity adsorbent with a homogeneous surface. Columns with PbSe were used for the separation of oxygen- and nitrogen-containing compounds.

INTRODUCTION

The investigation and application of inorganic salts in gas chromatography have been described by numerous workers [1–5]. It has been shown that alkali metal halides can be successfully used for high-temperature analyses of mixtures of polyphenyls and polynuclear aromatic hydrocarbons. Among the shortcomings of such adsorbents is the hydrophilicity of the surface and, therefore, the necessity for thorough drying of the carrier gas [4]. In this work the properties of the surface of lead selenide (PbSe), a crystalline adsorbent with a cubic lattice of the NaCl type, were investigated using gas chromatography (GC). The PbSe surface, mainly formed by (100) faces, consists of staggered metal and non-metal atoms. The determination of the thermodynamic characteristics of adsorption on PbSe is of interest from the point of view both of investigating the molecular adsorbate–adsorbent interactions and of assessing the possibility of using PbSe in analytical GC.

EXPERIMENTAL

PbSe powder with a specific surface area of 0.5 m^2/g and particle size 0.16–0.2 nm, manufactured at the Stavropol chemical reagent plant (U.S.S.R.), was used as the adsorbent. Investigations were performed on Tsvet-100 (U.S.S.R.) and Chrom-5 (Czechoslovakia) gas chromatographs with the use of a flame ionization detector and pure helium as the carrier gas. Glass columns (0.5–1.2 m × 1.5–3 mm I.D.) were used. To study the thermal stability of PbSe the sample was heated in a stream of helium for 10 h in the range 150–300°C. The GC characteristics of PbSe were constant up to 250°C, but at higher temperatures a decrease in the retention values of different classes of compounds was observed.

The following properties were determined for hydrocarbons and oxygen- and nitrogen-containing compounds by GC on PbSe in the range 60–250°C: retention volumes V_g (per gram of adsorbent), relative retention volumes V_{rel} ($V_{rel} = V_g / V_{g\ n\text{-alkane}}$), Kováts retention indices and differential initial heats of adsorption q_1 with slight filling of the surface. The heats of adsorption were calculated from the log V_g *vs.* inverse temperature dependence.

RESULTS AND DISCUSSION

Table I gives the values of V_{rel} and q_1 on PbSe. The V_{rel} and q_1 values of *n*-alkanes are smaller than those for alkylbenzenes with the same number of carbon atoms in the molecule; therefore, during adsorption on PbSe the electrostatic interaction of the aromatic ring π-bonds with the adsorbent surface occurs. The presence of alternating cations and anions on the PbSe surface also leads to a strong adsorption of molecules having an oxygen- or a nitrogen-containing group. A change in the geometry of molecules, resulting in a decrease in the number of contacts with the adsorbent surface, leads to a decrease in the adsorption values on PbSe. Thus, isopropylbenzene is adsorbed more weakly than *n*-propylbenzene and 2-methyl-1-propanol more weakly than *n*-butanol.

It was of interest to compare the adsorption characteristics on PbSe and on known adsorbents of different types. WSe_2 is an example of a non-specific adsorbent with a layered structure. The main role in adsorption on WSe_2 is played by non-polar basal faces filled with selenium atoms. The silica adsorbent Silochrome is a polar adsorbent of type II according to Kiselev's classification [1]. From Table I the heats of

TABLE I

RELATIVE RETENTION VOLUMES, V_{rel} (WITH RESPECT TO *n*-NONANE), AT 120°C AND HEATS OF ADSORPTION, q_1 (kJ/mol), ON PbSe, WSe_2 [6] AND SILOCHROME [7]

Adsorbate	q_1			
	V_{rel} (PbSe)	PbSe	WSe_2	Silochrome
n-Octane	0.36	49	50	41
n-Nonane	1.00	55	57	47
n-Decane	2.86	61	63	52
Ethylbenzene	0.61	53	45	60
n-Propylbenzene	1.53	60	51	67
Isopropylbenzene	1.07	54	–	64
di-*n*-Butyl ether	2.15	65	51	–
1-Butanol	5.80	–	–	–
2-Methyl-1-propanol	4.30	–	–	–
Nitrobenzene	5.62	–	–	–

adsorption of n-alkanes, adsorbed non-specifically on PbSe and WSe_2 [6], are seen to be close in value, but to exceed q_1 on the polar adsorbent Silochrome [7]. However, the partially ionic nature of bonding in PbSe leads to an increase in the contribution made by specific interactions of molecules, in which electron density is concentrated on the periphery of individual bonds, as compared with WSe_2 [6] where the bonds inside the layers are mainly of the covalent type. For instance, in contrast to WSe_2, on PbSe the heats of adsorption of di-n-butyl ether and n-propylbenzene are higher than that for n-nonane, although the total polarizabilities of these molecules are similar. Also, the magnitude of the contribution made by the energy of specific interactions between aromatic hydrocarbons on PbSe is lower than that on Silochrome [7] as the surface of PbSe crystals is uniformly occupied by cations and anions that are similar in size [1]. Fig. 1 shows the dependence of log V_{rel} (with respect to n-nonane) for n-alkanes, ethers and esters on the number of carbon atoms, n, in the molecule of PbSe, $WeSe_2$ [6] and Silochrome [7].

