Journal of Chromatography, 446 (1988) 79–86
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 1367

USE OF MODIFIED TUNGSTEN SELENIDE AS AN ADSORBENT FOR GAS CHROMATOGRAPHY

T. B. GAVRILOVA*, T. M. ROSHCHINA and E. V. VASIL'EVA
Adsorption and Chromatography Laboratory, Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow (U.S.S.R.)

SUMMARY

Tungsten selenide (WSe_2) is a crystalline adsorbent with a lamellar structure. In order to remove the residual non-homogeneity of the tungsten selenide surface, samples were subjected to adsorption modification with small amounts of liquid phases of different polarities [poly(ethylene glycol) 1500 and Dexil 300]. The effect of the modifying agent on the adsorption and chromatographic properties of tungsten selenide was studied. It was shown that on application of PEG 1500 in amounts lower than 0.3 mg/m^2 the surface of the adsorbent becomes more homogeneous and non-polar. Modifications with Dexil 300 gave no positive results. Columns with tungsten selenide modified with small amounts of PEG 1500 were used in the chromatographic analysis of organic substances.

INTRODUCTION

In gas chromatography, much attention is paid to the adsorption properties of inorganic salts and to the use of inorganic salts in analytical practice[1–5]. However, the surfaces of many inorganic salts are to a certain extent geometrically and chemically non-homogeneous. One of the efficient methods for the elimination of the residual non-homogeneity of the adsorbent surface is adsorption modification.

A number of papers[2,3,6–9] reported studies of the effect of the nature and amount of modifying agents on the adsorption and gas chromatographic properties of carbonic, silicic and other adsorbent supports. It was demonstrated that the application of a modifier in amounts less than or equal to a dense monolayer broadens the range of use of the initial adsorbents in gas chromatography and increases the efficiency of columns and the separation selectivity. On the other hand, adverse effects related to the heterogeneity of the adsorbent surface are fully or partly eliminated.

Both non-polar (*e.g.*, Apiezons, squalane, Dexil) and polar [poly(ethylene glycols) and organic substances containing carboxy, nitrile, nitro groups] compounds are employed as modifying agents. The choice of the optimal modifying agent is mostly governed by its ability to adsorb strongly on non-homogeneous areas of the surface and by the possibility of control of the selectivity of chromatographic columns[2,3,9].

Investigations of the properties of the tungsten selenide (WSe_2) surface showed

0021-9673/88/$03.50

that adsorption of hydrocarbons and other low-polarity molecules on the most homogeneous samples is basically determined by dispersion forces of interaction with non-polar basal faces filled with selenium atoms. Tungsten selenide features a high selectivity towards molecules with different geometric structures and for this reason is suitable for the separation of structural isomers and stereoisomers[10]. However, asymmetry of the chromatographic peaks of compounds with active functional groups indicates the existence of non-homogeneous areas on the tungsten selenide surface. In order to eliminate the residual non-homogeneity of the surface we carried out adsorption modification of tungsten selenide with liquid stationary phases of different polarities.

EXPERIMENTAL

Tungsten selenide powders with a 2 m^2/g surface area were compacted under a pressure of 7–9 MPa. After grinding the tablets, the 0.22–0.25 mm and 0.25–0.3 mm fractions were selected. The samples were subsequently heated for 10 h at 150°C in a current of helium. PEG 1500 or Dexil 300 was applied to the tungsten selenide by adsorbing the modifier from chloroform solutions. After solvent evaporation the chromatographic columns with the modified samples were conditioned at 150°C for 20 h in a current of the carrier gas (helium). Using this technique, we obtained samples containing 0.1–1 mg/m^2 of the modifier.

Gas chromatographic experiments were run on a Tsvet-102 chromatograph equipped with a flame ionization detector. The column dimensions were 0.5–1.0 m × 1.5–3 mm I.D.

Adsorption of molecules with different geometric and electronic structures (hydrocarbons and oxygen-, nitrogen- and halogen-containing compounds) was studied at surface coverages close to zero. Retention volumes per unit adsorbent mass, V_g, and relative retention volumes, $V_{rel} = V_g/V_{g,n\text{-alkane}}$, were determined[2].

RESULTS AND DISCUSSION

Fig. 1 shows the dependence of the retention volumes, V_g, of different molecules on the amount of PEG 1500 applied to tungsten selenide. The application of 0.1 mg/m^2 of PEG does not affect the V_g values of hydrocarbons. At the same time, a strong decrease in adsorption and an increase in the symmetry of the chromatographic peaks of molecules with peripheral functional groups (*e.g.*, alcohols and ketones) were observed.

