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PROBLEMS OF MOLECULAR ADSORPTION CHROMATOGRAPHY

A. V. KISELEV

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

In this review we have tried to show that molecular gas and liquid chromatography on adsorbents have a number of advantages for analytical and preparative applications. The vast amount of experimental data obtained on adsorbents with known and reproducible chemical and geometrical structure, together with the combined use of static and chromatographic methods, makes the development of a molecular theory of gas adsorption possible on the basis of molecular-statistics and semi-empirical, or effective, potential functions of intermolecular interactions. Advances made in this field so far warrant further applications of this theory to gas adsorption chromatography. Of practical interest is the fact that forecasts of certain parameters and phenomena can be made on the basis of this theory. The theory of adsorption from solutions and liquid chromatography has been developed to a lesser degree. However, here, too, the main qualitative aspects of this theory have been established. Further efforts should be made to develop the theory of adsorption from liquid solutions and apply this theory to equilibrium, non-equilibrium, molecular and macromolecular sieve liquid chromatography.

INTRODUCTION

About ten years ago molecular adsorption chromatography was mainly used in the separation of gas mixtures. Today this method is used on a much larger scale. It has been applied to the separation of various mixtures from hydrogen isotopes and isomers, to proteins and even to viruses. This development is related to a number of achievements in science and technology: (1) greater control of the homogeneity and specificity of the molecular adsorbents by means of the individual synthesis of adsorbents and the chemical modification of their surface; (2) expansion of the working range of the gas chromatographic columns, up to 500°; (3) employment of strongly adsorbable carrier gases at high pressures, the result of which is a narrowing of the gap between gas and liquid chromatography; (4) advances in liquid molecular adsorption chromatography on the basis of adsorbents whose nature and degree of porosity can be controlled; (5) the development of molecular and macromolecular sieves, especially of the non-swelling type; (6) the development of highly sensitive detection methods in liquid chromatography.

The following factors—the relatively simple physicochemical basis of the chromatographic separation of molecules and macromolecules on adsorbents, the possibility of controlling the geometrical structure of the adsorbents and the chemical nature of their surface, and the fact that most of the adsorbents are non-volatile and have a high thermal and chemical stability—all make an adsorbent particularly valuable for use in analytical temperature-programmed columns as well as for preparative gas and liquid molecular-adsorption chromatography and its use on an industrial scale.

In addition to the more usual applications of gas adsorption chromatography, it is now an important tool in physicochemical investigations of the surface chemistry of solids, in studies of isotherms, the heat and entropy of adsorption, and the heat capacity of adsorption systems. Owing to the fact that the equipment is simple to operate and that it can be used over a wide temperature range, gas chromatography has made possible the achievement of rapid advances in the investigation of the adsorption of a large variety of organic, inorganic, and elemento-organic compounds. The investigation of the adsorption of many of these compounds is practically impossible using the usual vacuum techniques. Both gas chromatographic analysis of solutions which are in contact with solid surfaces and direct liquid molecular adsorption chromatography have opened wide possibilities for investigating such adsorption processes. All these developments provide the necessary experimental basis for studying adsorbate-adsorbent and adsorbate-adsorbate molecular interactions of the most diverse types of molecules. Such interactions take place during adsorption from the gas phase and from solutions.

A good deal of highly reproducible experimental data has been obtained by using homogeneous and chemically well-defined adsorbents whose surface has a known geometrical structure. These results may serve as a basis for the development of a quantitative statistical molecular adsorption theory and provide a theoretical basis for chromatographic separation of complex molecules. With the aid of modern electronic computers, such a theory derived from the properties of the surface and the adsorbed molecule would make it possible to select adsorbents with properties optimal for a definite purpose as well as to calculate adsorption equilibria and retention indices for a given system. Besides their theoretical significance, such calculations would facilitate the identification of the components of the mixture being separated and give data necessary for designing industrial-scale chromatographic equipment.

Such are the general aspects of the theoretical and applied problems under further development of molecular adsorption chromatography. The complete solution of these problems will require considerable effort on the part of many scientists. The purpose of the present paper is to analyse some of the results achieved in this field and to indicate the difficulties that may be encountered in future work.

MOLECULAR THEORY OF ADSORPTION AND GAS ADSORPTION CHROMATOGRAPHY

Problems of molecular adsorption theory

At the present time an adsorption theory for adsorption from the gas phase on homogeneous crystal surfaces is being developed on the molecular level, *i.e.* by considering the geometrical and electronic structure of the solid body surface and of the molecule being adsorbed (see refs. 1-5). On the whole, this theory includes

molecular-statistical calculation of equilibrium constants, virial coefficients, retention volumes at zero, low and average levels of surface coverage, as well as other thermodynamic constants, *e.g.*, heat and entropy of adsorption and the heat capacity of the adsorption systems. The calculation of configurational integrals, which are part of these thermodynamic terms, is carried out with the aid of semi-empirical expressions for the potential energies of the adsorbate-adsorbent and adsorbate-adsorbate interactions.

For analytical applications of this theory, especially in the case of highly sensitive detectors together with very low concentrations of the adsorbed molecules and fairly high temperatures, the adsorbate-adsorbate interaction is insignificant, and thus one only needs to consider the adsorbate-adsorbent interaction, *i.e.* the Henry constants and their dependence on temperature. At higher surface concentrations, one should introduce into the equation the next virial coefficient which takes into account the paired adsorbate-adsorbate interaction in the field of the adsorbent, etc., or take into account in some other way the adsorbate-adsorbate interaction.

The calculation of the potential energy of the adsorbate-adsorbent interaction from semi-empirical potential functions is a separate problem. The potential energy of adsorption of the molecule, in its most favourable orientation on the surface, equals the heat of adsorption at absolute zero (including the correction for the zero energy). Owing to the relatively slight dependence of the heat of adsorption on temperature, the magnitude of the potential energy of adsorption also approximately expresses the heat of adsorption at the temperature of the gas chromatographic column. At fairly low temperatures the order of the retention volumes usually corresponds to that of the heats of adsorption. Thus the first approximation in the molecular adsorption theory is already of interest, *i.e.* the definition of the potential energy of adsorption for the most favourable orientation of the molecules on the adsorbent surface. In this section we shall consider some data obtained from the calculation of the potential energy of adsorption for adsorption of different molecules on a series of crystalline adsorbents. An analysis will also be made of the Henry constants obtained by molecular-statistical calculations and of the retention volumes at zero sample size.

Up to now molecular-statistical calculations of retention volumes have only been made for a few compounds, whereas calculations of the potential energy of adsorption have been carried out for a relatively large number of compounds. To compare the calculated values with experimental ones requires calorimetric, isosteric, or gas chromatographic determinations of the heat of adsorption. The most convenient method, especially for compounds of low volatility, consists of the gas chromatographic determination of the retention volumes at different temperatures. However, the precision of such determinations is somewhat low, and thus it is necessary to carry out repeated measurements and make a statistical analysis of the data obtained.

The calculated potential energy of adsorption and a comparison of this calculated energy with the measured heat of adsorption

Graphitised thermal carbon black. The surface of this adsorbent is almost entirely formed of the basal faces of large crystals of graphite^{5,6}. Therefore calculations were made for adsorption on the basal face of a graphite crystal. For adsorption of simple molecules on graphite the potential functions of the paired molecule-carbon atom interaction were used, *e.g.* $\varphi_{C...Ar}$ or $\varphi_{C...NH_3}$. For the adsorption of complex hydro-

carbon molecules and their derivatives the atom-atom potential functions $\varphi_{C\dots C}$, $\varphi_{C\dots H}$, $\varphi_{C\dots O}$, or group-atom potential functions $\varphi_{C\dots CH_3}$, $\varphi_{C\dots CH_2}$, $\varphi_{C\dots CH}$, etc. were used. The summation of the energy of paired interactions was made with respect to all atoms or atomic layers on the semi-infinite lattice of a graphite crystal (see refs. 1-3,5), and for complex molecules, with respect to the atoms or linkages which form these compounds, so that the potential energy of the molecule is:

$$\Phi = \sum_{C} \sum_{i} \varphi_{C\dots i} \quad (1)$$

where $\varphi_{C\dots i}$ is the potential energy of interaction of a C atom of the lattice with an atom or linkage i of the molecule. The equation for $\varphi_{C\dots i}$ was written in the form of the Buckingham or Lennard-Jones potential augmented by the term for dipole-quadrupole dispersion-attraction. In the first case we obtain:

$$\varphi_{C\dots i} = -C'_{Ci} r_{Ci}^{-6} - C''_{Ci} r_{Ci}^{-10} + B_{Ci} \exp\left(-\frac{r_{Ci}}{\rho_{Ci}}\right) \quad (2)$$

The constants C'_{Ci} and C''_{Ci} were calculated with the aid of the KIRKWOOD-MÜLLER equation^{7,8} or an analogous equation⁹ for the polarisability and diamagnetic susceptibility of C and i linkages. The constant B_{Ci} was determined from the equilibrium conditions and was expressed in terms of the equilibrium distance z^0_{Ci} of the atom or linkage centres i from a plane passing through the centres of the C atoms of the outer basal plane, for the most favourable orientation of the molecules relative to this plane (*i.e.* the maximum number of molecular linkages which are in contact with the basal plane). The constant ρ_{Ci} was taken to be equal to 0.28 Å, as for the molecular crystals. In the case of adsorption of a dipole molecule a term was introduced into eqn. 2 for the energy of the inductive attraction of the dipole to the polarised C atom in the

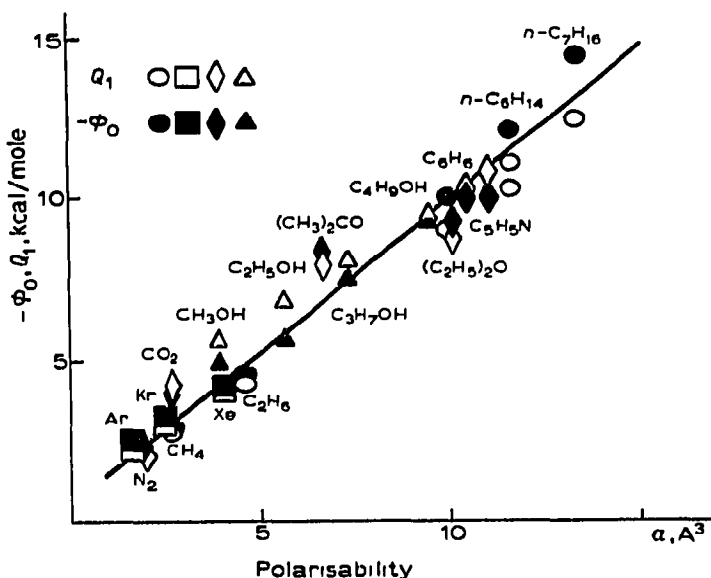


Fig. 1. Dependence of the calculated potential energy of adsorption, $-\Phi_0$, and the experimental heat of adsorption, Q_1 , for different substances adsorbed on the basal plane of graphite and on graphitised thermal carbon black, respectively, at low surface coverage as a function of the adsorbate polarisability, α .

lattice¹⁰ or for the energy of the reflected force of the dipole in the carbon layer of the lattice¹¹. In both cases the contribution due to this energy is small. Detailed calculations of the constants, the summation of the expression (2) in eqn. 1, and the calculation of $-\Phi_0$ for the equilibrium distances z^0_{C1} have been described in original studies which have been reviewed^{3,5}. Fig. 1 shows a comparison of some results obtained by AVGUL AND KISELEV⁵, CROWELL *et al.*¹², and CURTHOYS AND ELKINGTON¹³ of the calculation of Φ_0 together with the calculated heat of adsorption Q_1 (for zero surface coverage) derived on the basis of experimental measurements (calorimetric, isotheric, and in many cases gas chromatographic). The values $-\Phi_0$ and Q_1 in Fig. 1 are plotted as the function of the molecule polarisability α . The calculated values agree well with the experimental data. Furthermore, the values of $-\Phi_0$ and Q_1 fall approximately on the same line as those obtained by plotting the data for *n*-alkanes. This holds true for the molecules of group A (noble gases, saturated hydrocarbons) which are incapable of specific molecular interaction, group B which have π -bonds or lone electron pairs, and group D which contains functional HO- or HN-groups; groups A, B, and D are according to the classification by KISELEV^{1,5,14,15}. This indicates that graphitised thermal carbon black is non-specific in nature^{1,5,14-16}; *i.e.* it belongs to the adsorbents of the first type according to the above-mentioned classification.

Boron nitride. The lamellar structure of BN crystals is analogous to that of graphite except that at the intersection of the hexagonal basal planes there are alternate B and N atoms instead of C atoms. When the composition of the crystal corresponds exactly to the BN formula and the lattice is practically free of defects, the basal plane BN exhibits properties of a non-specific adsorbent. CROWELL AND CHANG¹⁷ have carried out calculations of the potential energy of adsorption and measurements of the heat of adsorption for noble gases, and CURTHOYS AND ELKINGTON¹³ for adsorption of hydrocarbons. As can be seen from the plots based on these data in Fig. 2,

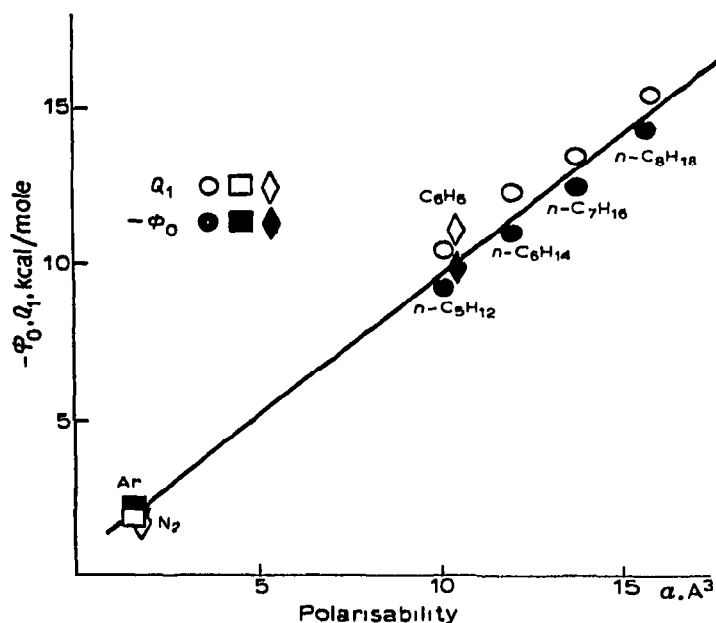


Fig. 2. Dependence of the calculated potential energy of adsorption, $-\Phi_0$, and the experimental heat of adsorption, Q_1 , on boron nitride at low surface coverage as a function of the adsorbate polarisability, α .

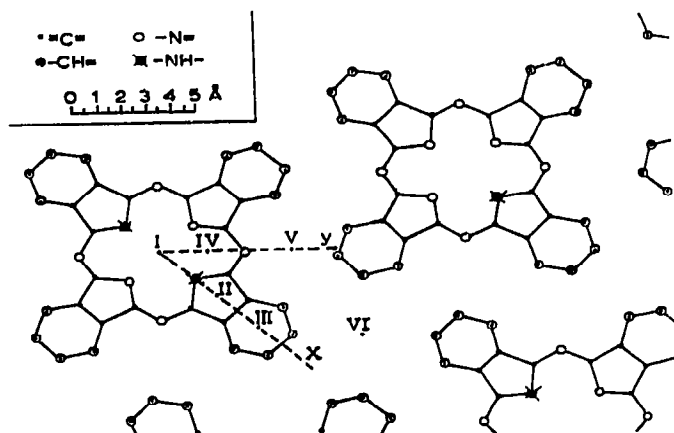


Fig. 3. Diagram showing the packing of phthalocyanine molecules on the surface of graphitised thermal carbon black¹⁸.

the values of $-\Phi_0$ and Q_1 are in good agreement (for hydrocarbons Q_1 was obtained by a gas chromatographic method).