The same functional groups make a much greater contribution to adsorption on Silochrome than on PbSe, which is mainly explained by the formation of hydrogen

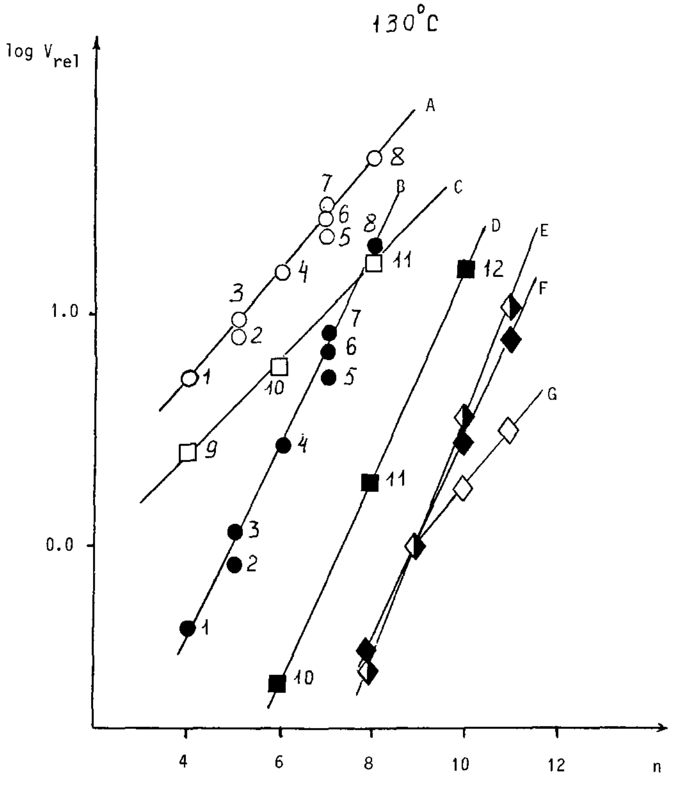

Fig. 1. Dependence of log V_{rel} on the number of carbon atoms in the molecule (n) for n-alkanes (E, F, G), ethers (C, D) and esters (A, B) on PbSe (B, D, F), Silochrome (A, C, G) and WSe_2 (E). 1 = Ethyl acetate; 2 = methyl butyrate; 3 = n-propyl acetate; 4 = ethyl butyrate and n-propyl propionate; 5 = *sec.*-butyl propionate; 6 = n-butyl propionate and n-propyl butyrate; 7 = amyl acetate; 8 = amyl propionate; 9 = diethyl ether; 10 = di-n-propyl ether; 11 = di-n-butyl ether; 12 = di-n-amyl ether.

TABLE II

VALUES OF $\Delta I = I - I_{\text{squalane}}$ ON DIFFERENT STATIONARY PHASES AT 100°C

Adsorbate	PbSe	Silochrome [10]	Tween-80 [8]	OV-225 [8]
Benzene	12	14	214	217
Ethanol	483	634	420	320
Methyl ethyl ketone	289	550	278	333
Pyridine	326	679	365	369

bonds between oxygen-containing molecules and the surface hydroxyl groups of Silochrome [1,7]. The contribution of a methylene unit to the value of the energy of adsorption of *n*-alkanes, determined by the slope of the log V_{rel} *vs*. *n* linear dependence, increases from Silochrome to PbSe (0.46 on PbSe) and then to WSe_2 (Fig. 1). It is of interest that lead selenide is much superior to squalane [2] in its selectivity towards the homologous series of *n*-alkanes (contribution per CH_2 group = 0.3) but is inferior to the known non-polar adsorbents [2].

The most commonly considered characteristic of the stationary phase in GC is its conventional chromatographic polarity [2,8]. To determine the polarity and selectivity of columns with PbSe, as was done by others [2,8–10], we calculated the differences between Kováts retention indices, I, of standard substances on PbSe and on squalane stationary phase: $\Delta I = I_{\text{PbSe}} - I_{\text{squalane}}$. The results for PbSe, Silochrome [10], and medium-polarity liquid phases [8] are given in Table II. The ΔI values on PbSe show that, with respect to oxygen- and nitrogen-containing compounds, the adsorbent belongs to the class of medium-polarity chromatographic materials and that PbSe is less polar than Silochrome. The small ΔI value for benzene indicates that PbSe is of low selectivity towards mixtures of unsaturated hydrocarbons. Nevertheless, PbSe can be recommended for the separation of molecules having active functional groups.

