

CHROM. 5213

GAS CHROMATOGRAPHY ON MONOLAYERS

A. V. KISELEV, N. V. KOVALEVA AND YU. S. NIKITIN

Laboratory of Adsorption and Gas Chromatography, M.V. Lomonosov State University of Moscow and Laboratory of Surface Chemistry, Institute of Physical Chemistry, U.S.S.R. Academy of Sciences, Moscow (U.S.S.R.)

SUMMARY

Densely adsorbed layers of polyethylene glycols of different molecular weights on graphitised carbon black and of polyarylate Ph-I on macroporous silica gel were prepared. It has been found that monolayers of polyethylene glycols possess the property of specific molecular interaction and that the contribution of the energy of specific interaction to the total heat of adsorption increases with the decreasing molecular weight of the polyethylene glycol. The deposition of polyarylate as a thin adsorbed layer on to the surface of macroporous silica gel results in a decrease in the specific adsorption. In addition, the retention of *n*-alkanes and particularly of aromatic hydrocarbons on a polyarylate film is markedly decreased in relation to porous polyarylates and a number of other porous polymers.

INTRODUCTION

Modification of non-porous and wide-pore supports by means of adsorbed dense monolayers presents the possibility of obtaining quite homogeneous surfaces of different chemical composition with low energies of adsorption¹⁻⁸. Furthermore, monolayer films held by adsorption forces on a large surface area of a strongly adsorbing support (adsorbent) are significantly more stable to heat than thick layers of these compounds on supports with small and weakly adsorbing surfaces such as are used in gas-liquid chromatography¹⁻³. Further, exchange processes on the surfaces of monolayers take place much more rapidly than in the bulk of liquids¹.

Monolayers which are particularly stable to heat are obtained by chemically modifying the supports^{1,8,9}. Graphitised carbon black¹⁻⁷ and wide porous silica gels^{1,8} are usually used as the supports for the monolayers. If polymers or large organic molecules with various functional groups are used as the modifying compounds, then it is possible to obtain quite homogeneous specific adsorbents, selective for different classes of organic compounds.

In the present work dense layers of different polymers on graphitised carbon black and on macroporous silica gel were prepared and studied.

MONOLAYERS ON GRAPHITISED CARBON BLACKS

The influence of the molecular weight (M) of the polyethylene glycols (PEG) on the density and structure of the monolayer was investigated, and the adsorption of various compounds on the surface of PEG monolayers of different molecular weight was studied.

Channel carbon black, which had been heated at 3000° for 6 h in a current of argon and which had a specific surface area $s = 80 \text{ m}^2/\text{g}$, was used as the support. PEGs with average molecular weights of 300, 3,000 and 15,000 were used. The adsorption isotherms of these polymers as determined from aqueous solutions were used to calculate the capacity of the monolayer, *i.e.*, the amount of polymer, a_m , required to cover the surface of the carbon black with a dense monolayer¹⁰. The PEG was deposited on the surface of the carbon black by adsorption from solution resulting in uniform coverage of the surface of the carbon black by the polymer¹⁰. The deposition of the polymer in amounts greater than the monolayer capacity was carried out by the usual method of depositing a liquid phase on a support as in gas-liquid chromatography³. The adsorption properties of the initial carbon black and of the modified samples were studied by means of gas chromatography using a Shimadzu GC-3A gas chromatograph. Before loading the column the samples were evacuated at 150° to about 10^{-3} torr (below the decomposition temperature of these polymers). The column temperatures were 75, 100, 130 and 150° . The compounds used as adsorbates were those whose molecules by their capability of molecular interaction belong to groups A, B and D according to the author's classification¹.

The dependence of the specific retention volumes V_g (ml/g of carbon black) of n -alkanes on the coverage of the surface of the carbon black by PEG is shown in Fig. 1. Molecules of n -alkanes belong to group A and are not capable of specific interaction with the functional groups of PEG. This dependence is also shown for benzene and diethyl ether in Fig. 1—these are molecules of group B which are capable of specific interaction with the terminal hydroxyl groups of PEG—as well as for n -alcohols—molecules of group D—which are capable of specific interaction with both the terminal hydroxyl groups of PEG and its ether groups. Molecules of group D are also capable of specific interaction with each other, forming associates.

The retention volumes of n -alkanes decrease sharply with increasing coverage of PEG up to a certain coverage, after which they remain unchanged. The sharp decrease in the retention volumes is explained by the lowering of the non-specific dispersion interaction with the adsorbent which is related to the smaller concentration of active centres on the surface as the carbon black is covered with polymer. The smaller concentration of active centres on the surface of the monolayer as compared with those on the support is connected first of all with the quite large van der Waals distance between the macromolecules when compared to that of the chemical bonds between the carbon atoms on the surface of the carbon black. This is also characteristic for adsorption on dense monolayers and on molecular crystals¹¹⁻¹³.