Phthalocyanine. The basal plane of the phthalocyanine crystal shown in Fig. 3 is an example of a specific adsorbent, since it contains different functional groups: $=C=$, $-CH=$, $-N=$, $HN=$ ¹⁸. Although these groups are conjugated and thus facilitate a more regular distribution of the electron density, the resulting surface of the adsorbent is chemically heterogeneous. At the edge of the plane corresponding to the plane of the molecule there is a higher electron density locally. Thus this adsorbent belongs mainly to the third type according to the classification by KISELEV^{1,5,14,15}, even though it contains $HN=$ centres which belong to the second type of adsorbent. The planes in a phthalocyanine molecule formed by CH linkages possess a weaker molecular field. KOUZNETSOV *et al.*¹⁸ have obtained, by gas chromatographic methods, the heat of adsorption for different compounds including those from group A (*n*-alkanes), which are incapable of specific molecular interactions, group B (acetone, ethers, aromatic hydrocarbons) and group D (phenols and amines) which are capable of such interactions^{1,5,14,15}. The Φ_0 values for *n*-alkanes were calculated by the method described above with the use of the Lennard-Jones equation for calculating $\varphi_{j\dots i}$. The force centres *j* of the adsorbent were taken as $=C=$, $-CH=$, $-N=$, and $=NH$ groups. The calculation of $\varphi_{j\dots i}$ for $i = CH_3$ and CH_2 at different distances, *z*, of the linkage centres in the molecule *i* from the basal plane containing adsorbing centres *j* was carried out for points I-VI in the plane $x, y, z = 0$ (Fig. 3). The absolute value of Φ_{0i} reaches its maximum above the centre of the phthalocyanine molecule (above point I in Fig. 3). It decreases linearly with the increase in the distance away from this point and parallel to the *x* and *y* axes, which are at a 45° angle to each other, the potential being somewhat greater for the *x* axis than for the *y* axis. Between these axes the change of potential was slight and could be easily compensated for. In Fig. 4 the calculated $-\Phi_0$ values for C_5 - C_{11} *n*-alkanes and some aromatic hydrocarbons are compared with the experimental values for the heat of adsorption Q_1 for graphitised thermal carbon black coated with phthalocyanine (10% by wt.); such an amount of phthalocyanine is sufficient to provide almost complete shielding of the carbon black. From Fig. 4a it can be seen that for the non-specific adsorption of molecules of group A (*n*-alkanes) and weakly specific adsorption of molecules of group B with conjugated

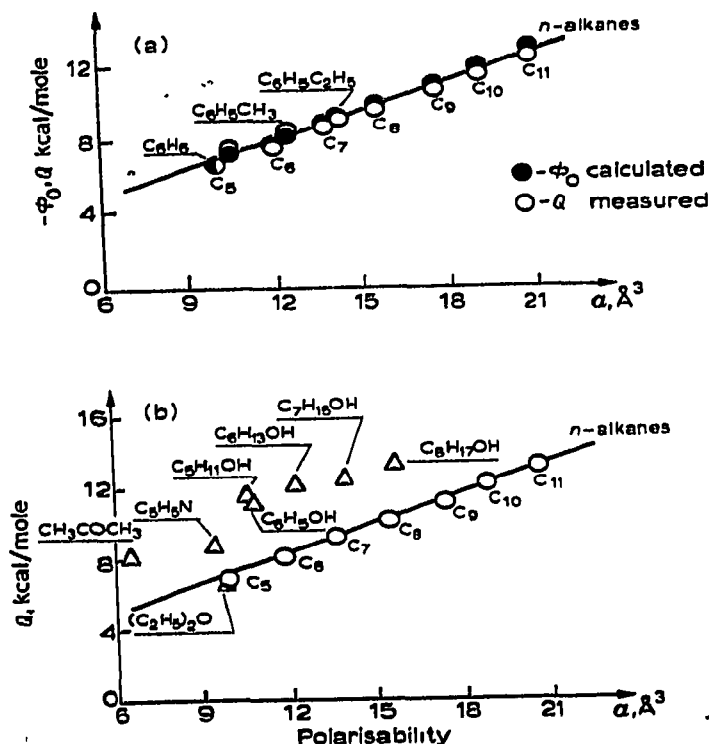


Fig. 4. Dependence of the calculated potential energy of adsorption, $-\Phi_0$, and the experimental heat of adsorption, Q_1 , on graphitised thermal carbon black coated with 10% by wt. phthalocyanine as a function of the adsorbate polarisability α . (a) $-\Phi_0$ (solid points) and Q_1 (open points) for n -alkanes and aromatic hydrocarbons; (b) Q_1 for n -alkanes (solid line) and for a number of specifically adsorbing substances.

π -bonds (aromatic hydrocarbons), the calculated values for the potential energy of a non-specific interaction, $-\Phi_0$, are close to the measured Q_1 , values, as shown in Figs. 1 and 2.

Fig. 4b shows the values for the heat of adsorption Q_1 for dipole molecules of group B (acetone, ether, pyridine) and also for molecules of group D (alcohols). These values are considerably larger than the known heats of adsorption^{1,5,14-16} of the corresponding molecules of group A (n -alkanes) which do not undergo specific molecular interaction. The distance between the point for Q_1 in the case of specifically adsorbable molecules and the corresponding point (for the same polarisability value α (ref. 16)) on the straight line for n -alkanes indicates the contribution to the total heat of adsorption Q_1 due to the energy of specific molecular interaction Q_{specific} ; see refs. 1,5,14-16.

$$Q_{\text{specific}} = Q_{1(\text{B,D})} - Q_{1(\text{A})} \quad (3)$$

where, $Q_{1(\text{A})}$ is the heat of adsorption of the corresponding molecule used for the comparison, the molecule being incapable of specific interaction. A theoretical calculation of the specific interaction energy has not yet been made in this case.

Some non-porous ionic adsorbents. The surface of ionic adsorbents is often heterogeneous not only because of the presence of growth steps or dislocations on individual planes but also because of sharp differences in these planes with respect to their crystallographic indices, *i.e.* because of the difference in the population of cations and anions. The simpler cases are those of laminar and cubic lattices (the latter

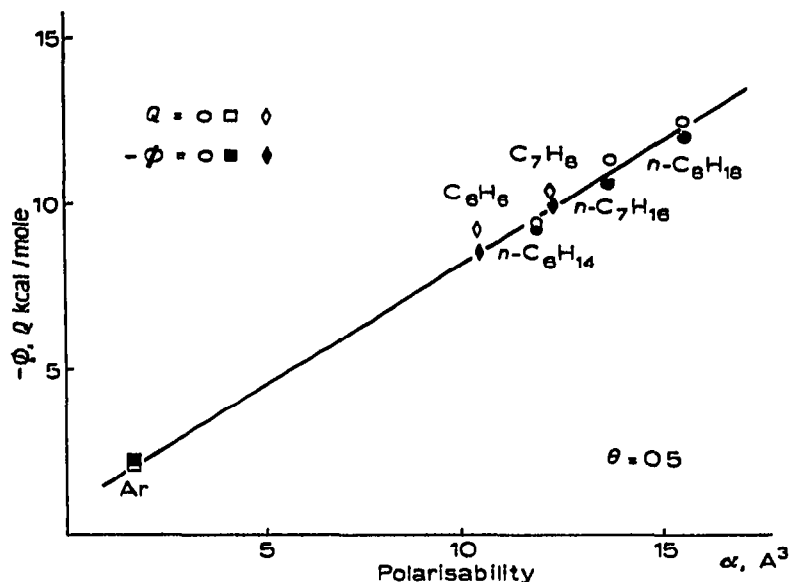


Fig. 5. Dependence of the calculated potential energy of adsorption, $-\Phi$, and the experimental heat of adsorption, Q , for different substances adsorbed on magnesium oxide at the level of surface coverage $\theta = 0.5$ as a function of the adsorbate polarisability α .

being of the NaCl type). In the latter case all (100) planes are identically populated by cations and anions. If the dimensions of these cations and anions are small and similar to one another, the electrostatic field changes periodically parallel to the surface in a rapid sequence. Owing to this, the contribution of the specific interaction energy to the total heat of adsorption of relatively large-size molecules is small. Fig. 5 shows a comparison of the calculated values for the potential energy of adsorption, $-\Phi$, (with compensation for the induction potential) and the measured heat of adsorption, Q , (for MgO cubic crystals whose surface was half-filled by molecules of noble gases¹⁰ and hydrocarbons⁹). Here, the values for $-\Phi$ and Q are similar, and the specific adsorption of benzene is low.

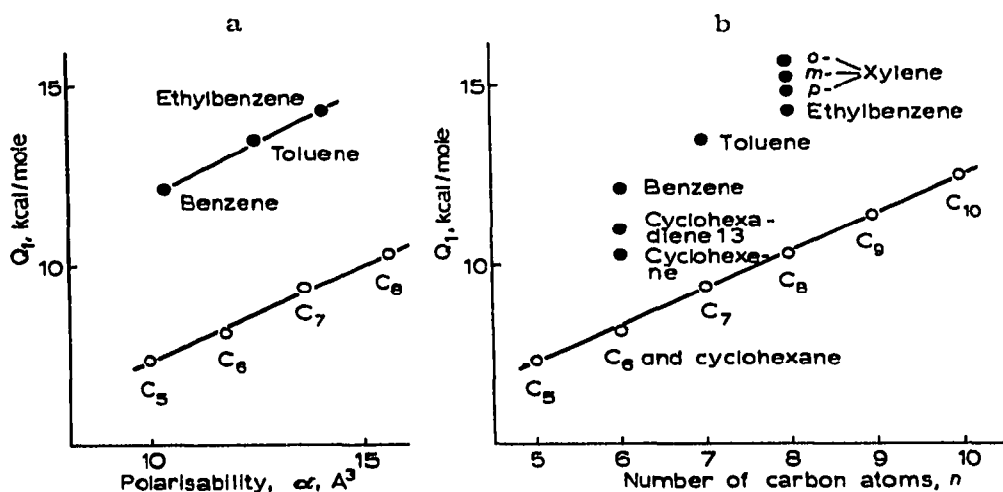


Fig. 6. Dependence of the heat of adsorption Q_1 for different substances separated on barium sulphate at low surface coverage as a function of the adsorbate polarisability α (a) and of the number of carbon atoms n in the molecules (b).

In a similar case, when the cations and especially multi-charged cations protrude on the surface of the crystal and the negative charge is distributed within large complex anions, the adsorbent exhibits very strong specific adsorptions (specific adsorbent of the second type according to the classification of KISELEV^{1,5,14,15}). This can be seen from Fig. 6 which shows the comparison of the heats of adsorption, Q_1 , for *n*-alkanes and cyclohexane, cyclohexene, cyclohexadiene, benzene, toluene, ethylbenzene and *o*-, *m*-, *p*-xylene with barium sulphate as the adsorbent. The data were obtained by a calorimetric method²⁰ and a gas chromatographic method²¹. The contribution to the heat of adsorption of benzene due to specific interaction energy, Q_{specific} , amounts to ~ 5.0 kcal/mole. The heats of adsorption on salt surfaces depend to a great extent on the methods of preparation and treatment of the sample.

Zeolites. The cavity surface of porous crystals of cationised zeolites carries positive charges concentrated within the exchange cations. The negative charges are distributed among many weakly charged oxygen ions surrounding Al and Si atoms. Because of this, zeolites are classified as specific adsorbents of the second type. From Fig. 7 it can be seen that the contribution to the heat of adsorption, Q , of the B- and D-type molecules due to specific interaction energy is rather large. The heats of adsorption of the A-, B-, and D-type molecules shown in Fig. 7 were mainly measured by the calorimetric^{22,23} and isotheric methods^{24,25}, but for small molecules gas chromatography²⁰ was also used.

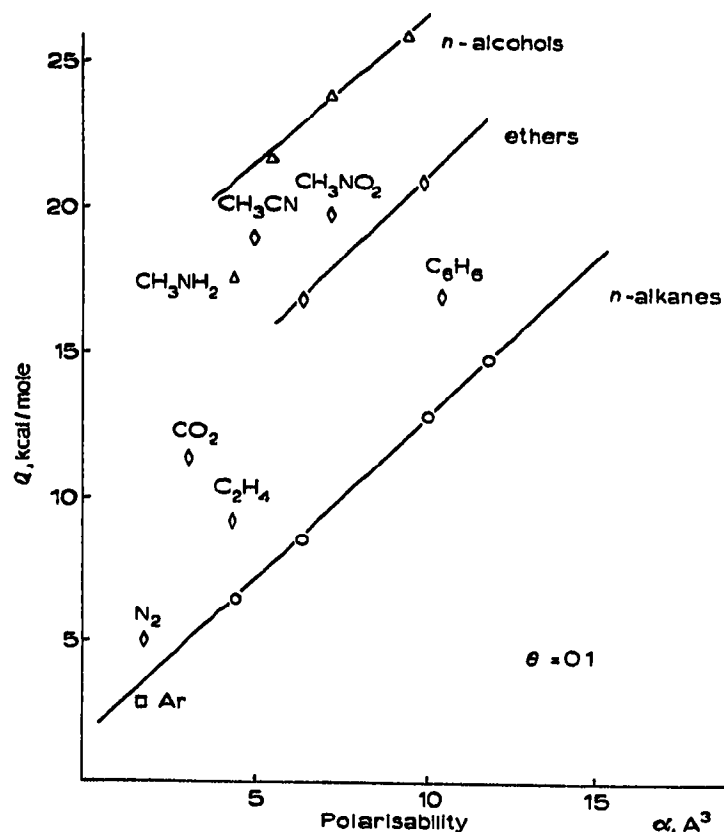


Fig. 7. Dependence of the heat of adsorption Q for different substances adsorbed on zeolite NaX with a degree of surface coverage $\theta = 0.1$ as a function of the adsorbate polarisability α .

Owing to the local distribution of the cations and the specific structure of the porous crystal network, the molecular field inside the zeolite cavity, and especially near its surface, is quite heterogeneous (here, the dispersion and electrostatic attraction forces must be taken into account). However, this heterogeneity can be allowed for²⁷, and thus we can obtain the average statistical value for the potential adsorption energy. This has been done for the adsorption of some gaseous compounds and a number of *n*-alkanes²⁸ on zeolites of the A-type²⁷. The calculated $-\Phi_0$ values for the potential adsorption energy and the measured heat of adsorption in this case are also similar.

Pure silica and silica containing impurities. The surface of non-porous and porous silica, as a rule, is covered by hydroxyl groups (see refs. 1, 14, 15, 29–33). The concentration of these groups on the surface and within the bulk of the particles depends on the nature and crystalline structure of the silica (for amorphous silica, on the nature of the sample). The concentration of hydroxyl groups also depends on whether the sample has been subjected to hydrothermal or simple thermal treatment or thermal treatment *in vacuo*. The concentration of hydroxyl groups on the surface can be determined by means of the deuterium-exchange method (see ref. 33) or by means of IR spectroscopy³². Reproducible values for the concentration of hydroxyl groups on the silica surface (*e.g.* aerosil, aerosilgel³⁴, silica gel) can be obtained when reproducible conditions are used for the hydroxylation procedure or the dehydroxylation of the surface. The concentration of hydroxyl groups is independent of the specific surface area³³.

The presence of hydroxyl groups on the silica surface determines the specific nature of this adsorbent, which is classified as one of the second types of adsorbent. This specific behaviour is demonstrated by hydrogen bonding with molecules of the B- and D-group^{1,14,15,35}. The removal of HO-groups from the surface by heating the sample causes a decrease in the degree of specific molecular interaction. This behaviour of the silica surface is to a great extent determined by the chemical purity of the sample.