It seems that on application of 0.1 mg/m^2 of poly(ethylene glycol) the molecules of the modifier are located on the surface of the polar side faces of the tungsten selenide crystals, which does not have any effect on the retention volumes of molecules adsorbed on non-polar basal faces filled with selenium atoms.

An increase in the amount of the modifier to 0.3–0.5 mg/m^2 reduces the retention volumes of all the adsorbates under study as the poly(ethylene glycol) screening of the force centres of tungsten selenide lowers the total adsorption energy.

We compared the V_{rel} values of a number of adsorbates on the initial and modified tungsten selenide samples with the aim of evaluating the contribution of specific interactions to adsorption (Table I).

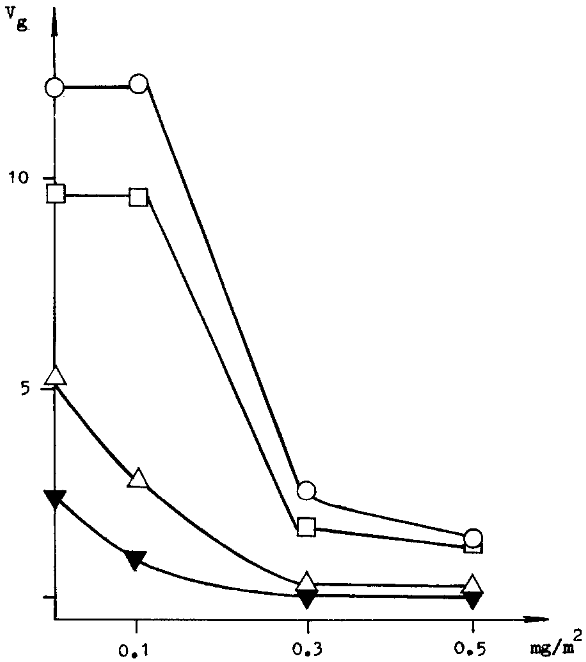

Fig. 1. Dependence of V_g of various compounds at 120°C on the amount of PEG 1500 applied to the surface of WSe_2. ○, *n*-Nonane; □, *n*-propylbenzene; △, ethanol; ▼, acetone.

TABLE I

RELATIVE RETENTION VOLUMES, V_{rel} (WITH RESPECT TO *n*-NONANE), ON THE INITIAL AND MODIFIED WSe_2 SURFACE AT 120°C

Adsorbate	V_{rel}						
	WSe_2	*Amount of Dexil-300 (mg/m²)*		*Amount of PEG 1500 (mg/m²)*			
		0.1	*0.3*	*0.1*	*0.3*	*0.5*	*1.0*
n-Octane	0.34	0.33	0.34	0.33	0.32	0.37	0.39
Ethylbenzene	0.31	0.30	0.37	0.29	0.27	0.42	0.52
n-Propylbenzene	0.79	0.81	1.00	0.77	0.70	0.96	1.15
o-Xylene	0.53	0.54	0.60	0.54	0.56	0.62	0.79
Bromobenzene	0.38	0.42	0.61	0.36	0.33	0.64	0.95
Di-*n*-butyl ether	0.88	0.87	0.88	0.72	0.66	0.68	0.74
n-Butanol	0.92	–	–	0.41	0.32	0.35	0.44
Acetonitrile	0.10	–	–	0.09	0.05	0.07	0.11
Acetone	0.21	0.19	0.22	0.07	0.03	0.03	0.07

On samples containing PEG in the range 0.1–0.3 mg/m^2, mono-n-alkylbenzenes are retained more weakly than n-alkanes having an identical number of carbon atoms in the molecule and di-n-butyl ether is adsorbed more weakly than n-nonane. The order of emergence of these molecules is the same as that on other non-specific adsorbents[1,2]. Therefore, the presence of π-electron bonds in an aromatic hydrocarbon or of a free electron pair on the oxygen atom in the ether molecule makes a small contribution to adsorption on the tungsten selenide surface modified with small amounts of poly(ethylene glycol). Therefore, the adsorption of low-polarity molecules on samples containing 0.1–0.3 mg/m^2 of PEG is mostly governed by dispersion forces and takes place on non-polar basal faces.

The screening of non-homogeneous areas leads to a strong decrease in the V_{rel} of molecules with a high dipole moment (acetone, butanol).