Molecules of alcohols may form hydrogen bonds with the functional groups of PEG. The increase in the contribution of the energy of the corresponding specific interaction to the total energy of adsorption in the region of low surface coverage of carbon black by PEG apparently predominates over the decrease in the dispersion interaction. Therefore, the retention volumes of alcohols, as can be seen from Fig. 1,

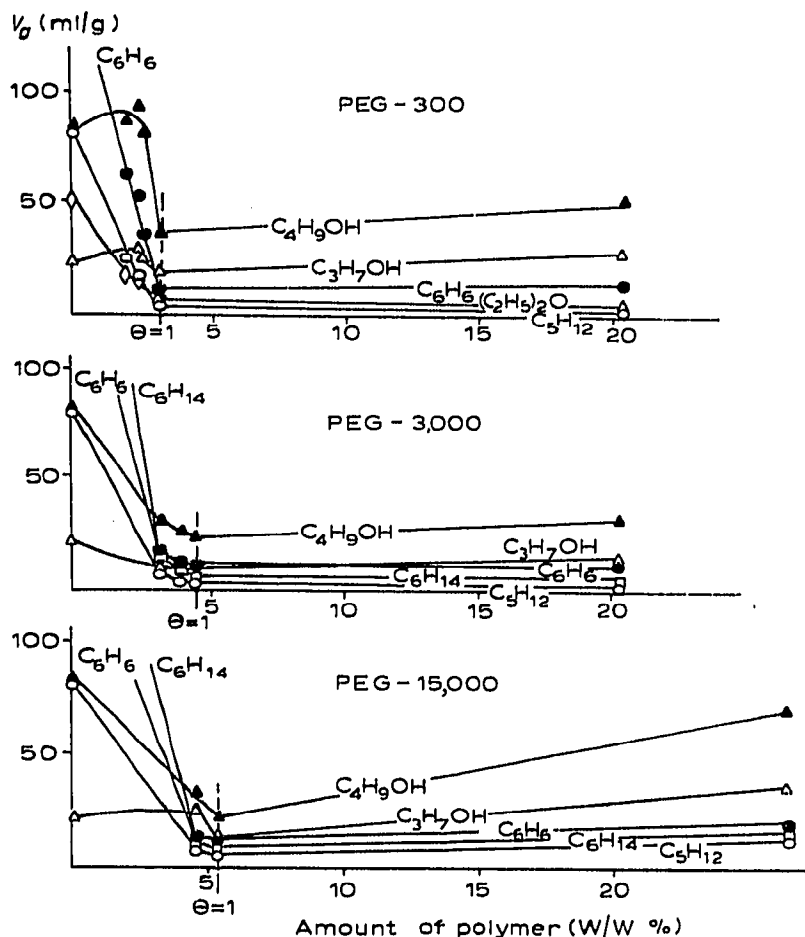


Fig. 1. Dependence of the retention volumes, V_{θ} (ml/g), on the surface coverage of graphitised channel carbon black by polyethylene glycols of different molecular weights PEG-300, PEG-3000 and PEG-15000. The adsorbates are shown on the figure. The dashed line indicates the monolayer capacity determined from the isotherms of adsorption from solution.

increase with increasing coverage of carbon black by PEG-300 up to 2.3% PEG per unit weight of carbon black, which corresponds to a surface coverage of carbon black by polyethylene glycol of approximately 75%. If the amount of PEG is increased further, up to 3% PEG per unit weight of carbon black, *i.e.* the surface of the carbon black is practically completely covered with a dense monolayer of PEG, the retention volume of the alcohols decreases. It is evident that in this region the decrease in the dispersion interaction predominates over the increase in the specific interaction. With an even greater amount of PEG-300 on the surface of the carbon black, the retention volumes of the alcohols again increase and this is the result of the solution of the alcohols in the polymolecular film of PEG.

No increase in the retention volumes of alcohols with increasing surface coverage of carbon black has been observed for the larger macromolecules PEG-3000 and 15000. The packing of these macromolecules in the deposited layers is less orderly (and therefore some of the functional groups, capable of specific interaction with molecules of alcohols, are inaccessible or are oriented less favourably for the formation of hydrogen bonds) than in the case of adsorption of alcohols on the more

orderly packed layer of the smaller macromolecule PEG-300. In the case of diethyl ether and benzene the decrease in the energy of dispersion interaction predominates over the increase in specific interaction with increasing surface coverage of the carbon black by PEG, and is independent of its molecular weight.