The presence on the silica surface of impurities which form strong Lewis acid centres (such as Al and B) causes an increase in the bond energy formed with electron-donor molecules. The effect is especially noticeable upon dehydroxylation when strong Lewis acid centres become exposed. This can be directly observed by comparing the heat of adsorption of electron-donor molecules on pure aerosilgels and aerosilgels containing aluminium before and after dehydroxylation at high temperatures (the surface area of the macroporous aerosilgels in these experiments remains unchanged). Fig. 8 shows some calorimetric data obtained by Ash *et al.*³⁶ for the heat of adsorption of vapours of N,N,N-triethylamine, a strong organic base. Relatively pure aerosilgel and aerosilgel containing 0.36% by wt. aluminium served as the adsorbent. The samples were kept *in vacuo* at 200° and 1100°. Both samples containing HO-groups following the 200° treatment showed, with respect to triethylamine, only molecular specificity on the surface (weak Brönsted acid centres). After gradual coverage of the monolayer on the hydroxylated silica surface, the heat of adsorption of triethylamine was about 20 kcal/mole. This value corresponds to a specific molecular adsorption leading to the formation of a SiOH...N(C₂H₅)₃ hydrogen bond. Strong dehydroxylation of the surface, when the sample is treated at 1100° (without altering the surface area) in the case of pure aerosilgel, leads to the formation of

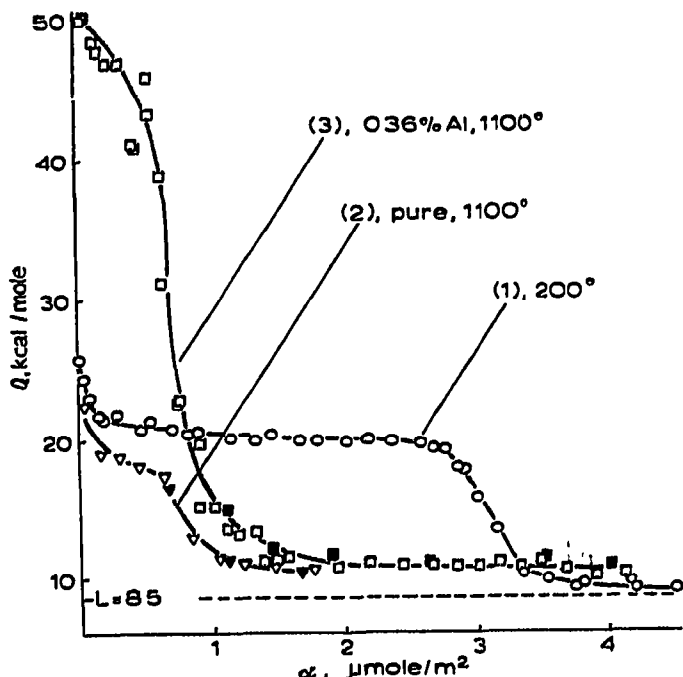


Fig. 8. Heat of adsorption of triethylamine on silica. 1 = on silica gel with the hydroxylated surface stored *in vacuo* at 200°; 2 = on pure aerosilgel with dehydroxylated surface stored *in vacuo* at 1100°, 3 = on aerosilgel containing 0.36% by wt. Al with a dehydroxylated surface stored *in vacuo* at 1100°.

siloxane groups which are incapable of specific molecular interaction. In this case the heat of adsorption of triethylamine decreases to 10 kcal/mole. This value corresponds to the energy for the non-specific interaction of triethylamine with a silica surface. In the case of the aerosilgel containing an aluminium impurity, dehydroxylation of the surface at 1100° results in the formation of a large number of Lewis electron-acceptor centres besides the siloxane groups. The molecules of triethylamine on these centres undergo chemisorption with a heat of adsorption of approximately 50 kcal/mole. Only when all such centres accessible to the N,N,N -triethylamine molecules are filled, does the heat of adsorption sharply decrease to a level corresponding to non-specific adsorption on the siloxane groups of the remaining sample surface. Thus, there are three main levels of interaction energy: the highest, ~ 50 kcal/mole, corresponding to chemisorption of $N(C_2H_5)_3$ molecules on the acceptor centres of the impurity; ~ 20 kcal/mole, a level corresponding to the specific molecular adsorption of $N(C_2H_5)_3$ molecules on silanol groups; and ~ 10 kcal/mole, a level corresponding to the molecular non-specific adsorption of $N(C_2H_5)_3$ molecules by the siloxane groups. Analogous results have been obtained by DAY *et al.*³⁷ for the heat of adsorption of tetrahydrofuran (a molecule of the B-group) on aerosilgel containing 0.36% of aluminium by wt.). The heat of adsorption of cyclopentane (a molecule of the A-group) at the usual temperature of calorimetric measurements is not affected either by the change of silanol groups into siloxane groups or by the exposure of the aluminium centres³⁷.

In accordance with this, the chromatograms of B- and D-type molecules on

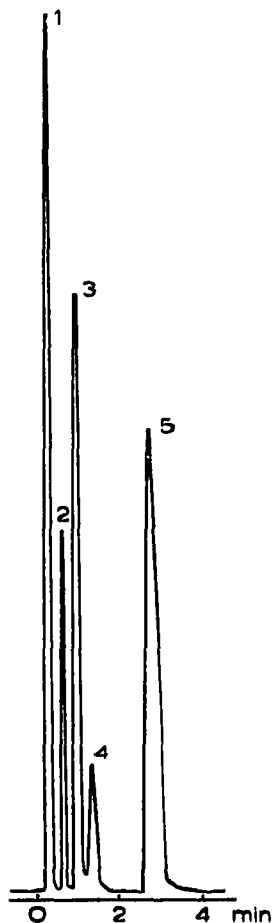


Fig. 9. Chromatogram obtained for Silochrom C-80. 1 = Cyclohexane; 2 = *n*-decane, 3 = aniline; 4 = nitrobenzene, 5 = acetophenone. Column temperature, 200°, column length, 100 cm, sample size, 0.4 μ l; carrier gas flow rate, 40 ml/min, flame ionisation detector.

aerosilgels respond with a high degree of sensitivity to the presence of aluminium or boron centres on the silica surface. Thus a separation on columns made of ordinary silica gel containing Al_2O_3 as an impurity only gives chromatograms with symmetrical peaks in the case of hydrocarbons (especially saturated hydrocarbons, *i.e.* molecules of the A-type). Aromatic hydrocarbons, ethers and ketones are only eluted from the column with difficulty, and the corresponding chromatograms are characterised by expanded peaks¹⁵. On the other hand, such compounds as amines, pyridines, quinoline and other strong organic bases remain on the column *i.e.* they are held by chemisorption on strongly acidic centres distributed on the silica surface³⁹. In the case of porous glass adsorbents, the role of such centres is performed by boron atoms³⁹.

In addition, in accordance with Fig. 8, the HO-groups on pure silica are neither too active energetically nor heterogeneous. From Fig. 9 it can be seen that the hydroxylated surface of chemically pure aerosilgel (Silochrom C-80) does not behave like a chemisorbent towards various molecules of the B- and D-groups, including an amine (aniline), but merely like a specific molecular adsorbent of the second type, which forms hydrogen bonds of different strengths with the molecules of B- and D-groups⁴⁰. The dehydroxylation of a pure silica surface, which decreases its specificity,

only decreases the retention of such molecules and has little effect on the retention of A-group molecules.

The approximate energy values of the specific interaction (in this case the energy of the hydrogen bond) of different molecules belonging to the B-group with the silanol groups have been determined by several workers³⁵⁻³⁷. IR spectroscopic investigation showed that, with respect to the energy of the hydrogen bond, the surface silanol groups are similar to phenol groups⁴¹. The conjugation of unshared electron pairs in O and N atoms for furan and pyridine molecules, respectively, with the π -electron system of the ring results in a decrease in the specific interaction energy as compared with tetrahydrofuran and triethylamine molecules, whose respective O and N atoms have lone electron pairs^{1,35}. For molecules containing several functional groups, the geometrical structure of the molecule is of special significance. In the case of dioxane, the presence of two ether groups isolated from each other by methylene groups does not result in a doubling of the value for the energy of the specific interaction with silanol groups on the silica surface³⁵. This is due to the fact that the favourable orientation of one ether group of the chairlike molecule of dioxane precludes the other ether group approaching close enough to the silanol group to form a strong hydrogen bond with the surface. All these factors affect the retention volumes in chromatographic columns filled with Silochroms.

Silica modified by grafted silylalkyl groups. The heat of adsorption on a silica surface which has been modified by reaction with $\text{ClSi}(\text{CH}_3)_3$ has been investigated by BABKIN *et al.*⁴². It was found that for molecules of relatively large size—benzene, *n*-hexane, and carbon tetrachloride—the initial heat of adsorption measured is considerably less than the corresponding heat of condensation. These results agree with the calculated data for the interaction potential energy, $-\Phi_0$, for the adsorption of benzene and hexane on a silica surface densely packed with methyl groups from the grafted $-\text{Si}(\text{CH}_3)_3$ groups⁴³. Such low values for the heat of adsorption are due to the low concentration of force centres on the outer surface, since the distance of the neighbouring methyl groups from one another is not equal to the C-C bond length (1.5 Å) but is considerably greater and at least equal to the sum of the van der Waal's radii of these groups (4.0 Å). The force field of the silica surface itself, like that of the graphitised carbon black when it was modified by dense monolayers of organic compounds (see below), becomes almost completely shielded. For the same reason, in the case of relatively low concentrations of force centres on the surface, the energy for non-specific adsorption on molecular crystals is smaller than on atomic crystals. Thus the heat of adsorption of *n*-alkanes on phthalocyanine is considerably smaller than on graphite.

A comparison of heats of adsorption and the contribution to their values due to the energy of specific interactions on different adsorbents. Fig. 10 shows the dependence of the heat of adsorption, at a low degree of surface coverage, for *n*-alkanes adsorbed on a number of surfaces described above. From Fig. 10 it can be seen how the heat of adsorption of non-specifically interacting molecules can be varied within a wide range. This means that the retention of these compounds in the chromatographic column can be varied to a much greater extent.

Furthermore, the *relative* role of specific interactions in adsorption on molecular crystals and monolayers containing functional groups can be quite significant, since the contribution of the non-specific interaction energy in this case is small. Thus the

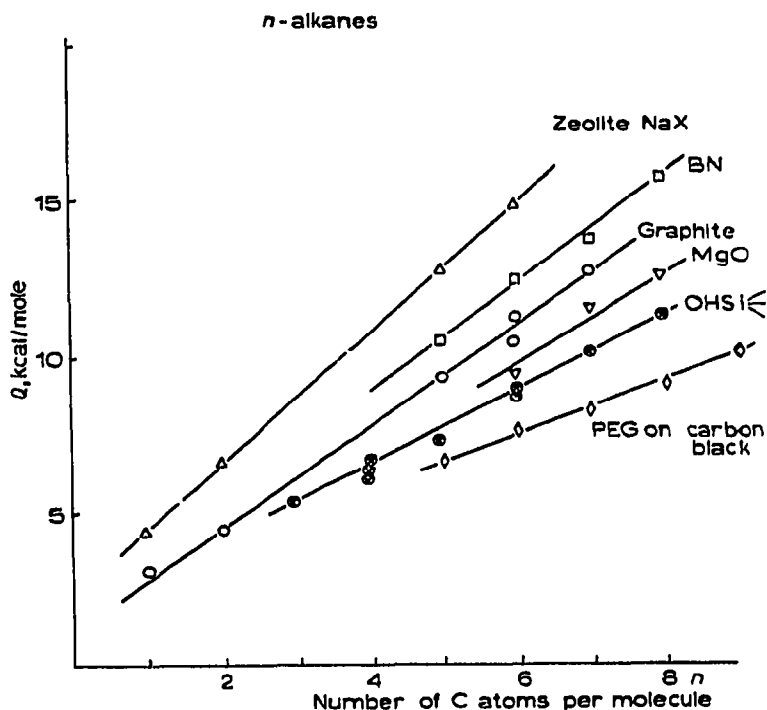


Fig. 10. Dependence of the heat of adsorption of *n*-alkanes at low degrees of coverage on the number of carbon atoms in the molecule for different adsorbents

specific interaction with the basal surface of phthalocyanine crystals is strong (see Fig. 4b). It is especially strong for adsorption on metal phthalocyanines. This fact has been utilised for carrying out precise separations⁴⁴.

From Fig. 11a it can be seen that the shielding of the surface of graphitised

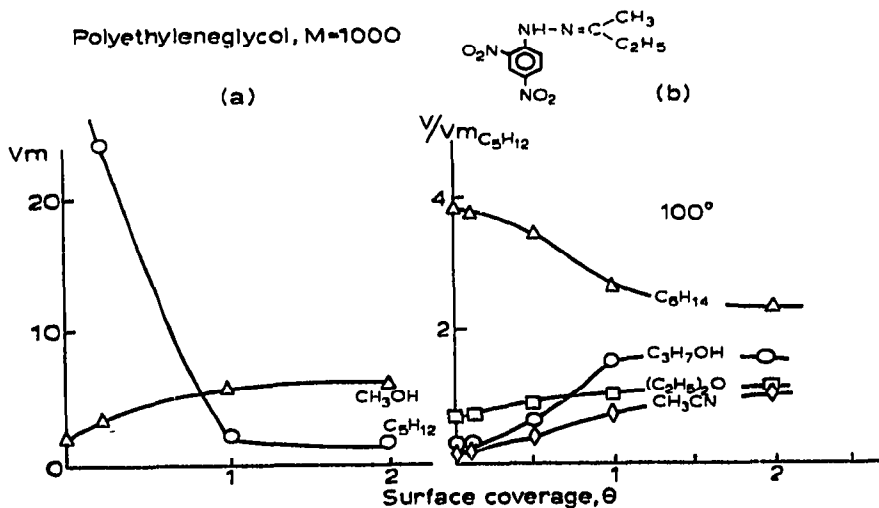


Fig. 11. (a) Dependence of the specific retention volume for *n*-pentane and methanol on the degree of coverage, θ , of the surface of the graphitised carbon black coated with polyethyleneglycol. (b) Dependence of the specific retention volumes of *n*-hexane, *n*-propanol, diethyl ether, and acetonitrile, relative to the retention volume of *n*-pentane on the degrees of coverage, θ , of the acetylene black surface coated with the 2,4-dinitrophenylhydrazone of methyl ethyl ketone

TABLE I

APPROXIMATE VALUES OF THE TOTAL HEAT OF ADSORPTION AT A LOW SURFACE COVERAGE, Q_{total} , AND THE CONTRIBUTION TO THESE VALUES DUE TO SPECIFIC INTERACTIONS WITH THE ADSORBENT, $Q_{specific}$, FOR DIFFERENT COMPOUNDS (KCAL/MOLE)

The adsorbents are arranged in order of the decreasing $Q_{specific}$ for benzene adsorption.

Adsorbent	C_6H_6		$(C_2H_5)_2O$		$n-C_3H_7OH$	
	Q_{total}	$Q_{specific}$	Q_{total}	$Q_{specific}$	Q_{total}	$Q_{specific}$
BaSO ₄	12.2	5.0	—	—	—	—
Zeolite NaX	18.0	5.2	21.0	8.6	—	—
Silica gel with hydroxylated surface (degree of coverage $\theta = 0.5$)	10.2	2.8	15.0	7.3	16.0	11.1
Polyacrylonitrile	9.4	2.8	9.0	2.8	9.6	4.8
Polyethyleneglycol (monolayer on carbon black)	9.1	2.5	6.1	0.0	9.4	4.6
2,4-Dinitrophenylhydrazine of methyl ethyl ketone (monolayer on carbon black)	8.3	1.2	8.1	1.5	8.3	2.8
Phthalocyanine (10% by wt. on graphitised carbon black)	7.9	0.7	6.9	0.0	10.4	5.0
Graphitised thermal carbon black	9.2	0.0	8.6	0.0	8.1	<0.5

carbon black, a non-specific adsorbent of the first type, with a dense monolayer of polyethyleneglycol sharply lowers the adsorption of the A-group molecules (*n*-alkanes) but increases the adsorption of D-group molecules (methanol). By modifying graphitised carbon black with a monolayer of polyethyleneglycol, we can obtain an adsorbent of a third type. In this case we have the electron density concentrated locally at the edge of the ether group; this electron density provides high specific activity with respect to molecules of the D-group and at the same time gives a low background for non-specific interactions⁴⁵.

In Fig. 11b, the result of the modification of the surface of the graphitised carbon black with a dense monolayer of 2,4-dinitrophenylhydrazine of methyl ethyl ketone is shown. In this case, different centres appear on the surface, but the surface on the whole acquires the properties of an adsorbent of the third type characterised by the strong retention of alcohols⁴⁶.

The change in the contribution to the total heat of adsorption of the energy due to specific interaction and the change in the total heat of adsorption of molecules of different groups on adsorbents of different types are evident from the data summarised in Table I.