An increase in surface coverage with poly(ethylene glycol) (0.5–1 mg/m^2) enhances the electrostatic interactions of all adsorbed molecules of groups B and D (according to Kiselev's classification[1]) with the ether and terminal hydroxy groups of poly(ethylene glycol).

Other dependences were observed on adsorption of poly(ethylene glycol) on graphitized carbon blacks, which are the most homogeneous and non-polar of all adsorbents. It was shown in earlier studies[3,6–8] that the application of small amounts of poly(ethylene glycol) (0.1–0.3 mg/m^2) to graphitized carbon black strongly reduces the energy of non-specific interaction, the retention volumes of n-alkanes decreasing drastically. However, the modification of graphitized carbon black with poly(ethylene glycol) is simultaneously accompanied by an increase in the contribution of the specific interaction energies of molecules of groups B and D. Therefore, the retention volumes of alcohols increase until 0.4 mg/m^2 of PEG 1000 has been applied to the adsorbent surface[3,6], which is explained by the fact that the polymer molecules on graphitized black are oriented almost linearly along its surface; as a result, strong specific interactions on adsorption of alcohols can take place not only with the ether groups but also with the terminal hydroxy groups of poly(ethylene glycol).

With small amounts of PEG (0.1–0.3 mg/m^2) present on tungsten selenide, the adsorption of molecules is mainly determined by dispersion interaction forces. A considerable decrease in the adsorption values of molecules capable of strong specific interaction and hydrogen bond formation can be explained by adsorption of PEG on the most non-homogeneous areas of the surface of tungsten selenide crystals, mostly on the polar side faces. It appears that in this instance strong bonds between the terminal hydroxy groups of PEG and the non-homogeneous areas on the surface hinder the participation of these groups in specific interactions.

Hence the character of changes in the properties of the surface on PEG modification depends on the initial adsorbent support.

Our results show that the modification of tungsten selenide with small amounts of poly(ethylene glycol) makes it possible to increase greatly the homogeneity of the adsorbent. The main role in adsorption is still played by non-polar basal faces.

Table I gives the V_{rel} values obtained on tungsten selenide modified with Dexil 300. The presence of the non-polar modifier has no effect on the adsorption properties of tungsten selenide, the asymmetry of the chromatographic peaks remains unchanged and substances capable of electrostatic interaction show large adsorption values. Therefore, Dexil-300 modification is not efficient from the viewpoint of the imrovement of the chromatographic process on tungsten selenide.

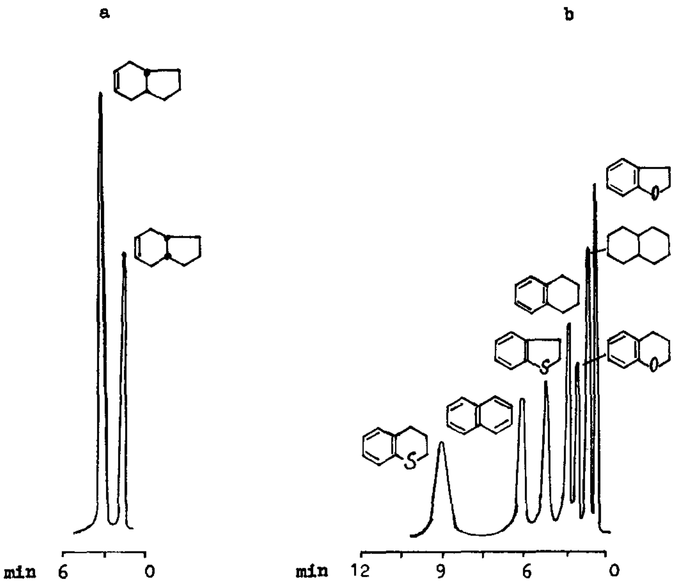

Fig. 2. Chromatograms of (a) bicyclic compounds (at 100°C) and (b) heterocycles (at 150°C) on WSe_2 modified with 0.1 mg/m^2 of PEG 1500. Column: 100 cm × 0.15 cm I.D.

Columns with tungsten selenide modified with small amounts of PEG were used to separate mixtures of organic substances belonging to various classes. The chromatogram in Fig. 2a illustrates the separation of steric isomers (*cis*- and *trans*-bicyclononenes) which differ considerably in their geometic structures and in the arrangement on the surface. The separation is due to the difference in the number of contacts of the links of the molecules with the flat surface. The analysis time on tungsten selenide with 0.1 mg/m^2 of PEG is shorter than that on other non-polar carbonic adsorbents[11].