A sharp break in the curves showing the dependence of the retention volumes on the surface coverage of carbon black by PEG is observed at approximately the same surface coverage of carbon black by polyethylene glycol both for compounds capable and incapable of specific interaction. These amounts are shown in Fig. 1 as vertical dashed lines and correspond to the formation of a sufficiently dense monolayer of macromolecules screening the surface of the carbon black. The capacities of the monolayers evaluated by different methods are compared in Table I. They are taken from the van der Waals dimensions of the monomer of the PEG macromolecule, from the adsorption isotherms determined for solutions and from the gas chromatographic data in Fig. 1. Only in the case of the low molecular weight polymer PEG-300

TABLE I

CAPACITIES OF DENSE MONOLAYERS OF PEG DEPOSITED ON GRAPHITISED CHANNEL CARBON BLACK

<i>Modifying agent</i>	<i>Capacity of dense monolayer (mg/m²)</i>		
	<i>Calculated from the van der Waals dimensions of the monomer unit of the macromolecule</i>	<i>Determined from adsorption isotherms from solution data</i>	<i>Determined from gas chromatographic data</i>
PEG-300	0.44	0.43	0.42
PEG-3000	0.44	0.60	0.57
PEG-15000	0.44	0.74	0.73

does the capacity of the dense monolayer of the stretched-out macromolecule, calculated from the van der Waals dimensions of the monomer unit of the macromolecule, correspond to the capacity of this polymer layer determined from its adsorption isotherm from solutions. Apparently, among the PEG samples investigated, only PEG-300 molecules, with the lowest molecular weight, straighten out almost completely and pack densely on the surface of carbon black under the influence of the adsorption forces. In the case of PEG-3000 and particularly in the case of PEG-15000 complete stretching out of the macromolecules on the surface of carbon blacks does not occur. It is possible that these macromolecules are in fact not completely linear.

The macromolecules of these higher molecular weight polymers do not contact the surface of the carbon black with all their units and this is in agreement with other data¹⁴. In agreement with this is the fact that the concentration of ether groups and terminal hydroxyl functional groups of PEG, capable of specific interaction with adsorbate molecules on the surface of a dense monolayer, is greater in the case of PEG-300 than in the case of PEG-3000 and PEG-15000.

TABLE II

RETENTION VOLUMES, V_g (ml/g), AT 100° AND CORRESPONDING RELATIVE RETENTION VOLUMES, $V_g/V_g(C_6H_{12})$, ON DENSE MONOLAYERS OF PEG OF DIFFERENT MOLECULAR WEIGHT DEPOSITED ON GRAPHITISED CHANNEL CARBON BLACK

Adsorbate	Carbon black		Monolayer					
			PEG-300		PEG-3000		PEG-15000	
	V_g	$V_g/V_g(V_g(C_6H_{12}))$	V_g	$V_g/V_g(V_g(C_6H_{12}))$	V_g	$V_g/V_g(V_g(C_6H_{12}))$	V_g	$V_g/V_g(V_g(C_6H_{12}))$
$n-C_6H_{12}$	80	1.00	2.50	1.00	2.5	1.00	2.50	1.00
$n-C_8H_{14}$	253	3.17	5.30	2.12	5.35	2.14	5.38	2.14
C_6H_6	172.5	2.18	11.2	4.46	10.20	4.08	9.15	3.66
$(C_2H_5)_2O$	51.7	0.65	3.36	1.35	2.85	1.14	2.75	1.10
$n-C_3H_7OH$	23.2	0.18	14.6	5.81	10.45	4.18	8.10	3.40
$n-C_4H_9OH$	82	1.03	39.6	15.7	24.4	9.76	19.10	7.64

In accordance with this, on dense monolayers of PEG with different molecular weights the retention volumes of the n -alkanes which are adsorbed non-specifically are the same, but the retention volumes of compounds, capable of specific interaction with the functional groups of PEG, decrease with increasing molecular weight of the PEG. This is evident from Table II. It is also evident from Table II that PEG monolayers are particularly selective with respect to alcohols.

In order to evaluate the contribution of the energy of specific interaction of various molecules on monolayers of PEG to the total heat of adsorption it is convenient to compare the heats of adsorption of these molecules with those incapable of specific interaction (*viz.* n -alkanes)^{1,7,15,16}. The dependence of the heats of adsorption on the total polarisability of molecules^{7,16} belonging to groups B and D

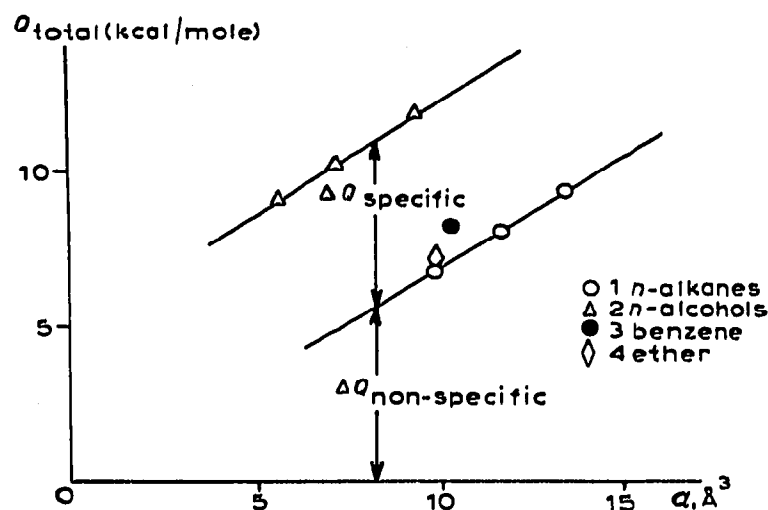


Fig. 2. Dependence of heats of adsorption, Q , at low surface coverage with a dense monolayer of PEG-300 (deposited on channel carbon black treated at 3000°), on the polarisability, α , of the adsorbate molecules. The contributions of the energy of non-specific interaction, $\Delta Q_{\text{non-specific}}$, and of the specific interaction, $\Delta Q_{\text{specific}}$, with the monolayer are indicated by arrows.

were therefore compared with the corresponding dependence for *n*-alkanes, molecules of group A (Fig. 2).