Molecular-statistical calculation of Henry constants

Representation of the adsorption isotherm in virial form. In addition to calculating, by the methods of the molecular theory of adsorption, the potential energy of adsorption, which is close to the heat of adsorption, the calculation of the retention volumes as a function of concentration (*i.e.* adsorption isotherms), or at least at zero surface coverage (*i.e.* Henry constants), is of even greater interest. The adsorption equilibrium for many cases can be expressed through the virial form of the equation for the adsorption isotherm:

$$p = \Gamma \exp(C_1 + C_2\Gamma + C_3\Gamma^2 + \dots) \quad (4)$$

where p is the pressure of a given adsorbate in the gas phase; Γ is the Gibbs adsorption per unit surface area of the adsorbent; and $C_1, C_2, C_3 \dots$ are coefficients which depend on the temperature. This equation is obtained by the molecular-statistical method⁴⁷ and by substituting into the Gibbs equation the equation for a two-dimensional state in the virial form^{1,48}. For a low surface coverage, eqn. 4 expressed as an equation of the Gibbs adsorption isotherm in the virial form changes to:

$$p = K_1' \Gamma + K_2' \Gamma^2 + \dots \quad (5)$$

where $K_1' = \exp C_1$; $K_2' = C_2 \exp. C_1$. In the molecular-statistical theory of adsorption^{4,40} this equation is usually written in reverse in the form of a series of powers of p

$$\Gamma = K_1 p + K_2 p^2 + \dots \quad (6)$$

Here, K_1 is Henry's constant, which is related to the absolute value (calculated per unit surface area) of the retention volume V_s through the equation (ref.15) :

$$V_s = K_1 RT \quad (7)$$

The remaining constants K_2, K_3, \dots take into account the adsorbate-adsorbate interaction (paired, tripled, etc.) in the adsorbent field.

Molecular-statistical equations for virial coefficients. Eqn. 6 is obtained by the general molecular-statistical method using a large partition function and assuming that the gas far away from the adsorbent surface is an ideal gas^{4,40}. The quantitative calculations of coefficients K_1 and K_2 in the case of gas adsorption chromatography on fairly homogeneous surfaces are simpler than in the case of gas-liquid chromatography. This is due to the fact that the force centres of the adsorbent are tightly held. The virial coefficients are expressed through the corresponding statistical partition functions, Z , by following equations (ref. 49):

$$K_1 = \frac{v}{skT} \left(\frac{Z_1}{Z_1^0} - 1 \right), \quad (8)$$

$$K_2 = \frac{v^2}{s(kT)^2} \left[\frac{2Z_2 - Z_1^2}{(Z_1^0)^2} \right] \quad (9)$$

Here, Z_1 and Z_1^0 are the partition functions for a single molecule within the volume v when the interaction of the molecule with the adsorbent surface is possible and subsequently when such interaction is absent in the same volume; Z_2 is the partition function within the volume v for two molecules when their paired interaction with one another in the adsorbent field is possible.

Measurements in gas chromatography are usually carried out at fairly high temperatures except in the separation of hydrogen isotopes and isomers⁵⁰. Thus the calculation of the partition functions Z can be made according to classical approximations. By assuming that the partition function which is related to intramolecular motion remains practically unchanged during adsorption (which holds true for non-specific adsorption), POSHKUS AND AFREIMOVICH⁵¹ obtained the following equation for the Henry constant, K_1 , through the corresponding configurational integrals:

$$K_1 = \frac{\int [s_i]^{\frac{1}{2}} \exp(-W/kT) [\exp(-\Phi/kT) - 1] \sin\vartheta dx dy dz d\vartheta d\varphi d\psi d\alpha_1 \dots d\alpha_t}{8\pi^2 s kT \int [s_i]^{\frac{1}{2}} \exp(-W/kT) d\alpha_1 \dots d\alpha_t} \quad (10)$$

Here, W is the potential energy of the isolated molecule which does not interact with the neighbouring molecules of the adsorbate, this energy being dependent on the angles of the internal rotation of the molecule, $\alpha_1 \dots \alpha_t$; $-\Phi$ is the potential energy of interaction of the molecule with the adsorbent surface, this energy being the function of the x, y, z coordinates of the centre of the mass, Euler's angles ϑ, φ, ψ describe the orientation of the quasi-rigid core of the molecule in space and $\alpha_1 \dots \alpha_t$, the internal rotation angles; the function $[s_i]$ is the determinant of the matrix composed of the quadratic equation coefficients for the rotational kinetic energy of the molecule expressed by projection of the angular velocity of rotation of the core and the derivatives of the internal angles of rotation. Thus this equation for K_1 is sufficiently general in form and is not linked to any model of localised or mobile adsorption. However, this equation involves the assumption that the interaction with the adsorbate molecule does not affect the state of the adsorbent which is considered as a field source only, causing deviation of the gas near the surface from its ideal state far away from the surface. For fairly rigid adsorbents, especially in the case of non-specific adsorption, this assumption holds true.

In many cases of practical importance, eqn. 10 for Henry constants can be simplified. For a homogeneous crystal surface, $-\Phi$ is a periodic function of x and y . Often, for example in the case of adsorption on the basal plane of graphite, this periodicity can be neglected by assuming that the regular distribution of the adsorbent density is parallel to the basal plane^{3,5,52}. The determinant $[s_i]$ depends on the internal angles of rotation of the linkages i of the molecule. However, if the molecule has a rigid core and if t symmetrical spindles (as, for example, in butane and n -pentane molecules) are attached to it, $[s_i]$ becomes constant and eqn. 10 can be abbreviated. If the whole molecule is quasi-rigid, *i.e.* if internal rotations are impossible, $W = 0$. In this frequently occurring case, only the term for the potential energy for the interaction of the isolated adsorbate molecule with the adsorbent remains in the expression for K_1 and:

$$K_1 = \frac{1}{8\pi^2 s kT} \int [\exp(-\Phi/kT) - 1] \sin\vartheta dx dy dz d\vartheta d\varphi d\psi \quad (11)$$

Finally, when the molecule is of the one-atom type, the expression for the Henry constant becomes very much simplified and contains only the x, y, z coordinates of the centre of the molecule.

The calculation of the next virial coefficient K_2 is carried out by taking into account the potential energy of the paired adsorbate-adsorbate interaction (this energy is a part of the partition function Z_2 in eqn. 9) in the case of simultaneous interaction of both molecules with the adsorbent (the partition function Z_1 is included in eqn. 9).

The approximation of the additivity of paired adsorbate-adsorbate interaction in the calculation of interaction energy in the equation for K_2 as well as for paired $j \dots i$ interactions in the calculation of $-\Phi$ (see eqn. 1) is quite satisfactory, since to disregard the interactions of many bodies which strongly depend on their mutual orientation apparently does not lead to large errors.

Eqns. 8, 10, 11 have been used in the work of KISELEV *et al.*^{1, 15, 40, 51-55} for the calculation of the Henry constant K_1 (retention volumes V_g for zero sample size) at different temperatures, as well as for the change in the chemical potential, $\Delta\mu$, in the case in which the adsorbate molecule transfers from the gas phase at standard pressure p^0 to the surface with a low value of adsorption Γ (with the assumption that up to this value of Γ the adsorbate-adsorbate interactions can be neglected):

$$\Delta\mu = -RT \ln K_1 + RT \ln (\Gamma/p^0) \quad (12)$$

The calculation of isotheric heat of adsorption Q_1 and the differential molar change in the entropy of the adsorbate, ΔS , at low surface coverage requires the calculation of the first derivative with respect to temperature of $\ln K_1$ (and thus also the corresponding configurational integrals) with the assumption that v and s are constants:

$$Q_1 = -RT^2 \frac{\partial \ln K_1}{\partial T} \quad (13)$$

and

$$\Delta S = R \left(\ln K_1 + T \frac{\partial \ln K_1}{\partial T} - \ln \frac{\Gamma}{p^0} \right) \quad (14)$$

On the other hand, the calculation of the differential molar change in the adsorbate heat capacity, $\Delta \bar{c}_{v,s}$, requires the calculation of the second derivative of $\ln K_1$ with respect to temperature (and thus the corresponding configurational integrals⁵⁴ as well):

$$\Delta \bar{c}_{v,s} = - \frac{\partial Q_1}{\partial T} = R \left(2T \frac{\partial \ln K_1}{\partial T} + T^2 \frac{\partial^2 \ln K_1}{\partial T^2} + 1 \right) \quad (15)$$

A comparison of the calculated values of $\ln K_1$ and the experimental values. Such a comparison has been made by KISELEV *et al.*^{1, 5, 40, 51-55} for the adsorption of a series of simple and complex molecules on graphitised thermal carbon black and by BRÄUER *et al.*^{27b} for the adsorption of some simple molecules on various cationic forms of

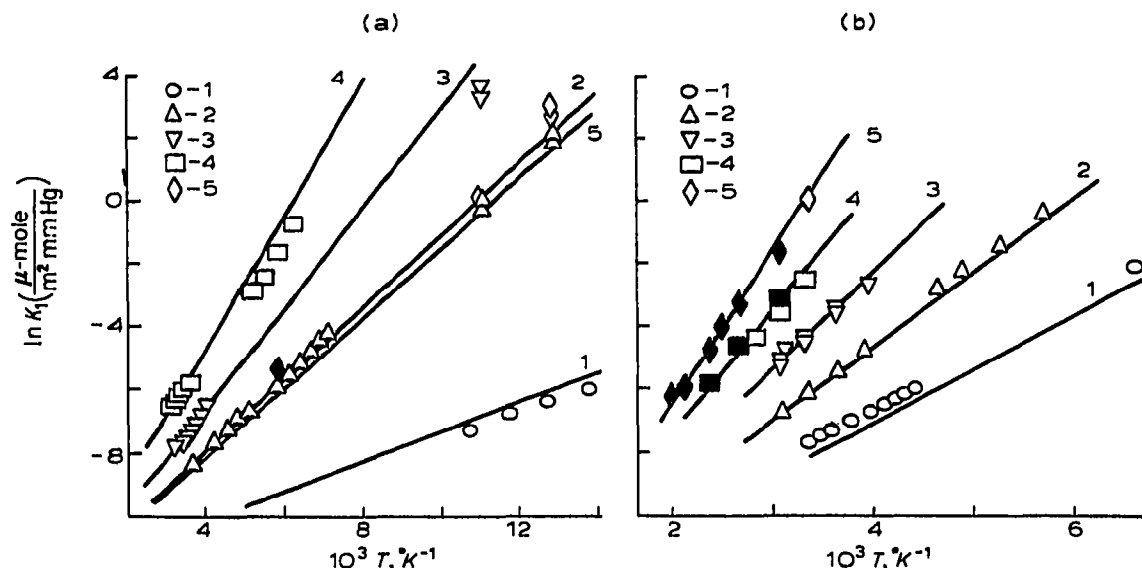


Fig. 12. Dependence of the calculated (lines) and the measured (points) Henry constants as a function of the reciprocal of the absolute temperature on graphitised carbon black. (a) 1 = Neon, 2 = argon, 3 = krypton, 4 = xenon, 5 = nitrogen. (b) For C_1 - C_6 *n*-alkanes

zeolite A. In the latter case, account is taken of the heterogeneous distribution of the molecular field in different directions inside the cavities of a porous crystal.

Fig. 12 shows a comparison of the calculated dependences of $\ln K_1$ on $1/T$ with the experimental data for adsorption on graphitised thermal carbon black. For noble gases and nitrogen, calculations were made by means of eqn. 11. The adsorbate-adsorbate interaction potential $\varphi_{C...1}$ was calculated from eqn. 2, and the summation with respect to the carbon atoms of the semi-infinite lattice of the graphite in the calculation of $\Phi(z)$ (see eqn. 1) was carried out by the CROWELL method³ for a regular distribution in carbon density along the basal planes. The constants C'_{C1} and C''_{C1} for these adsorbents were calculated from the KIRKWOOD-MÜLLER theoretical equation^{7,8} and an equation analogous to this one⁹. From Fig. 12a, it can be seen that the lines calculated in this manner agree satisfactorily with the experimental data.

In the case of hydrocarbons (*n*-alkanes from C_1 to C_6), atom-atom potentials $\varphi_{C...C}$ and $\varphi_{C...H}$ and group-atom potentials $\varphi_{C...CH_3}$ and $\varphi_{C...CH_2}$ were used. In the determination of the corresponding C'_{C1} and C''_{C1} constants of these potential functions, the calculation of the configurational integrals and the values of $\ln K_1$ for adsorption of the first alkanes considered as quasi-rigid gave results which deviated somewhat from the experimental data (within $\pm 10-15\%$). In order to use these potential functions for all hydrocarbons, a constant correcting factor was introduced for the constants C'_{C1} and C''_{C1} (ref. 54). POSHKUS⁵⁵ (see also ref. 56) has shown that the effective potential function $\varphi_{C...C}$ obtained for the adsorption of hydrocarbons on graphite is very close to the effective potential function calculated for other cases where there is molecular interaction between carbon atoms. This is indicated by data on the compressibility of graphite⁵⁷, the properties of molecular crystals of hydrocarbons⁵⁸, and the second virial coefficient of gaseous methane⁵⁹. This means that the effect of interactions between many bodies is insignificant and that the approximation of the additivity of paired interactions is satisfactory.

By using these effective potential functions for atom-atom and group-atom interactions and by taking into account the differences in the adsorption of different rotational isomers (*trans*- and *skew*-forms of *n*-butane and *n*-pentane), KISELEV *et al.*⁵⁵ calculated $\ln K_1$ as the function of $1/T$ for all C_1-C_6 *n*-alkanes. From Fig. 12b it can be seen that in the case of the adsorption of complex molecules, the calculated values are close to the experimental values. Analogous results have been obtained for quasi-rigid molecules of benzene, ethylene, and acetylene.

The calculated values for $\Delta\bar{c}_{v,s}$ (ref. 60) can be compared with the calorimetric measurements⁶¹ only for the case of adsorption of benzene on graphitised thermal carbon black; and these values are in good agreement. The value of $\Delta\bar{c}_{v,s}$ in this case amounts to approx. 5 cal/mole·deg; this indicates that in the treatment of gas chromatographic data obtained at wide intervals of column temperature, Q_1 as a function of temperature should be taken into account.

Molecular-statistical and thermodynamic estimation of the separation of components leaving a column and the order of the appearance of these components. This problem is of great interest in gas chromatography, since the order of emergence of the peaks for two given components depends on the nature and the geometry of their molecules, the adsorbent surface and on the temperature.

Usually the order of the $\ln V_s$ values for two components on the same adsorbent corresponds to the order of the values of the heat of adsorption¹⁶. However,

with a change in temperature a reversal in the order of appearance of the peaks is often observed. The molecular-statistical calculation of the $\ln V_s$ values and the heat of adsorption is not sufficiently precise because of the small changes in these values on changing over from adsorption of one molecule to that of another of similar structure. However, the difference in these values can be calculated fairly accurately, since in both cases the calculations involve the same assumptions and approximations.

In the papers⁶² for this symposium (see also ref. 63) POSHKUS examines the separation of deuterio-substituted molecules in great detail from the point of view of the molecular statistical theory. He also cites the relevant literature on the subject. The quantum-statistical effects related to the intramolecular vibrations rapidly decrease with increase in temperature. Translational and rotational quantum effects increase the adsorption of the heavier molecules among the series of the isotopes investigated, but these effects rapidly disappear with the increase in the mass and moment of inertia of the molecule and increase in temperature. Thus, under conditions of chromatographic measurement, the difference in the potential functions of the interaction of deuterated hydrocarbons with the surface is of great importance. This difference is mainly due to the lesser polarisability of the deuterated linkages of the molecule. KISELEV AND POSHKUS^{62,63} give an equation, obtained by quasi-classical approximation, describing the relative difference in the retention volumes for a number of organic substances in the H- and D-substituted forms of the molecules. In the same work, the corresponding expressions for the differences in the heat and entropy of adsorption and the changes in the heat capacity of the adsorbate are given. In accordance with the molecular adsorption theory, the retention volumes and the heats of adsorption on graphitised carbon black^{64,65} and carbonised Saran⁶⁶ are smaller for D-substituted compounds than those for H-substituted compounds.

The separation of various geometrical isomers and positional isomers on graphitised thermal carbon black and the possibility of using gas adsorption chromatography in the investigation of molecular structure have been reviewed in detail by KISELEV *et al.*⁵⁶. In the paper by KOUZNETSOV AND SHEHERBAKOVA⁶⁷ presented at this symposium, new results on the use of gas chromatography, based on non-specific adsorbents having a homogeneous plane surface, for the estimation of the molecular structure of a number of hydrocarbons are reported.