Fig. 2b shows a chromatogram for the separation of bicyclic hydrocarbons and their oxygen- and sulphur-containing analogues. Tetralin, chroman and thiochroman have similar geometric structures. Chroman is eluted the first from the tungsten selenide packed column, followed by tetralin and then thiochroman. This elution sequence is a result of the increase in polarizability in the oxygen, CH_2 group and sulphur series and consequently of the enhancement of the dispersion interaction of these molecules with the tungsten selenide surface, much like the situation on the surface of hydrogen-treated graphitized thermal carbon black[2,3,12].

The separations shown in Fig. 2 support the statement that the main role in the adsorption of molecules on the modified tungsten selenide surface is played by basal faces.

The increase in the separating ability of columns packed with tungsten selenide through an increase in surface homogeneity on modification with PEG permits the use of this adsorbent in the separation of substances capable of specific interactions.

Halogen derivatives of cyclopropanes are used in the synthesis of complex polycyclic systems containing high-energy small rings. Fig. 3a shows a chromatogram for the separation of chlorine derivatives of cyclopropanes. PEG-modified WSe_2

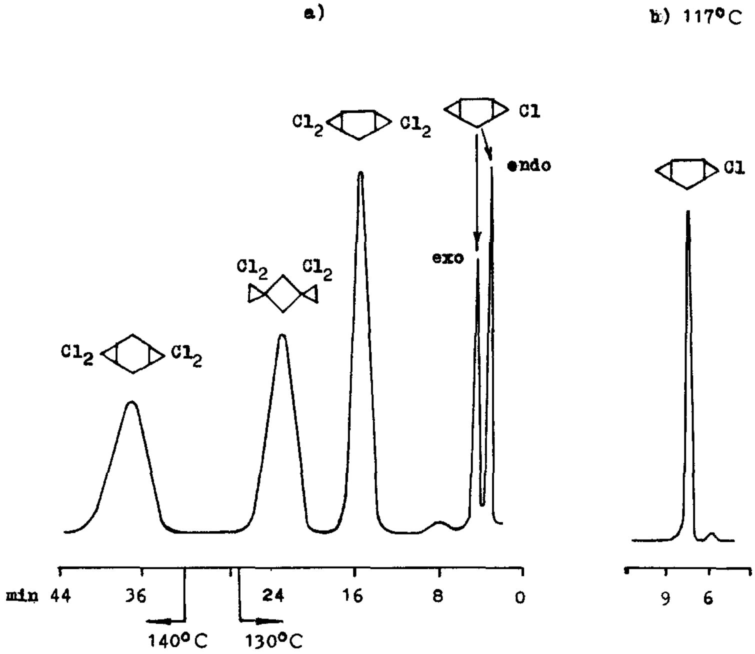

Fig. 3. Chromatograms of a mixture of chlorine derivatives of cyclopropanes: (a) on WSe_2 modified with 0.1 mg/m^2 of PEG 1500 with a 100 cm × 0.2 cm I.D. column; (b) on 5% SE-30 applied to Chromaton N with a 200 cm × 0.2 cm I.D. column.

provides a complete separation of the isomers of tetrachlorodispiro[2.2.2]hexane and 4,4,8,8-tetrachlorotricyclo[5.1.0.$0^{3,5}$]octane; 7-monochlorotricyclo[4.1.0.$0^{2,4}$]heptane shows two peaks belonging to its *endo* and *exo* isomers.

It should be noted that on a packed column containing SE-30 stationary phase 7-monochlorotricyclo[4.1.0.$0^{2,4}$]heptane is eluted as a single peak (Fig. 3b), which means that the selectivity of the column with modified tungsten selenide is much higher

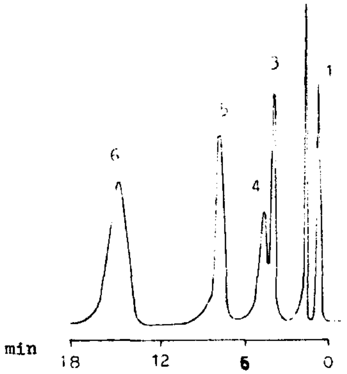

Fig. 4. Chromatogram of a mixture of oxo compounds on WSe_2 modified with 0.3 mg/m^2 of PEG 1500. Column: 100 cm × 0.15 cm I.D. Peaks: 1 = valeraldehyde; 2 = dipropyl ketone; 3 = ethyl butyl ketone; 4 = enanthaldehyde; 5 = di-*n*-butyl ether; 6 = methyl hexyl ketone.