The contribution of the energy of specific interaction, $\Delta Q_{\text{specific}}$, was determined as the difference between the experimental heat of adsorption and the non-specific component which was found from the characteristic straight line which shows the dependence of the heats of adsorption of molecules of group A (*n*-alkanes), at low coverage, on the polarisability (Fig. 2 and Table III). On a dense monolayer of PEG-300 $\Delta Q_{\text{specific}}$ for alcohols is 5.5 kcal/mole, *i.e.* the energy of a hydrogen bond characteristic for alcohols. On increasing the molecular weight of the PEG the contribution of the specific interaction decreases for all compounds which are capable of specific interaction with the functional groups of PEG. This also shows that the concentration and availability of the functional groups on the surface of the monolayer decreases with increasing molecular weight of the deposited polymer and the orientation of these functional groups becomes less advantageous for specific interaction with molecules adsorbed from the gas phase.

It may be seen from Table III that the strongest specific interaction with the functional groups of PEG is observed for molecules of group D—for alcohols. At the same time the total energy of interaction of these molecules with a PEG monolayer is small. The large contribution of $\Delta Q_{\text{specific}}$ together with the comparatively small contribution $\Delta Q_{\text{non-specific}}$ permits the advantageous use of such a monolayer for the chromatographic separation of mixtures of alcohols. The separation of mixtures

TABLE III

APPROXIMATE VALUES OF HEATS OF ADSORPTION, Q , AND CONTRIBUTION OF ENERGY OF SPECIFIC INTERACTION, $\Delta Q_{\text{specific}}$, TO THEM, WHEN VARIOUS MOLECULES ARE ADSORBED ON THE SURFACE OF A DENSE MONOLAYER OF PEG DEPOSITED ON GRAPHITISED CHANNEL CARBON BLACK

Adsorbent	C_6H_6		$(C_2H_5)_2O$		<i>n</i> - C_3H_7OH		<i>n</i> - C_4H_9OH	
	Q	$\Delta Q_{\text{spec.}}$	Q	$\Delta Q_{\text{spec.}}$	Q	$\Delta Q_{\text{spec.}}$	Q	$\Delta Q_{\text{spec.}}$
PEG-300	8.3	1.3	7.1	0.3	10.3	5.6	12.0	5.6
PEG-3000	8.2	1.1	7.0	0.2	9.4	4.7	11.2	4.7
PEG-15000	8.4	0.9	7.1	0.0	8.9	3.6	10.9	3.6

of all alcohols from C_1 to C_4 is shown in Fig. 3. On channel carbon black (as distinct from graphitised thermal carbon black¹) mixtures of the alcohols are not separated even at 100° and the peaks are very unsymmetrical. On samples modified by monolayers of PEG, a mixture of these same alcohols is separated even at 70°. In connection with this, the most effective columns are those filled with carbon black supporting a dense monolayer of PEG-300 which has the lowest molecular weight of the PEGs which were investigated.

As well as polyethylene glycol even lower molecular weight compounds, *e.g.* molecules of 2,4-dinitrophenylhydrazones⁷, may be used as modifiers for carbon black. It is evident from Fig. 3 that dense monolayers of these compounds deposited on the surface of channel carbon black ($s = 80 \text{ m}^2/\text{g}$) are even more selective for alcohols than a PEG monolayer.