Table III gives the values of V_g and of selectivity coefficients α ($\alpha = V_{g,1}/V_{g,2}$) on PbSe for compounds with similar physico-chemical properties. High α values for the pairs *n*-propanol–*n*-heptane and ethanol–methyl ethyl ketone indicate interactions of

TABLE III

V_g (cm^3/g) AND SELECTIVITY COEFFICIENTS, α, ON PbSe AT 120°C

M = molecular mass; T = boiling point (°C); μ = dipole moment (D).

Adsorbate	M	T	μ	V_g	α
n-Propanol	60	97.8	1.66	1.53	14.5
n-Heptane	100	98.4	–	0.11	
Ethanol	46	78.3	1.68	0.51	1.4
Methyl ethyl ketone	80	79.5	2.75	0.36	
2-Methyl-2-propanol	74	82.2	1.66	1.72	1.7
2-Propanol	60	82.4	1.68	1.00	
n-Propyl acetate	102	101.6	1.86	0.96	1.4
Methyl butyrate	102	102.5	1.70	0.69	

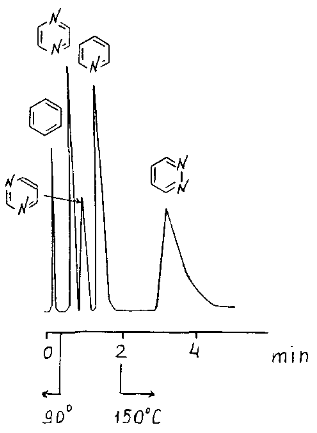

Fig. 2. Chromatogram of benzene and nitrogen-containing heterocyclics. Column, 60 × 0.3 cm I.D.

the hydrogen-bond type during the adsorption of alcohols on PbSe. The differences in the energies of adsorption for molecules with close boiling points and dipole moments (2-propanol and 2-methylpropanol; methyl butyrate and *n*-propyl acetate) is mainly determined by the number of contacts between the units of a molecule and the adsorbent surface. PbSe thus has a sufficiently high separation ability with respect to the molecules with similar physico-chemical properties.

The chromatograms shown in Figs. 2 and 3 demonstrate the possibility of using PbSe in gas-adsorption chromatography. Owing to the manifestation of sufficiently strong electrostatic interactions, the separation of 1,4-, 1,3- and 1,2-diazines can be achieved on PbSe (Fig. 2). The elution sequence of these compounds is explained by the increase in dipole–dipole interactions. The adsorption of benzene is noticeably weaker than that of heterocyclic compounds, *i.e.*, the presence of a free electron pair on the

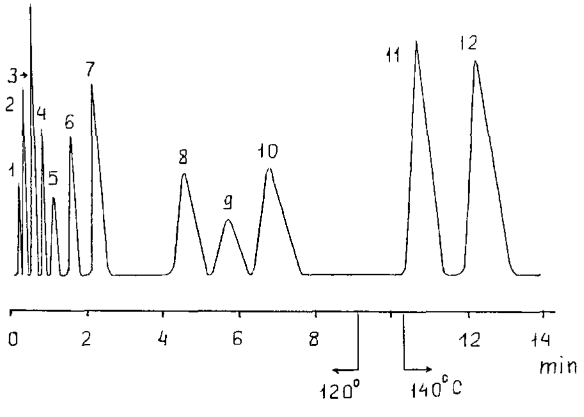

Fig. 3. Chromatogram of a mixture of ethers and esters on PbSe. Column, 120 × 0.2 cm I.D. 1 = Diisopropyl ether; 2 = di-*n*-propyl ether; 3 = ethyl acetate; 4 = methyl butyrate; 5 = *n*-propyl acetate; 6 = di-*n*-butyl ether; 7 = ethyl butyrate; 8 = *sec.*-butyl propionate; 9 = *n*-butyl propionate; 10 = amyl acetate; 11 = di-*n*-amyl ether; 12 = amyl propionate.

nitrogen atom makes a considerable contribution to the adsorption on PbSe, as distinct from non-polar adsorbents [11].

The sensitivity of retention values in adsorption on PbSe to the electronic and geometric structure of molecules makes it possible to apply this adsorbent to the separation of a mixture of ethers and esters (Fig. 3). For instance, PbSe has a sufficiently high selectivity for the separation of isomers such as *sec.*-butyl propionate, *n*-butyl propionate and amyl acetate.

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