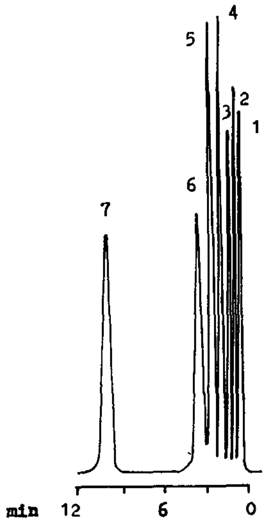

Fig. 5. Chromatogram of a mixture of esters on WSe_2 modified with 0.3 mg/m^2 of PEG 1500. Column: 100cm × 0.15 cm I.D. Temperature, 90°C. Peaks: 1 = ethyl acetate; 2 = propyl acetate; 3 = *sec.*-butyl acetate; 4 = propyl propionate; 5 = *sec.*-butyl propionate; 6 = isobutyl propionate; 7 = amyl butyrate.

than that of the column with the stationary phase; it can also be seen that the separation time on tungsten selenide with 0.1 mg/m^2 of PEG 1500 is shorter. Fig. 4 shows a chromatogram for the separation of oxo compounds with carbon numbers of 5–8. The selectivity of the adsorbent with respect to the structure of the molecules made it possible to separate isomeric molecules of dipropyl ketone, ethyl butyl ketone and enanthaldehyde at 80°C. Good separations were observed for isomers of esters such as *sec.*-butyl acetate–propyl propionate and *sec.*-butyl propionate–isobutyl propionate (Fig. 5).

In conclusion, the modification of tungsten selenide with small amounts of poly(ethylene glycol) widens the range of application of tungsten selenide for the gas chromatographic analysis of organic substances, with a high selectivity of tungsten selenide with respect to molecules with similar physico-chemical properties and different spatial structures remaining unchanged.

REFERENCES

1 N. N. Avgul', A. V. Kiselev and D. P. Poshkus, *Adsorbtsiya Gazov i Parov na Odnorodnykh Poverkhnostyakh (Adsorption of Gases and Vapours on Homogeneous Surfaces)*, Khimiya, Moscow, 1975.
2 A. V. Kiselev and Ya. I. Yashin, *Adsorbtsionnaya Gazovaya i Zhidkostnaya Khromatografiya (Gas and Liquid Adsorption Chromatography)*, Khimya, Moscow, 1979.
3 A. V. Kiselev, *Mezhmolekulyarnye Yzaimodeistviya v Adsorbtsii i Khromatografii (Intermolecular Interactions in Adsorption and Chromatography)*, Vysshaya Shkola, Moscow, 1986.
4 T. B. Gavrilova, A. V. Kiselev and T. M. Roshchina, *J. Chromatogr.*, 192 (1980) 323.
5 T. B. Gavrilova, A. V. Kiselev, I. V. Parshina and T. M. Roshchina, *Kolloidn. Zh.*, 48 (1986) 421.
6 A. V. Kiselev, *J. Chromatogr.*, 49 (1970) 84.
7 A. V. Kiselev, N. V. Kovaleva and Yu. S. Nikitin, *J. Chromatogr.*, 58 (1971) 19.
8 L. Ya. Gavrilina, O. A. Emelyanova, V. I. Zheivot, A. V. Kiselev and N. V. Kovaleva, *Kolloidn. Zh.*, 40 (1978) 636.

9 A. Di Corcia and A. Liberti, *Adv. Chromatogr.*, 14 (1976) 305.

10 A. V. Kiselev, T. B. Gavrilova, T. M. Roshchina, I. P. Borovinskaya, A. G. Merzhanov and L. P. Shchepinova, *Inventor's Certificate of the U.S.S.R.*, No. 1 273 153; *Byul. Izobr.*, No. 44 (1986) 30.

11 T. B. Gavrilova, T. M. Roshchina, E. V. Vlasenko, Chr. Dimitrov, S. Ivanov, N. Petsev and I. Topalova, *J. Chromatogr.*, 364 (1986) 439.

12 P. B. Dallakyan and A. V. Kiselev, *Zh. Fiz. Khim.*, 59 (1985) 1278.