Thus, by modifying graphitised carbon black with polyethylene glycol of low

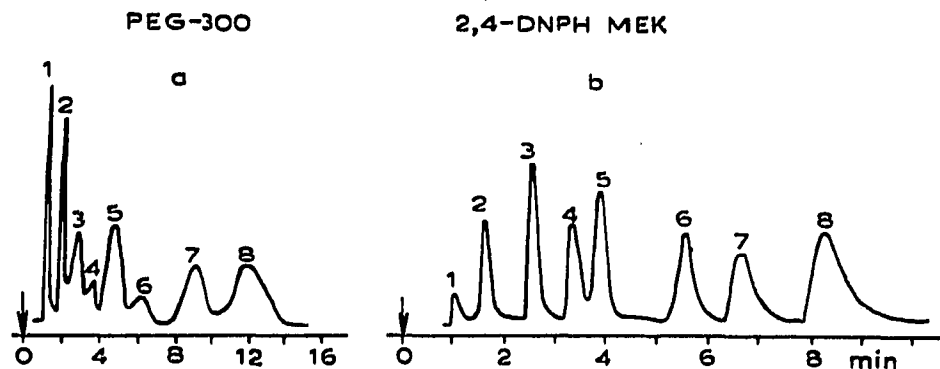
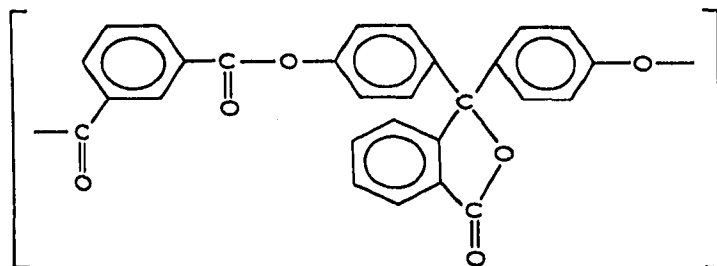


Fig. 3. Separation of a mixture of C_1 - C_4 alcohols on monolayers deposited on channel carbon black: (a) on a monolayer of PEG-300 ($t = 70^\circ$, $l = 100$ cm, $d = 0.3$ cm, flow rate of He = 38 ml/min); (b) on a monolayer of the 2,4-dinitrophenylhydrazone of methyl ethyl ketone ($t = 70^\circ$, $l = 100$ cm, $d = 0.3$ cm, flow rate of He = 40 ml/min). (1) CH_3OH ; (2) C_2H_5OH ; (3) *iso*- C_3H_7OH ; (4) *n*- C_3H_7OH ; (5) *tert.*- C_4H_9OH ; (6) *sec.*- C_4H_9OH ; (7) *iso*- C_4H_9OH ; (8) *n*- C_4H_9OH .

molecular weight by adsorption from an aqueous solution it is possible to form a dense monolayer consisting of straightened-out macromolecules oriented in a plane on the surface. Monolayers of PEG specifically adsorb molecules of groups B and D and may be used for the separation of alcohols at low temperatures. To improve the quality of such adsorbents it is necessary to use narrow fractions of linear macromolecules.

MODIFICATION OF SILICA GEL BY POLYARYLATE PH-I

As well as using graphitised carbon black which is a strong, but non-specific, adsorbing support for monolayers of molecules and macromolecules, specifically adsorbing adsorbents, in particular macroporous silica gel^{1,7} may also be used. The molecules and polymers containing functional groups capable of forming hydrogen bonds with the silanol groups of the surface¹⁷ must be held particularly firmly on the silica gels. An industrial macroporous silica gel of specific surface area $s = 17$ m²/g and mean pore diameter about 500 Å (ref. 1) was used as a support for the adsorption film. The modifying polymer for the silica gel consisted of polyarylate Ph-I¹⁸ of average molecular weight about 30 000. The macromolecule is made up of the monomer units (see scheme below) and consequently according to the author's classification¹ polymer Ph-I belongs to adsorbents of type III *i.e.* it is a specific adsorbent carrying on its surface negative charges concentrated mainly on the oxygen atoms of carbonyl and ether groups.



Polymer Ph-1 was deposited on the surface of the macroporous silica gel from a chloroform solution.

The specific surface area of the modified silica gel $s = 18 \text{ m}^2/\text{g}$ determined by low temperature adsorption of krypton¹⁹ did not differ much from the surface of the initial silica gel ($s = 17 \text{ m}^2/\text{g}$) but was significantly greater than the specific surface area of the initial porous polyarylate Ph-1 ($s = 3 \text{ m}^2/\text{g}$).

The average concentration of the polymer on the surface of the silica gel, determined by loss of weight during calcining of the modified sample at 800° in air, was $2.3 \text{ mg}/\text{m}^2$. This shows that a very thin adsorbed layer of Ph-1 was formed on the surface of the silica gel. For uniform surface coverage its thickness cannot exceed 2–2.5 monolayers if we accept $a_m \approx 0.9\text{--}1.0 \text{ mg}/\text{m}^2$ as the capacity of a monolayer, which value was obtained^{7,20} for the adsorption of polystyrene on aerosil and on macroporous silica gels. a_m may be evaluated roughly from the geometric dimensions of the separate monomers of the macromolecule Ph-1. For flat orientation of the aromatic rings of the basic framework of the polymer, the area occupied by one monomer of Ph-1 is approximately equal to 160 \AA^2 and consequently $a_m \approx 0.43 \text{ mg}/\text{m}^2$ if the Ph-1 macromolecules are completely unfolded when adsorbed on the surface of macroporous silica gel. This assumption is not likely to be true for such a rigid and difficultly soluble polymer as polyarylate Ph-1. Besides, on account of the presence of carbonyl groups in Ph-1 it is possible that the orientation of the macromolecules in the monolayer is not flat and this must also lead to an increase in a_m .