The investigation of the frequently observed inversion of the order of appearance of the components from a column upon a change in temperature is of great interest. KISELEV AND POSHKUS⁶⁸ have examined the conditions leading to the intersection of the plots of $\ln V_s$ as a function of $1/T$ in the case of low surface coverage. In this case (see eqns. 7, 12-14) we have:

$$\ln K_1 = \ln (V_s/RT) = Q_1/RT + [\Delta\bar{S}/R + \ln(\Gamma/p^0)] \quad (16)$$

The entropy of the adsorption $\Delta\bar{S} + R \ln(\Gamma/p^0)$ is usually negative^{15,48,60,70}. The value of $\Delta\bar{S}/R + \ln(\Gamma/p^0)$ as well as that of $K_1 = (\Gamma/p)_{\Gamma,p \rightarrow 0}$ and Q_1 are limited and finite. That is, they are independent of Γ . But all these values K_1 , V_s , Q_1 , and $\Delta\bar{S}/R + \ln(\Gamma/p^0)$ depend on temperature. With an increase in Q_1 , an increase in $\ln K_1$ and in the absolute value of the entropy of adsorption also occur. The dependence of these values on Q_1 is often linear¹⁵. This question has been examined in theoretical studies by BARRER AND REES⁶⁹, BARKER AND EVERETT⁴⁸, and KISELEV AND POSHKUS⁷⁰.

For adsorption on graphitised thermal carbon black the theoretical slopes of these relations were calculated for the noble gases and *n*-alkanes⁷⁰.

The difference between the $\ln K_1$ values for two adsorption systems at the same temperature, T , and for adsorption of two components on the same adsorbent is in accordance with eqn. 16:

$$\Delta \ln K_1 = \Delta Q_1/RT + \Delta[\Delta S/R + \ln(\Gamma/p^0)] \quad (17)$$

The temperature at which the retention of both components becomes equal, *i.e.* when $\Delta \ln K_1$ becomes zero, and an inversion of the order of appearance of the peaks occurs, is described by the equation:

$$T_{\text{inversion}} = - \frac{\Delta Q_1}{\Delta[\Delta S + R \ln(\Gamma/p^0)]} \quad (18)$$

The difference in the heats of adsorption and the entropies of adsorption are related here to the temperature $T_{\text{inversion}}$. The intersection of the plots of $\ln K_1$ against $1/T$ for two components takes place in the range of temperatures usually encountered in gas chromatographic measurements, if the small differences in the heats of adsorption ΔQ_1 correspond to sufficiently large differences in the entropy of adsorption $\Delta[\Delta S + R \ln(\Gamma/p^0)]$. The inversion temperature can be predicted both on the basis of experimental measurements of V_g as a function of T for the corresponding pair of components and by means of molecular-statistical calculations of $\ln K_1$ (or Q_1 and $\Delta S + R \ln(\Gamma/p^0)$). Fig. 13 shows the results of such calculation for the adsorption of benzene and cyclohexane on graphitised thermal carbon black. This calculation suggests that the inversion of the order of appearance of the peaks should take place at fairly high temperatures. Unfortunately, however, this cannot be confirmed owing to the fact that experimental data obtained so far are not sufficiently precise.

SOME ANALYTICAL APPLICATIONS OF GAS CHROMATOGRAPHY USING NEW ADSORBENTS

Graphitised thermal and acetylene carbon black

The advantages of graphitised carbon black as a non-specific adsorbent with

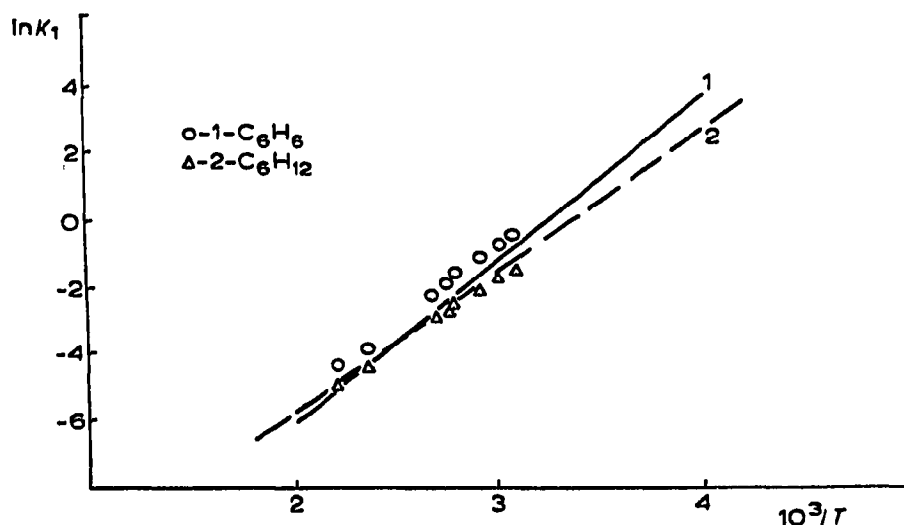


Fig. 13. Calculated (solid and dotted lines) and measured (points) dependence of $\ln K_1$ on $1/T$ for benzene (1) and cyclohexane (2) on graphitised thermal carbon black.

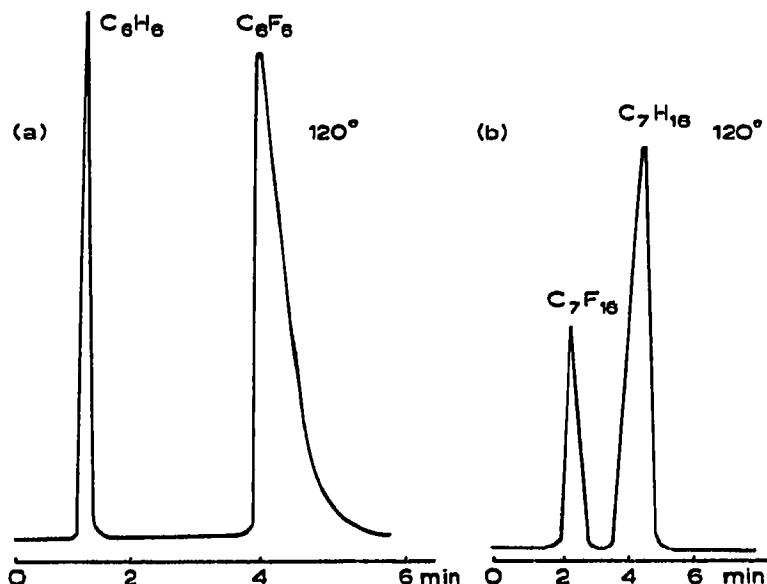


Fig. 14. Separation on graphitised thermal carbon black column: (a) benzene + perfluorobenzene; (b) perfluoroheptane + *n*-heptane. Experiments by I. A. MIGUNOVA and YA. I. YASHIN

the plane faces of the particles of graphite being formed by the basal planes are well known^{14,15,56,65,67}. In this work, therefore, we shall only cite examples of new applications of graphitised thermal and acetylene carbon black.

Graphitised thermal carbon black, an adsorbent with a plane surface, is particularly effective in the separation of structural and geometrical isomers. Several examples of separations of isomers are considered by KOUZNETSOV AND SHCHERBAKOVA⁶⁷ in their paper for this symposium. The theory for the separation of isotopes has been examined by KISELEV AND POSHKUS^{62,63}.

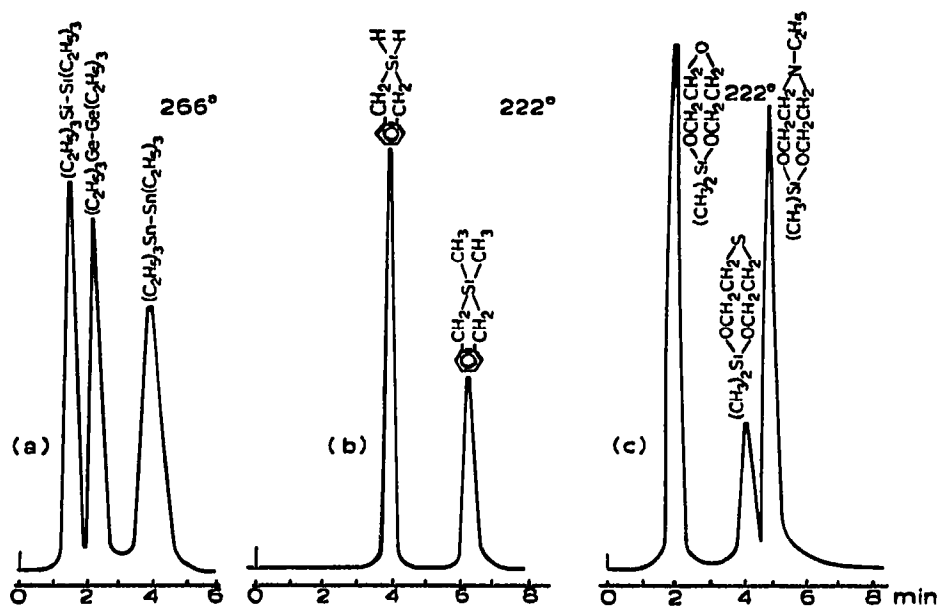
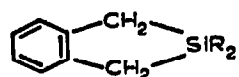


Fig. 15. Separation on graphitised thermal carbon black column: (a) bielemento-organic compounds containing silicon, germanium and tin; (b) organosilicon compounds; (c) heterocyclic compounds.

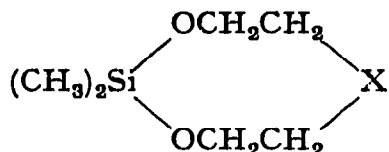
The separation on graphitised thermal carbon black of the usual and fluorine-saturated aromatic hydrocarbons is of interest. In the case of benzene the substitution of hydrogen by fluorine takes place in the plane of the aromatic ring and therefore does not lead to an increase in the distance between the carbon atoms of the molecule and the basal plane of the graphite. The polarisability of the fluorinated molecule is somewhat higher, and thus the energy of a non-specific interaction with graphitised thermal carbon black in the case of perfluorobenzene is greater. From Fig. 14a it can be seen that in accordance with this, perfluorobenzene leaves the column after benzene. In the case of the fluorination of methyl and methylene groups, their radius increases and the carbon atoms of fluorinated alkanes are at a greater distance from the basal plane of the graphite. Consequently, the energy of a non-specific interaction of fluorinated alkanes and cycloalkanes⁷¹ with the basal plane of the graphite is smaller than that of the unfluorinated alkanes and cycloalkanes. From Fig. 14b it can be seen that *n*-perfluoroheptane leaves the column first, while the *n*-heptane remains longer on the column.

As a chemically inert non-specific adsorbent, graphitised thermal carbon black is effective in the separation of elemento-organic compounds. Fig. 15a shows the separation of bielemento-organic compounds of silicon, germanium, and tin; Fig. 15b shows the separation of organosilicon compounds of the type



where $R = \text{CH}_3$ or H ; while Fig. 15c shows the separation of

heterocyclic organosilicon compounds of the type



where X is $>\text{O}$, $>\text{S}$, and $>\text{NC}_2\text{H}_5$ (ref.72). The

efficiency of this separation on graphitised thermal carbon black exceeds that obtained in gas chromatographic columns filled with various non-polar and polar liquid phases.

Graphitised thermal carbon black is a fine powder. The granular particles obtained after shaking and passing it through a sieve are irregular in shape and have low mechanical strength. This has a detrimental effect on the hydrodynamic conditions inside the column and decreases its efficiency. KISELEV *et al.*⁷³ investigated the optimal conditions for reinforcing the carbon black particles by treatment with an adhesive polymer (Apiezon L, 0.01% by wt.). This treatment yielded mechanically strong particles without affecting the properties of graphitised thermal carbon black as a non-specific adsorbent having a homogeneous plane surface. We have named this new material Carbochrom. From Fig. 16 it can be seen that in the separation of C_6 - C_{10} mixtures of *n*-alcohols the efficiency of the Carbochrom column is twice that of a column of the same length filled with untreated graphitised thermal carbon black.

It has been found that Carbochrom obtained from graphitised carbon black having a higher specific surface area is effective for the separation of more volatile mixtures. A suitable material for this purpose is acetylene black. During its preparation acetylene black is subjected to thermal treatment at 2500-3000° (ref. 74). Fig. 17a illustrate the dependence of the specific surface area of acetylene black on the amount of polyisobutylene and polyphenylmethylsiloxane used as adhesion modifying

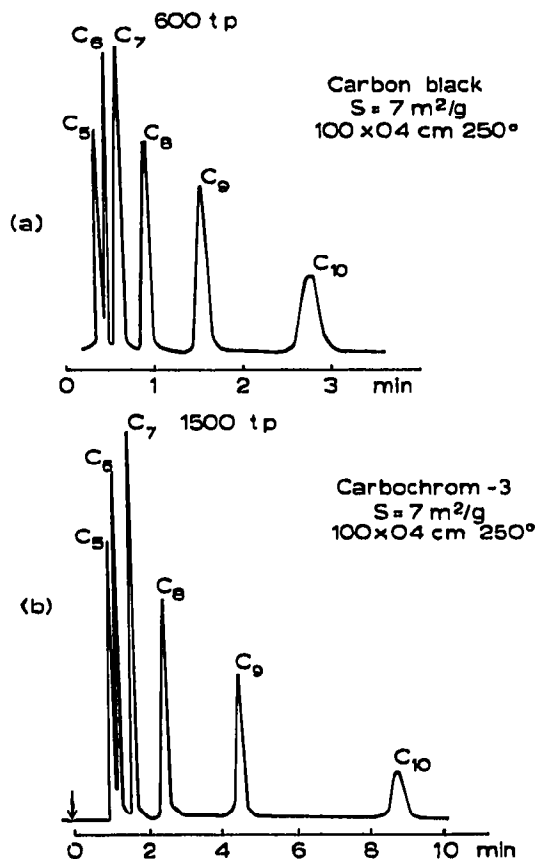


Fig. 16. Separation of C_5 - C_{10} n -alcohols (a) on graphitised thermal carbon black without modification with an adhesive material, (b) on Carbochrom (graphitised thermal carbon black + 0.01% by wt. Apiezon L)

agents⁷³. As shown in Fig. 17b, the addition of polyisobutylene (0.5% by wt.) considerably increases the efficiency of the acetylene black column.

Silochroms

Silochroms are prepared from aerosilogels subjected to an additional treatment for the purpose of obtaining the desired specific surface area and pore structure. As shown earlier (Figs. 8 and 9), the hydroxylated and dehydroxylated surface of pure silica is only capable of molecular adsorption, even with rather strong organic bases. In Fig. 18, some examples are shown illustrating the separation of compounds of the B-group, *i.e.* those which can specifically interact with the hydroxyl groups of the silica surface⁷⁶. The peaks obtained in chromatographic separations with columns containing pure macroporous silica are fairly symmetrical, and the temperature of the column need not be high. The relatively low energy of non-specific interactions makes it possible to utilise macroporous silochromes for the separation of high-boiling-point substances at relatively low temperatures. Data in Fig. 19 illustrate the separation, at 250° , of a mixture of phthalic acid esters on macroporous silochrome having a specific surface area of $80 \text{ m}^2/\text{g}$.

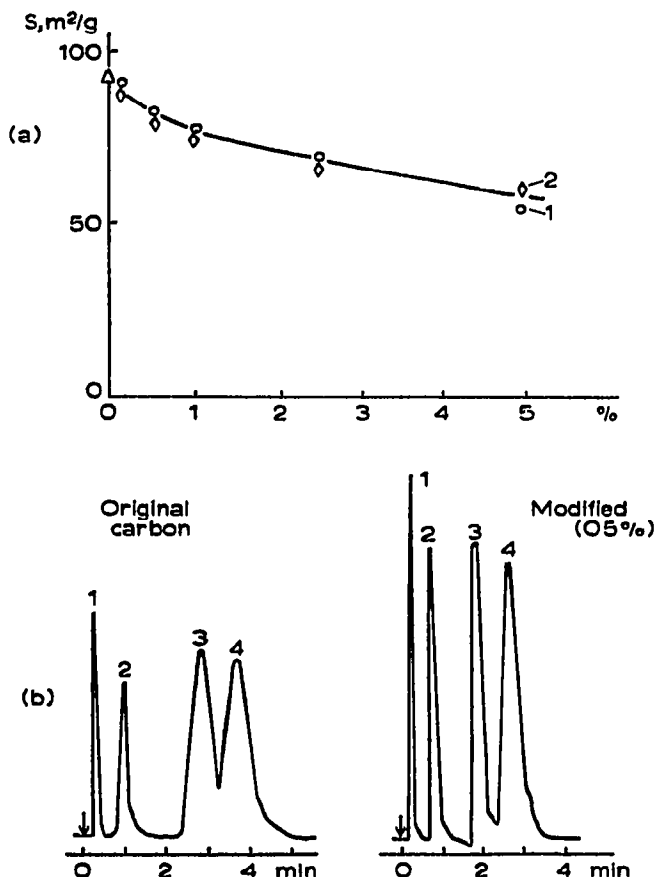


Fig. 17. (a) Dependence of the specific surface area, s , of acetylene black on the amount of adhesive material. 1 = Polyisobutylene; 2 = polyphenylmethylsiloxane. (b) Separation of aromatic hydrocarbons: 1 = benzene; 2 = toluene; 3 = cumene; and 4 = *p*-xylene; all on acetylene black and on acetylene black modified by the addition of 0.5% by wt. polyisobutylene.