The chromatographic investigation of these compounds was carried out using a Tswett-4 gas chromatograph provided with a flame ionisation detector. The samples were sieved and the fraction between 0.25–0.5 mm taken, dried *in vacuo* at 200° , loaded into the chromatographic column, $100 \times 4 \text{ cm}$, and given a preliminary heating in a current of nitrogen at 200° until a stable zero line was obtained. Compounds whose molecules belong to groups A, B and D were used as adsorbates.

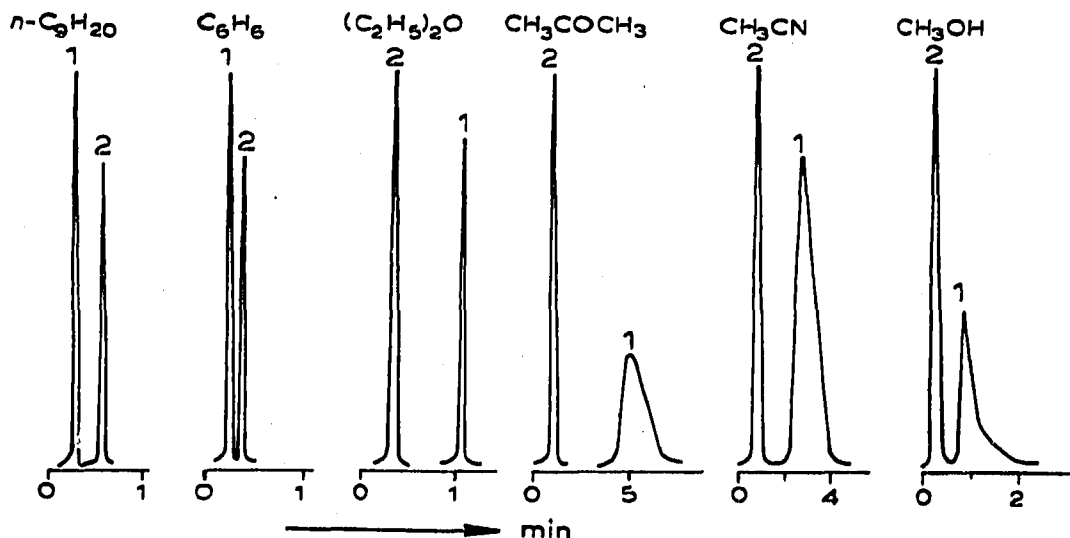


Fig. 4. Examples of chromatograms of a number of organic compounds on: (1) initial wide-pore silica gel; and (2) wide-pore silica gel modified with a thin layer of polyarylate. The adsorbates are shown on the figure. Experimental conditions: $t = 150^\circ$; column dimensions $100 \times 0.4 \text{ cm}$; flow rate of carrier gas (nitrogen) $40 \text{ ml}/\text{min}$; flame ionisation detector.

TABLE IV

RETENTION VOLUMES PER UNIT SURFACE AREA, V_s , AND HEATS OF ADSORPTION, Q , (AT LOW COVERAGES) ON POROUS POLYMER Ph-I AND ON A FILM OF Ph-I DEPOSITED ON MACROPOROUS SILICA GEL

Adsorbate	Dipole moment (Debye units)	V_s (ml/m ²) (150°)			Q (kcal/mole)		
		Silica gel support	Film Ph-I on silica gel	Porous Ph-I	Silica gel support	Film Ph-I on silica gel	Porous Ph-I
<i>Molecules of group A</i>							
Hexane	0	—	0.08	3.42	7.0	12.3	13.5
Heptane	0	—	0.15	6.32	8.6	14.1	15.6
Octane	0	—	0.29	10.82	9.9	15.5	17.6
Nonane	0	0.16	0.54	—	11.4	17.0	19.6
Decane	0	0.23	0.99	—	13.0	—	—
<i>Molecules of group B</i>							
Benzene	0	0.13	0.19	21.6	8.3	12.4	15.2
Toluene	0.37	0.30	0.39	49.6	9.7	14.2	17.4
<i>p</i> -Xylene	0	0.65	0.79	—	11.2	15.9	19.6
Cumene	—	0.74	1.06	—	12.2	16.1	—
Diethyl ether	1.17	1.25	0.27	3.95	13.5	10.9	14.1
Dipropyl ether	1.77	2.71	0.67	9.62	15.2	—	—
Acetone	2.85	7.21	0.67	10.4	15.1	12.0	14.1
Nitromethane	3.54	0.83	0.27	25.3	10.1	11.7	13.7
Acetonitrile	3.94	2.38	0.48	14.2	12.2	9.4	12.8
<i>Molecules of group D</i>							
Methanol	1.67	1.23	0.25	3.56	—	—	10.5
Ethanol	1.70	—	0.41	6.59	—	—	12.6
<i>n</i> -Propanol	1.66	—	0.77	14.5	—	—	14.6
<i>n</i> -Butanol	1.66	—	2.04	35.6	—	—	16.6

It can be seen from Fig. 4 and Table IV that a deposit of a thin layer of Ph-I on the surface of the silica gel leads to a noticeable increase in retention times, retention volumes per unit surface V_s and heats of adsorption of *n*-alkanes and aromatic hydrocarbons. On the other hand for ethers, ketones, acetonitrile and

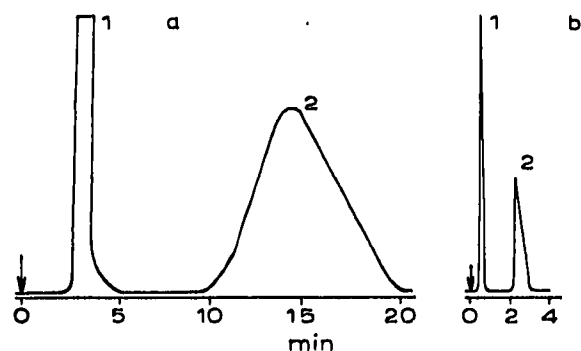


Fig. 5. Chromatograms of naphthalene on: (a) porous polyarylate Ph-I at 200°; and on (b) silica gel modified by a thin layer of this polyarylate Ph-I, at 180°. The rest of the conditions are the same as in Fig. 4. Solvents: (1) benzene, (2) naphthalene.

alcohols which are all capable of forming strong hydrogen bonds with the silanol groups of silica gel, after modification of the silica gel surface with the polymer Ph-1, a sharp decrease in these values is observed. At the same time the adsorption properties of the polymer film, deposited on the silica gel, are substantially different from the properties of the porous Ph-1 polymer. It may be seen from Fig. 5 that naphthalene emerges from a column of silica gel, modified by a film of Ph-1 with a very narrow peak and much more rapidly than from a column of the porous polymer Ph-1, despite the somewhat lower experimental temperature and the quite large surface of the modified silica gel. This difference appears even greater on comparing

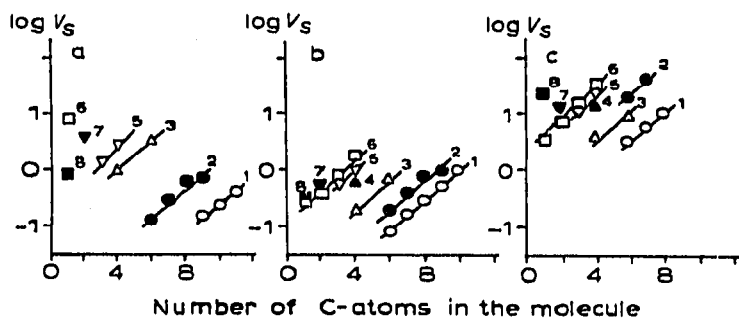


Fig. 6. Dependence of logarithm of retention volumes V_s at 150° of various adsorbates on the number of carbon atoms in the molecule for: (a) the initial silica gel; (b) silica gel modified with a thin layer of polyarylate Ph-1; and (c) the porous polyarylate Ph-1 itself. (1) *n*-Alkanes; (2) alkylbenzenes; (3) ethers; (4) ethyl acetate; (5) ketones; (6) *n*-alcohols; (7) acetonitrile; (8) nitromethane.

the retention volumes V_s referred to unit surface of the modified silica gel (Fig. 6 and Table IV).

The values of V_s on the porous polymer Ph-1, despite its small specific surface area as measured from adsorption of krypton, exceeds the value of V_s on silica gel modified by this polymer by one order of magnitude. Quite possibly the molecules of these adsorbates are capable of penetrating into the network of the porous polymer between its macromolecules which results in strong retention and high values of V_s and Q . High values of Q for *n*-alkanes are also characteristic of silica gel modified by a film of Ph-1. However, because of the fact that in this case the polymer was deposited as a very thin layer, the exchange processes (adsorption and desorption) take place much more quickly on the polymer film than in the porous polymer. The macromolecules of the polymer are probably arranged in a more orderly fashion on the surface of silica gel than in the network of the same porous polymer, being oriented to the surface of the support by their polar groups. This fact is demonstrated in particular by the smaller heats of adsorption of molecules of group B—diethyl ether, acetone and acetonitrile—on silica gel modified by a film of Ph-1, than on the same porous polymer Ph-1. Thus, the heats of adsorption of these adsorbates on a film of Ph-1 deposited on silica gel are less by 2–3 kcal/mole than the corresponding heats of adsorption on the porous polymer Ph-1. Thus a film of Ph-1 on silica gel is a less specific adsorbent with respect to these molecules of group B than the porous polymer Ph-1 itself. This demonstrates the fact that a film of Ph-1 is non-porous or at least significantly less porous in comparison to the polymer itself.