Barium sulphate

Data in Fig. 6 and Table I show the high specificity of BaSO_4 as an adsorbent of the second type. Thus barium and magnesium sulphates are suitable for separating molecules of the B-group, which undergo weak specific interactions with adsorbents of the second type. The selection of adsorbents such as these enhances the weak specific interaction. Fig. 20 shows a chromatogram²¹ for some aromatic hydrocarbons separated on barium sulphate. Even in this preliminary experiment with a low-efficiency column, there is complete separation of the *o*-, *m*-, and *p*-mixture of xylenes. This example shows that it is possible to control the adsorption properties, particularly the specificity of the adsorbents, using various inorganic crystalline substances (especially those having a lamellar structure). The modification of such adsorbents can often be achieved by the ion-exchange method. In this respect compounds with an organic cation should be effective. TARAMASSO AND VENIALE⁷⁰ showed that the separation of aromatic hydrocarbons on a beidellite-type adsorbent treated with long-chain alkyl-ammonium complexes can be highly efficient. Apparently in this case we have an effective combination of the non-specific behaviour of the organic layer and the residual specific behaviour of the mineral itself.

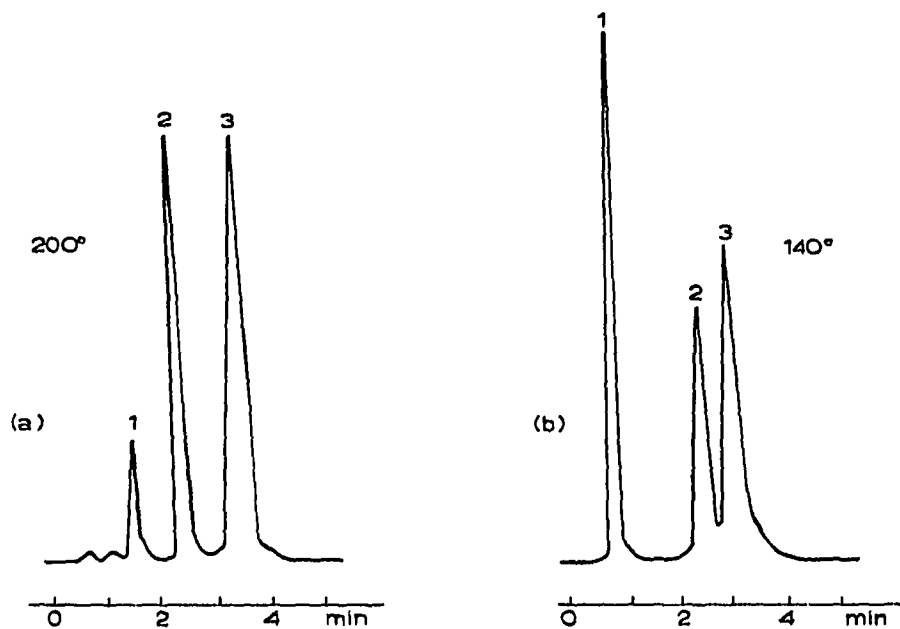


Fig. 18. Chromatograms obtained with Silochrom C-80. (a) Mixture of ketones: 1 = acetone; 2 = methyl ethyl ketone; 3 = diethyl ketone. Column temperature, 200°; sample size, 0.4 μ l. (b) Mixture of esters: 1 = ethyl formate; 2 = ethyl acetate; 3 = methyl isobutyrate. Column temperature, 140°, sample size, 0.4 μ l

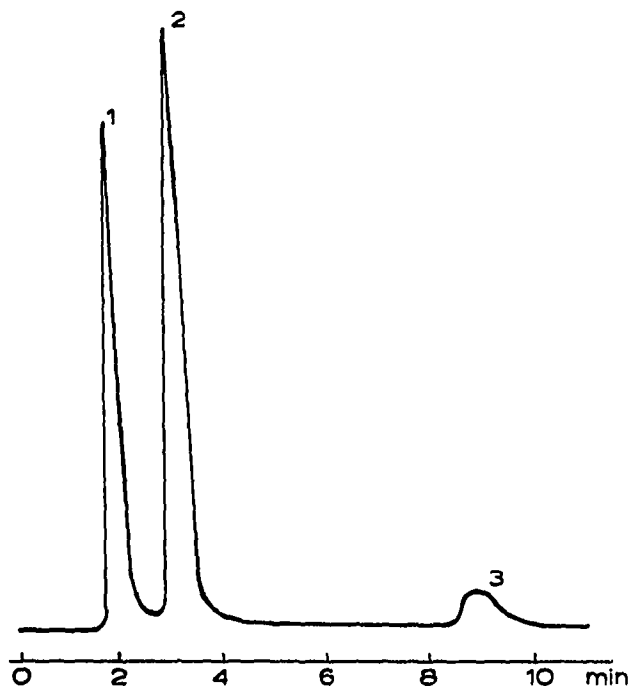


Fig. 19. Chromatograms obtained with Silochrom C-80 of a mixture of phthalic acid esters: 1 = dimethyl phthalate, 2 = diethyl phthalate; 3 = dibutyl phthalate. Column temperature, 270°, sample size, 0.4 μ l.

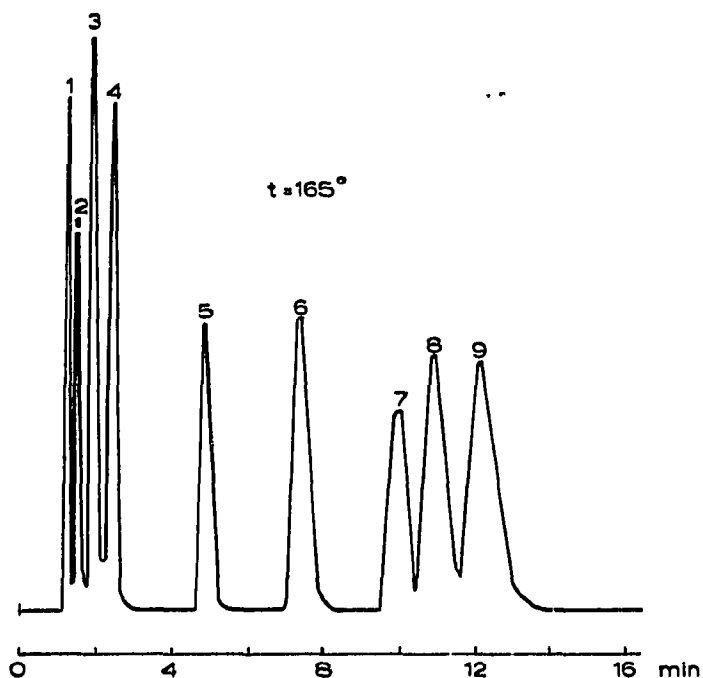


Fig. 20. Chromatograms for mixtures of aromatic hydrocarbons separated on BaSO_4 . Column temperature, 165° ; column length, 400 cm; column diameter, 0.6 cm; flame ionisation detector; carrier gas, nitrogen; carrier gas flow rate, 55 ml/min. 1 = Cyclohexane; 2 = cyclohexene, 3 = 1,3-cyclohexadiene, 4 = benzene; 5 = toluene, 6 = ethylbenzene, 7 = *p*-xylene; 8 = *m*-xylene; 9 = *o*-xylene.

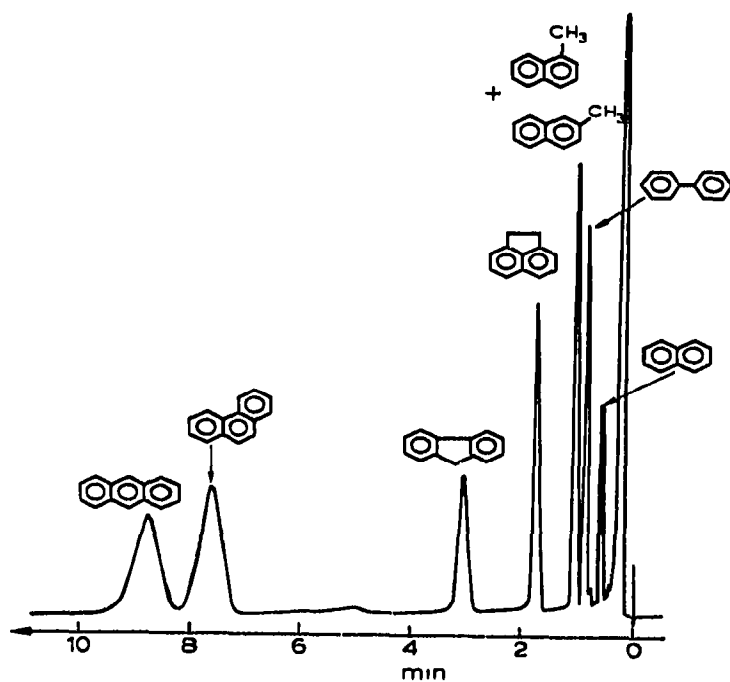


Fig. 21. Chromatogram for the separation of aromatic hydrocarbons on graphitised thermal carbon black containing 1% by wt. copper phthalocyanine. Column temperature, 265° ; column length, 1 m; carrier gas, hydrogen; carrier gas flow rate, 28 cm/sec.

Phthalocyanine and metal phthalocyanines

The characteristic adsorption properties of phthalocyanine have been illustrated in Fig. 4. The possibility of introducing metallic complex-forming ions leading to the formation of different phthalocyanines widens the prospect of controlling the specific nature of these adsorbents. These properties have been exploited successfully⁴⁴ in excellent separations of complex mixtures. An example of such a separation is shown in Fig. 21.

Adsorbents coated with dense monolayers

The coating of adsorbent supports having a large surface area with dense monolayers of various substances provides a number of advantages^{15,45,46,77}. These are:

(1) The shielding of the adsorbent support field with a dense monolayer of molecules or macromolecules (see Fig. 3) leads to a sharp decrease in the concentration of force centres on the coated surface as compared with the uncoated surface; this results in a considerable decrease in the adsorption energy.

(2) The detrimental effects due to heterogeneity of the adsorbent surface are completely or partially overcome.

(3) The degree of specificity of molecular interactions with the adsorbent surface can be controlled effectively by coating the adsorbent with monolayers of compounds containing such functional groups as $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, $-\text{CN}$, $>\text{O}$, $>\text{CO}$, $-\text{C}_6\text{H}_5$, etc.

(4) The monolayers are much less volatile than the corresponding volume phase, since the monolayers are located in the strong adsorption field of the adsorbent support.

Monolayers can be applied on the adsorbent support surface by adsorption from a solution (a particularly useful method when coating with non-volatile macromolecular polymers^{15,45,46,77}) or by adsorption from the carrier gas directly on to the adsorbent in the chromatographic column. The latter method is very convenient with substances that undergo chemisorption from the gas phase on the adsorbent support^{38,78a}. KISELEV AND YASHIN^{78b} have examined the effect on the order of appearance of the peaks in a separation of C_1 - C_4 alcohols on macroporous silica gel coated with various amounts of glycerine, sorbitol and triethanolamine. When the surface is almost completely covered with a dense monolayer, a change occurs in the relative retention volumes of this series of alcohols (see Fig. 11). The functional groups of glycerine, sorbitol, and triethanolamine become partially involved in a specific interaction with the HO-groups on the silanol surface, forming strong hydrogen bonds with them. Because of this, the strong specificity of the adsorbent is obstructed by the monolayer coating. Such modified adsorbents therefore show relatively weak adsorption of alcohols from the gas phase. As a result, the separation of alcohols can be carried out at a relatively low column temperature.

The specific nature of the monolayer surface becomes even less pronounced when the adsorbent support is coated with planar molecules which, like phthalocyanine (see Fig. 3), are located parallel to the surface of the adsorbent support. As a result, the adsorbent exhibits weak specificity. This makes it possible to separate the lower alcohols at yet lower temperatures. Fig 22 shows a comparison of the chromatograms obtained for C_1 - C_4 alcohols on macroporous silica gel with a specific

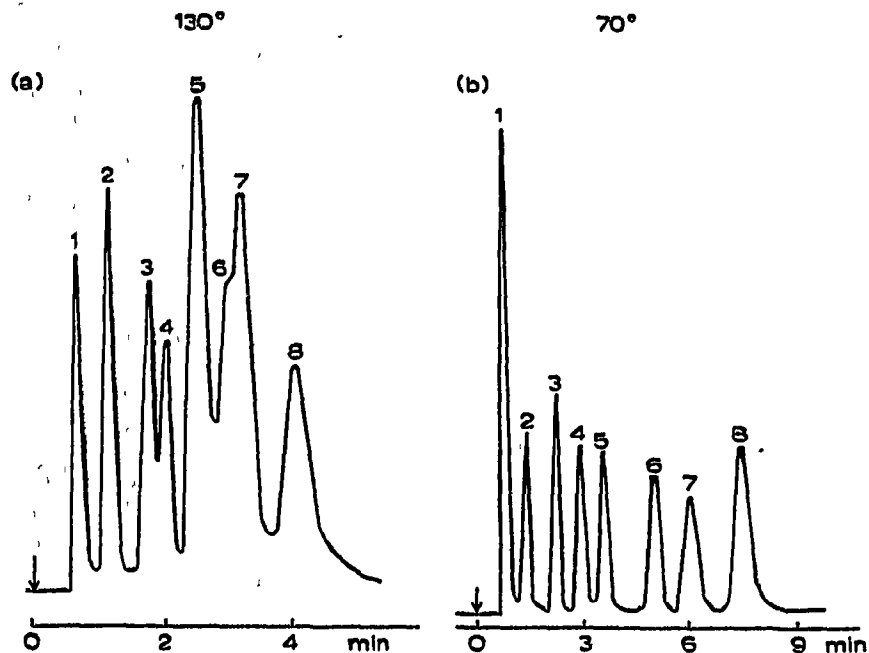


Fig. 22. Separation of C₁-C₄ alcohols on dense monolayers: (a) sorbitol on macroporous silica gel with specific surface area $s = 60 \text{ m}^2/\text{g}$; (b) 2,4-dinitrophenylhydrazone of methyl ethyl ketone on acetylene carbon black with specific surface area $s = 90 \text{ m}^2/\text{g}$.

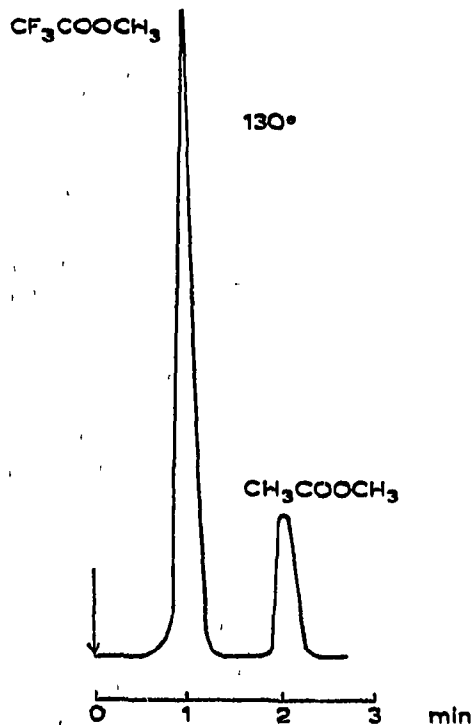


Fig. 23. Separation of the mixture CH₃COOCH₃ + CF₃COOCH₃ on Chromosorb-101.

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surface area, $s = 60 \text{ m}^2/\text{g}$, coated with a dense monolayer of sorbitol and on an acetylene carbon black adsorbent ($s = 90 \text{ m}^2/\text{g}$) coated with a dense layer of the 2,4-dinitrophenylhydrazone derivative of methyl ethyl ketone. In the latter case all eight C_1 - C_4 alcohols are well separated at a column temperature of 70° . The hydrazone monolayers on an acetylene carbon black surface do not affect the background of the flame ionisation detector at column temperatures up to 150° .