Thus, the adsorption properties of a thin layer of polyarylate Ph-1, deposited on silica gel, differ substantially both from the properties of the initial porous polymer Ph-1 and also from the properties of the support. Surfaces of silica gel modified by polyarylate Ph-1 sharply diminish its specificity and decrease the retention times and asymmetry of the chromatographic peaks of polar compounds: ethers, esters, ketones, nitriles and nitro-compounds. The use of polyarylate as a thin adsorption layer on silica gel permits a sharp reduction of the strong retention of *n*-alkanes and, in particular, of aromatic hydrocarbons characteristic of porous polyarylates and industrial porous polymers based on styrene and divinylbenzene. In addition to this, spreading of the chromatographic peaks is reduced.

CONCLUSION

The results presented here show that modification of adsorbent-supports which have the capability of different molecular interactions, by adsorption of dense monolayers of molecules and macromolecules, permits us to obtain new adsorbents with quite uniform surfaces, small energies of non-specific interaction, high specificity and selectivity, and sufficient thermal stability for numerous applications in gas chromatography.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to LE ZUNG, V. V. KHOPINA and G. A. CHIRKOVA who took part in the experimental work and to Dr. G. CURTHOYS (University of Newcastle, Australia) for the translation of this paper into English.

REFERENCES

- 1 A. V. KISELEV AND YA. I. YASHIN, *Gazo-adsorbciionnaya khromatografiya*, Izd. Nauka, Moscow, 1967; *Gas-Adsorption Chromatography*, Plenum Press, New York, London, 1969; *La Chromatographie Gas-Solide*, Masson, Paris, 1969.
- 2 A. V. KISELEV, in GOLDUP (Editor), *Gas Chromatography 1964*, Institute of Petroleum, London, 1964.
- 3 L. D. BELYAKOVA, A. V. KISELEV, N. V. KOVALEVA, L. N. ROZANOVA AND V. V. KHOPINA, *Zh. Fiz. Khim.*, 42 (1968) 177.
- 4 C. VIDAL-MADJAR AND G. GUIOCHON, *Bull. Soc. Chim. France*, (1966) 1096; in H. G. STRUPPE (Editor), *Gas-Chromatographie 1968*, Akademie-Verlag, Berlin (DDR), 1968, p. 295.
- 5 F. A. HOLDINGHAUSEN, D. FREITAG, N. RIED AND I. HALASZ, *Angew. Chemie*, (1968) 754.
- 6 A. V. KISELEV, N. V. KOVALEVA, O. G. KRYUKOVA AND V. V. KHOPINA, *Kolloid. Zh.*, 32 (1970) 527.
- 7 A. V. KISELEV, *J. Chromatogr.*, 49 (1970) 84.
- 8 V. I. KALMANOVSKY, A. V. KISELEV, G. G. SHESHENINA AND YA. I. YASHIN, *Gasovaya Khromatografiya*, vypusk 6, NIITEKHIM, Moscow, 1967, p. 45.
- 9 I. YU. BABKIN, A. V. KISELEV AND A. YA. KOROLEV, *Dokl. Akad. Nauk. SSSR*, 136 (1961) 373.
- 10 A. V. KISELEV, N. V. KOVALEVA, V. V. KHOPINA, G. A. CHIRKOVA AND YU. A. ELTEKOV, *Kolloid. Zh.*, in press.
- 10a A. V. KISELEV, N. V. KILEVAJA, V. V. KHOPINA AND YA. A. ELTEKOV, *Vysokomolekul. Soedin.*, in press.
- 11 C. F. PRENZLOW AND G. D. HALSEY, *J. Phys. Chem.*, 61 (1957) 1158.
- 12 M. W. BARNES AND W. A. STEELE, *J. Chem. Phys.*, 45 (1966) 461; 49 (1968) 2128.
- 13 A. V. KOUZNETSOV, C. VIDAL-MADJAR AND G. GUIOCHON, *Bull. Soc. Chim. France*, (1969) 1440.

- 14 R. R. STROMBERG, D. I. FRETOS AND E. PASSAGLIA, *J. Phys. Chem.*, 69 (1965) 3955.
- 15 A. V. KISELEV, *Zh. Fiz. Khim.*, 38 (1964) 2753; 41 (1967) 2470.
- 16 R. M. BARRER, *J. Colloid Interface Sci.*, 21 (1966) 415.
- 17 V. YA. DAVYDOV, A. V. KISELEV AND B. V. KUZNETSOV, *Zh. Fiz. Khim.*, 44 (1970) 1.
- 18 A. A. ASKADSKY, *Fiziko-Khimiya poliarilatov*, Izd. Khimiya, Moscow, 1968, p. 32.
- 19 A. V. KISELEV, A. YA. KOROLEV, R. S. PETROVA AND K. D. SHCHERBAKOVA, *Kolloid. Zh.*, 22 (1960) 671.
- 20 E. K. BOGACHEVA, A. V. KISELEV, YU. S. NIKITIN AND YU. A. ELTEKOV, *Vysokomol. Soedin.*, 10A (1968) 574.

J. Chromatogr., 58 (1971) 19-30