Porous polymers

Porous styrene-divinylbenzene copolymers such as the Chromosorbs-101 and -102 manufactured by the John Manville Co. and Polysorbs⁷⁰ are weakly specific adsorbents of the third type. Some of their adsorption properties with respect to the molecules of groups A, B, and D have been described by GVOZDOVICH *et al.*⁸⁰. The use of porous polymers in preparative chromatography is discussed in the paper by ZELVENSKY AND SAKODYNSKY⁸¹ at this symposium. Owing to their weak adsorption of water, porous polymers find wide applications in the analysis of various mixtures containing water^{82,83}. In Fig. 23 an example is given illustrating the separation of the B-group molecules, $\text{CH}_3\text{COOCH}_3$ and $\text{CF}_3\text{COOCH}_3$, on Chromosorb-101. Owing to the large radius of the fluorine atom, the volume of the CF_3 group is considerably greater than that of the CH_3 group, hence the main non-specific dispersion interaction of the fluorinated compound with Chromosorb-101, in this case the adsorption of B-group molecules on an adsorbent of the third type, is weaker, and $\text{CF}_3\text{COOCH}_3$ is the first to leave the column. This case is analogous to the separation of a mixture of perfluoroalkane and *n*-alkane on a non-specific adsorbent (see Fig. 14b). A more detailed analysis of the chromatographic separation of fluorinated compounds is discussed in the paper by GVOZDOVICH AND YASHIN⁸⁴ presented at this symposium.

LIQUID-MOLECULAR ADSORPTION CHROMATOGRAPHY

Some characteristics of liquid molecular adsorption chromatography

In 1903 TSWETT discovered chromatography as a liquid adsorption process⁸⁵. One reason for the slow development of liquid chromatography, apart from the fact that TSWETT's discovery at first received little attention, was the absence of sensitive and versatile detectors. In recent years liquid chromatography has become a subject of intense research. This interest is related to the development of new detection methods and to the fact that the shortcomings of gas chromatography had in the meantime become apparent. In its usual form (with a low pressure of weakly adsorbing carrier gas) gas chromatography can only be used in the separation and analysis of relatively volatile and thermally stable compounds. Highly compressed and strongly adsorbing carrier gases can be used to decrease the Henry constants in the case of heavy molecules^{86,87}. Actually this type of high pressure gas and fluid chromatography is similar to liquid chromatography, since the molecules of the carrier are concentrated and actively compete with the molecule of the components to be separated for the sites on the adsorbent surface.

In the case of liquid chromatography the separation takes place in the liquid layer immediately adjacent to the surface of the solid adsorbent. The separation proceeds at lower pressures and temperatures (usually at room temperature). Sepa-

ration in liquid molecular adsorption chromatography can be controlled by regulating not only the chemical nature and geometrical structure of the adsorbent surface but also the nature of the adsorbable mobile phase (eluant).

Depending on the diffusion rate of the components in solution and the pore size of the adsorbent, liquid chromatography can approach the conditions of equilibrium adsorption chromatography or molecular sieve chromatography. In this part of the paper we shall consider the first case, where the question of establishing a relationship between liquid adsorption chromatography and the theory of adsorption from solutions⁸⁸⁻⁹⁰ is of special significance. Unfortunately, however, this question has received very little attention as yet.

Adsorption isotherms from solution, equilibrium constants, and distribution function

Liquid molecular adsorption chromatography, in the case where the system approaches equilibrium, is based on the difference in the equilibrium constants for the solution-adsorbent system. Even where complete separation of the components of a mixture takes place, the elution peak of a given component contains at least two substances: the component from the mixture being analysed and the solvent. A characteristic of adsorption from solution is the mutual displacement of the molecules of the components of the solution on the adsorbent surface. That is, the adsorption of some molecules is inevitably accompanied by the desorption of others. The heat of adsorption of a given component from a liquid solution is determined by the difference in the energy of interaction of its molecules with the molecular fields of the adsorbent and the solution. Thus it is several times lower than the heat of adsorption of the same component from the gas phase. This makes it possible, firstly, to carry out liquid adsorption chromatography at significantly lower temperatures and, secondly, to utilise the changes in the molecular field both of the adsorbent and the eluant. In the case of mixed solvents being used during the elution of a given component of a mixture, adsorption takes place from at least a three-component system: a given component of the mixture being separated and the eluant which consists of the main

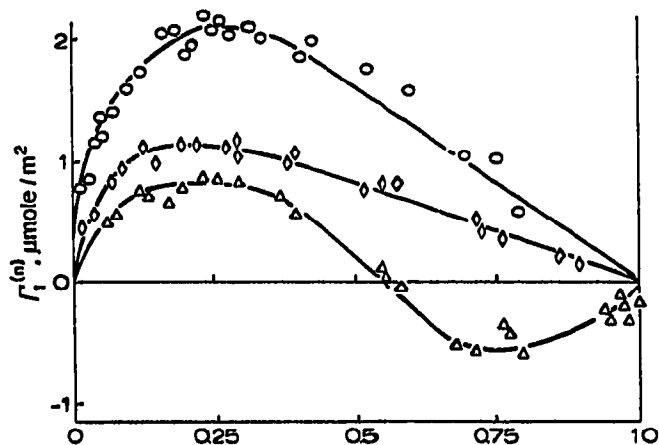


Fig. 24. Gibbs adsorption isotherm $\Gamma_1^{(a)}$ of toluene from solution in *n*-heptane on: \circ = hydroxylated silica gel, \diamond = oxidised carbon black; \triangle = non-oxidised carbon black. Mole fractions of the equilibrium bulk solution are on the abscissa.

solvent and a substance added to it. The increase in the concentration of this substance remains constant or is programmed.

The effect of the chemical nature of the adsorbent surface and its modifications in liquid adsorption chromatography is in general similar to that in gas chromatography. However, the competing interaction with the molecules of the solvent should be taken into account here. Fig. 24 shows the effect of decreasing the specificity of the adsorbent on the Gibbs adsorption isotherm $\Gamma_1^{(n)}$ from binary solutions of toluene (component 1) + *n*-heptane⁹¹. On going over to a non-specific adsorbent of the first type, graphitised carbon black, the magnitude of the Gibbs adsorption of the B-group molecules (toluene) from *n*-alkane solutions (molecules of the A group) sharply de-

TABLE II

EQUILIBRIUM CONSTANTS FOR A BINARY SOLUTION-ADSORBENT SYSTEM AT ROOM TEMPERATURE

<i>Mixture</i>	<i>Adsorbent</i>	<i>Equilibrium constant</i>
Benzene + <i>n</i> -hexane	Hydroxylated silica	9.1
Toluene + <i>n</i> -heptane	Hydroxylated silica	10.4
Benzene + <i>n</i> -hexane	Dehydroxylated silica	2.6
Toluene + <i>n</i> -heptane	Oxidised carbon black	3.0
Toluene + <i>n</i> -heptane	Non-oxidised carbon black	1.5

creases. In this case, at sufficiently high concentrations of toluene, its adsorption changes sign. It becomes negative (while the adsorption of *n*-heptane becomes positive), and the isotherm passes through the azeotropic point.

Table II gives a summary of the values for the equilibrium constants for the adsorption of an aromatic hydrocarbon from a solution in a saturated hydrocarbon on the surfaces of adsorbents in the order of their decreasing specificity^{91,92}. These values were calculated with the assumption that there is monomolecular adsorption, constant orientation of the molecules of the solution components near the surface, and equal areas occupied by these molecules on the adsorbent surface^{89,91}. With an increase in the degree of dehydroxylation of the silica surface or in the graphitisation of the carbon black, *i.e.* as one goes from specific adsorbents to non-specific, the equilibrium adsorption constant decreases. With the decrease in the equilibrium constant to 1.5 (in the case of adsorption on graphitised carbon black), the adsorption isotherm passes through the azeotropic point.

Fig. 25 shows the effect of the structure of aromatic compounds (benzene, naphthalene, biphenyl, phenanthrene) on the adsorption from solutions in non-specifically adsorbing solvents (*n*-alkanes) on the hydroxylated surface of silica gel. Here the adsorption is expressed in mole fractions of the surface solution $x_1^{(s)}$ calculated from experimental Gibbs adsorption values, $\Gamma_1^{(n)}$. In this case account is taken of the effect of the mutual displacement of the molecules of the aromatic compound and the solvent molecules. This effect is reflected in the ratio of the area occupied by the aromatic molecules to that occupied by the solvent molecules on the adsorbent surface⁹¹.

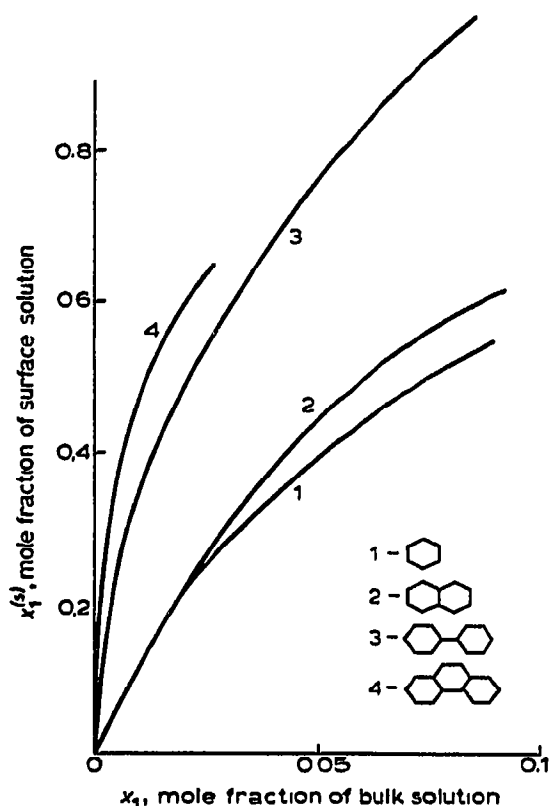


Fig. 25. Adsorption isotherms for benzene, naphthalene, biphenyl and phenanthrene from *n*-alkane solutions on silica gel with a hydroxylated surface. The adsorption values are given in mole fractions of the aromatic hydrocarbons in the surface solution, $x_1^{(s)}$.

In this case, the values for the activity in the bulk solutions are unknown, and the areas occupied by the component molecules are considerably different. Thus the equilibrium constants could not be calculated. But the order of these values in the case of strong specific adsorption of one of the components of the solution (aromatic hydro-

carbon) could be expressed by means of the distribution function $f = \frac{x_1^{(s)}}{x_2^{(s)}} / \frac{x_1}{x_2}$

when $x_1^{(s)} = x_2^{(s)} = 0.5$. Here, $x_1^{(s)}$, $x_2^{(s)}$ and x_1 , x_2 are the mole fractions of the components of the surface and bulk binary solutions, respectively. Table III summarises the values of f at $x_1^{(s)} = 0.5$ for the adsorption of a series of aromatic hydrocarbons from solutions in saturated hydrocarbons on a hydroxylated silica surface⁹². The successive order of the f values for polynuclear aromatic hydrocarbons from solutions in saturated hydrocarbons on specific adsorbents coincides with that of the retention times for polynuclear aromatic hydrocarbons in the case of the liquid adsorption chromatography (experiments of FROLOV AND YASHIN¹⁰⁰) and in the case of fluid gas chromatography at high pressures and with a strongly adsorbable carrier gas⁸⁶.

It will be necessary to establish in future work a clear relationship between the equilibrium constants for adsorption from solutions or at least the equilibrium values

TABLE III

DISTRIBUTION COEFFICIENT f IN THE ADSORPTION OF AROMATIC HYDROCARBONS ON A HYDROXYLATED SILICA SURFACE FROM SATURATED SURFACE SOLUTIONS

Mole fraction $x_1^{(g)} = 0.5$; at room temperature

Aromatic hydrocarbons	Distribution coefficient f
Benzene	12
Naphthalene	15
Biphenyl	47
Phenanthrene	90

of the distribution coefficients, f , examined and the corresponding retention characteristics in liquid adsorption chromatography.

The adsorption from tertiary solutions is much more complex. Owing to mutual displacement of different molecules of the component in the surface solution, at least one of the components is negatively adsorbed, as in the case of binary systems. The magnitude of the adsorption can be determined by analysing the composition of the equilibrium solutions by means of gas chromatography⁹³ or directly by liquid chromatographic analysis on adsorption columns.

The adsorption isotherms in this case are not in the form of curves, but of curved surfaces. They can be conveniently expressed by projection by means of the Gibbs triangle. Isotherms thus obtained for adsorption of dioxane, benzene, and n -hexane from tertiary solutions of these components⁹³ are shown in Fig. 26. The strong

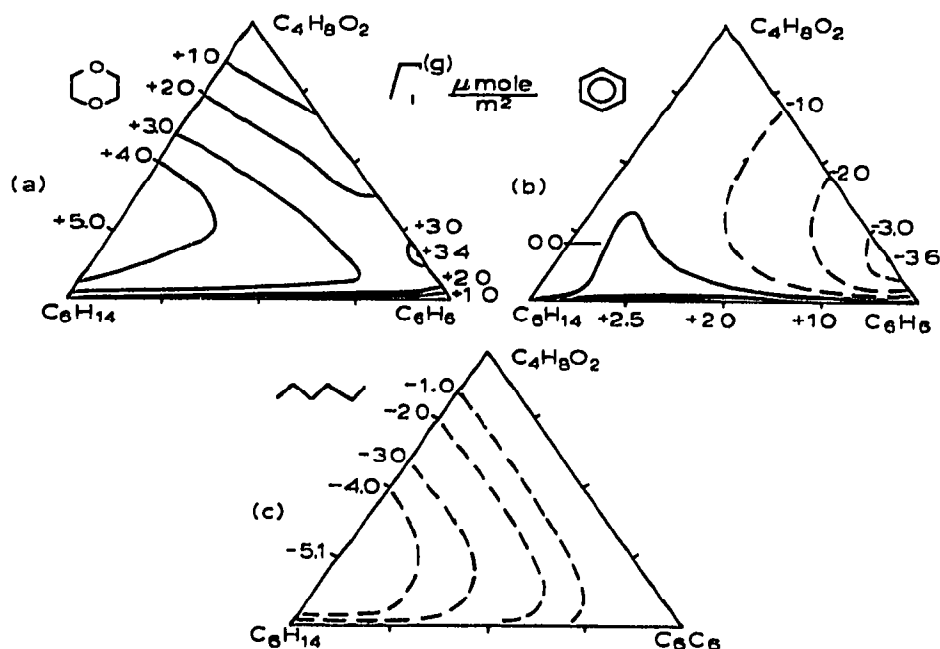


Fig. 26. Gibbs adsorption isotherms (micromoles/m²) of. a = dioxane, b = benzene; c = n -hexane on hydroxylated silica gel from their mixtures. The solid lines are projections of the positive surface adsorption; dotted lines are the projections of the negative surface adsorption.

specific interaction of dioxane molecules with the silanol groups on the surface makes the adsorption of dioxane positive throughout the whole range of concentrations. On the other hand, the adsorption of *n*-hexane is negative throughout. The adsorption of benzene whose molecules can only undergo weak specific interactions with the silanol groups on the adsorbent surface has different signs at different concentrations. The adsorption of benzene is positive at low concentrations of dioxane and negative at high concentrations of dioxane. This example shows the extent to which one can vary the adsorption of the component by changing the nature and concentration of the solvent mixture.

SNYDER⁹⁴ has made a comparison of the results obtained from liquid and gas adsorption chromatographic analyses of the same mixtures. In liquid chromatography, as in gas chromatography, the retention volumes on non-specific and weakly specific adsorbents (in particular on various types of carbon black) are practically independent of the nature of the functional groups, but are determined by the configuration and the electron polarisability of the molecules of the components. In separations with a specific adsorbent such as aluminum oxide, the retention volumes in liquid adsorption chromatography sharply increase when the molecules of the components contain polar groups or π -bonds⁹⁵ in the case where the solvent belongs to the A-group, *i.e.* where the solvent cannot undergo specific interaction with the adsorbent.

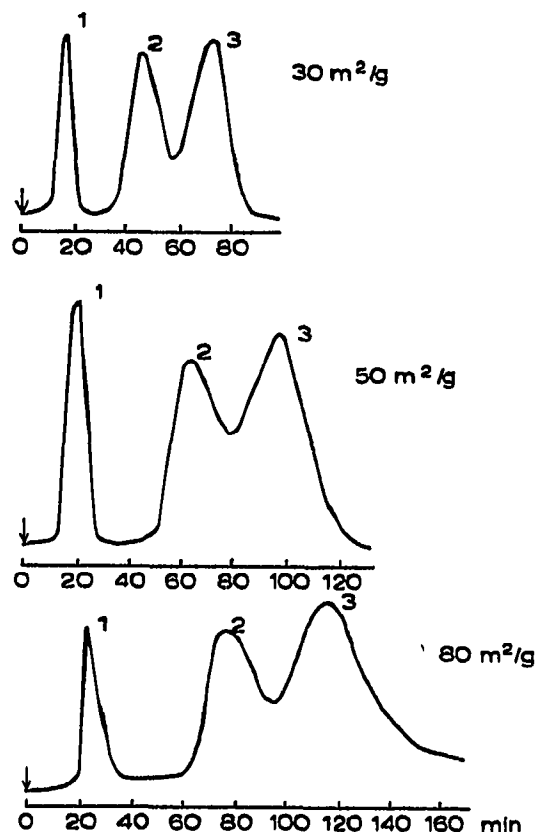


Fig. 27. Chromatogram obtained on aerosil gels of different geometrical structures for the mixture of isomers: 1 = *o*-dihydroxybenzene, 2 = *m*-dihydroxybenzene, 3 = *p*-dihydroxybenzene. Column length, 15 cm; column diameter, 0.6 cm; column temperature 18°; mobile CCl_4 phase flow rate, 0.5 ml/min; specific surface area (from top to bottom): 30, 50, 80 m^2/g .

The effect of the nature and porosity of the adsorbent on liquid chromatography of molecules

SNYDER⁹⁶ has studied the effect of various experimental parameters on the efficiency and selectivity of the separation in liquid chromatography. These are sample size, the nature of the adsorbent, the dimensions of the adsorbent particles, the nature of the mobile solvent and the rate of its flow, and the column diameter. The effect of the adsorbent porosity on the performance of a chromatographic column is of great interest; an increase in pore size, corresponding to a decrease in the specific surface area from 830 to 340 m²/g increases the efficiency (the number of theoretical plates) five times⁹⁷. By selecting the optimal pore size and controlling the porosity relative to the grain depth (*e.g.* by using surface-porous adsorbents such as were originally developed by ZHDANOV *et al.*⁹⁸), one can considerably raise the efficiency of liquid chromatographic columns and carry out separations in shorter periods of time⁹⁹.

Data in Fig. 27 illustrate the effect of pore size of aerosilgels in the chromatographic separation of dihydroxybenzene isomers¹⁰⁰. With the decrease in the surface area of the adsorbent and the increase in the average diameter of the pores, the retention times and peak width decrease. The best results are obtained on columns with a more macroporous aerosilgel.

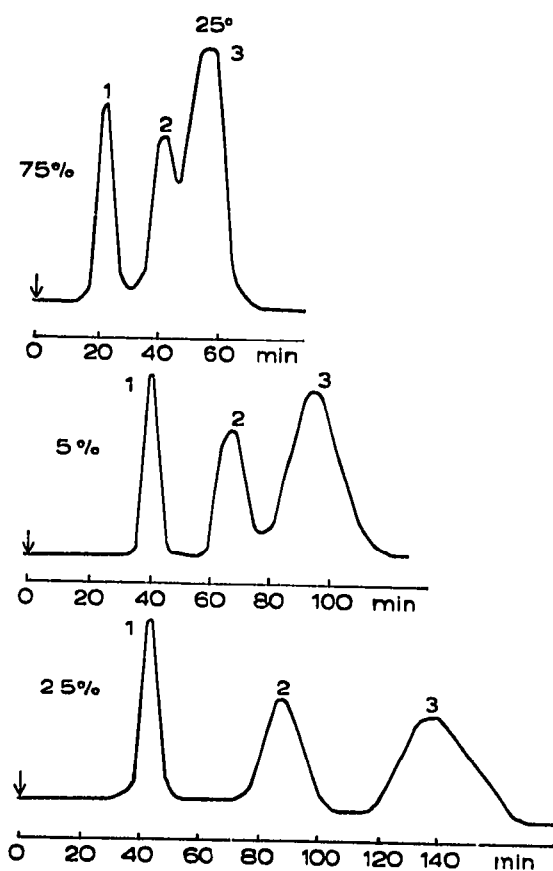


Fig 28. Chromatograms obtained on aluminium oxide at various concentrations of ethanol (the amount of ethanol is indicated on each chromatogram) in benzene as the main solvent. 1 = *o*-nitrophenol, 2 = *m*-nitrophenol; 3 = *p*-nitrophenol. Column length, 50 cm, column diameter, 0.8 cm, column temperature, 25°, flow rate, 0.44 ml/min

The effect of changes in the nature of the eluant and in temperature

The effect of changes in the nature of the solvent on the retention volumes and the separation selectivity in liquid adsorption chromatography is illustrated in Fig. 28 (ref. 100). The separation of nitrophenol isomers can be improved upon the addition of ethanol to benzene used as the main solvent. However, at higher concentrations of ethanol, separation becomes less efficient owing to a big decrease in the adsorption of nitrophenol. This makes it possible to control the adsorption of nitrophenol isomers and consequently the retention time. In applying the method of gradient elution, ALM *et al.*¹⁰¹ and SNYDER¹⁰² increased the concentration of the strongly adsorbing additive in the main solvent as a function of time.

An increase in the column temperature in liquid adsorption chromatography leads to more diverse results than in gas chromatography¹⁰³. This is apparently due to the fact that in adsorption from multi-component solutions the competition for the most favourable sites on the adsorbent surface results in different dependences of the adsorption of the various components on the temperature. From Fig. 29, it can be seen¹⁰⁰ that with an increase in temperature, the retention volumes of *o*- and *p*-nitrophenol on an aluminium oxide column, with benzene as the main solvent containing various amounts of ethanol, do not decrease but even increase slightly. With the increase in temperature the relative role of the specific interactions, in particular the formation of hydrogen bonds, of ethanol with the adsorbent decreases. The retention volumes when large molecules are being separated depend to a lesser degree on temperature. In this case the main contribution to the energy of adsorption is due

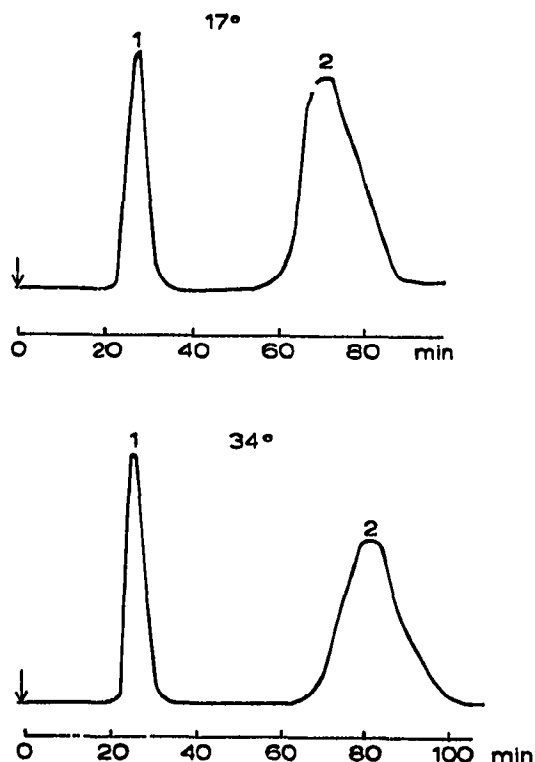


Fig. 29. Chromatograms obtained on an aluminium oxide column: 1 = *o*-nitrophenol; 2 = *p*-nitrophenol. Column temperature indicated on the chromatogram; column length, 50 cm; column diameter, 0.8 cm; mobile phase, 97.5% benzene + 2.5% ethanol; flow rate, 0.44 ml/min.

to dispersion interaction. Apparently at higher temperatures large molecules displace a fraction of the ethanol molecules from the more active sites and become themselves adsorbed more strongly than the ethanol molecules.

Gas chromatography versus liquid chromatography as applied to the separation of the same mixture

In many cases the time for analysis by liquid chromatography may approach that for gas chromatography^{104,105}. This is illustrated in Fig. 30, where the data obtained for the same mixture of *o*-, *m*-, and *p*-nitrophenol separated by gas and liquid chromatographic methods¹⁰⁰ are shown. The separation times by these methods

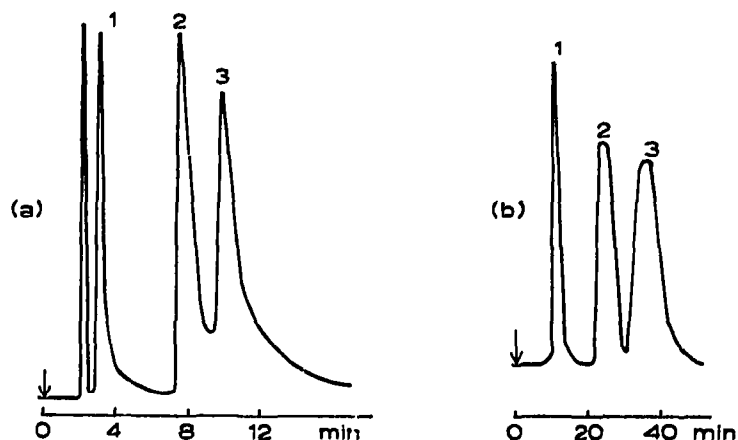


Fig. 30. Chromatograms of the mixture: 1 = *o*-nitrophenol, 2 = *m*-nitrophenol; 3 = *p*-nitrophenol. (a) Obtained by gas chromatography on a column (100 × 0.3 cm) with Chromosorb W + 3% OV-17 at 150°; (b) obtained by liquid chromatography on a column (50 × 0.8 cm) with aluminium oxide at 25°, mobile phase, 95% by wt benzene + 5% by wt. ethanol; flow rate, 0.44 ml/min.

are comparable, though the liquid chromatographic separation is more complete. From data in Fig. 31 it can be seen that the mixture of diaminodiphenylmethane isomers is completely separated on the liquid adsorption column, whereas on the gas-liquid column the mixture of 4,4'- and 3,3'-diaminodiphenylmethanes is not separated at all¹⁰⁰.

The examples cited show the importance of liquid molecular adsorption chromatography for analytical and preparative use. For the development of this method it is necessary to have more versatile and sensitive detectors and, what is especially important, new and homogeneous adsorbents with controlled geometric and chemical surface structure. It is important to develop further the theory of liquid chromatography on the basis of the adsorption theory for binary and tertiary systems as well as for solutions of a more complex nature under both static and dynamic conditions.

LIQUID MOLECULAR SIEVE CHROMATOGRAPHY BASED ON MACROPOROUS SILICA GEL AND AEROSILOGEL

Separation of synthetic polymers

The molecular sieve effect can be used in liquid molecular adsorption chromato-

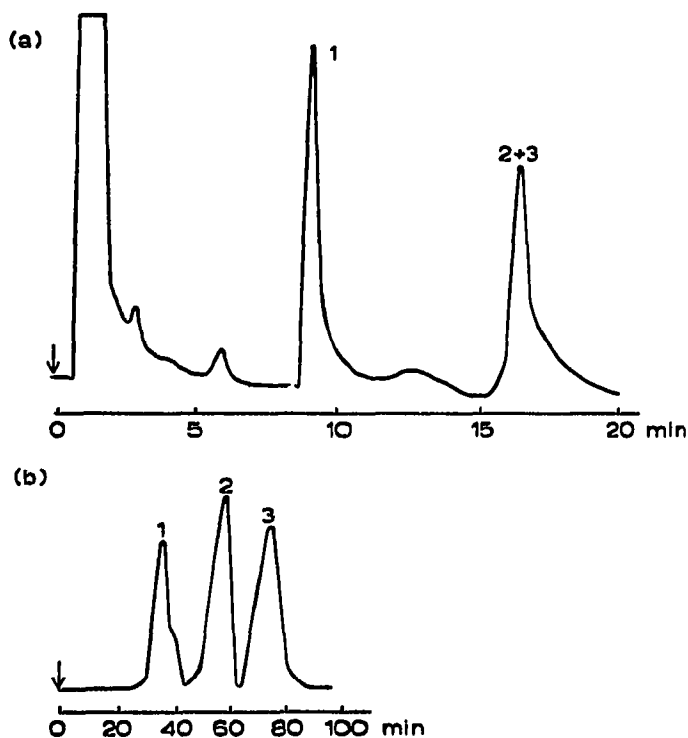


Fig. 31. Chromatograms of (1) 2,2'-diaminodiphenylmethane, (2) 4,4'-diaminodiphenylmethane; (3) 3,3'-diaminodiphenylmethane. (a) Obtained by gas chromatography on a column (100×0.3 cm) with Chromosorb W + 3% by wt. OV-17 at 200° ; (b) obtained by liquid chromatography on a column (15×0.6 cm) of aluminium oxide; mobile phase, 99% by wt. CCl_4 + 1% by wt. $\text{C}_2\text{H}_5\text{OH}$; column temperature: 18° , flow rate, 0.44 ml/min.

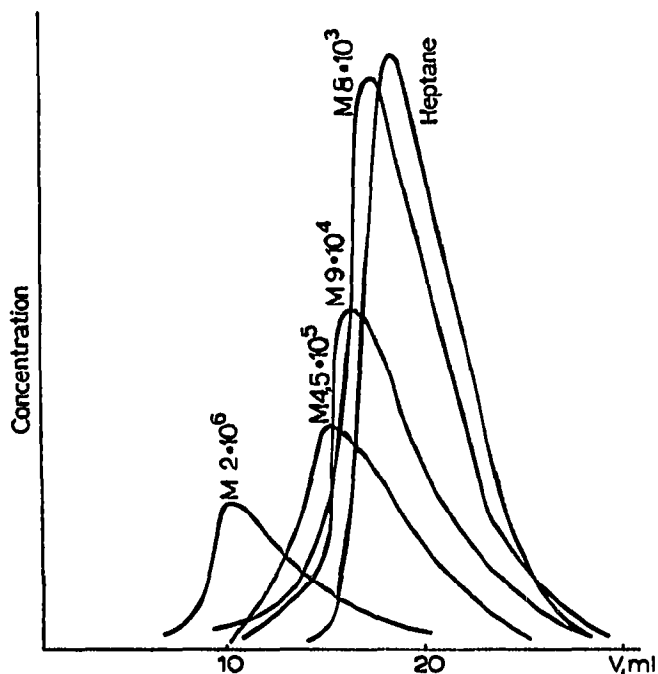


Fig. 32. Chromatograms for toluene solutions of polystyrene on: Silicrom with $d \approx 1500 \text{ \AA}$; column size, 40×0.6 cm; flow rate, 0.5 ml/min.

graphy as in gas adsorption chromatography. However, the slow diffusion rate prevents separation under equilibrium conditions with respect to the adsorption process. Thus molecular sieve separation, under conditions of liquid chromatography, finds its application not so much on the basis of the differences in adsorption as on the basis of the differences in diffusion rate through the pores of the adsorbent. The ordinary molecular sieve effect is the limiting case of this phenomenon, that is the molecules of a given component of the mixture cannot pass through the pores of the

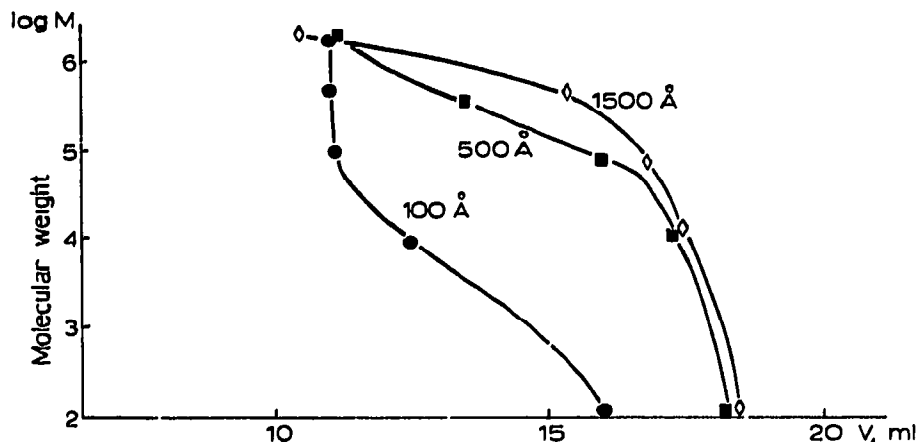


Fig. 33. Dependence of retention volumes for polystyrene as a function of molecular weight obtained on silica gels with effective pore diameters 1500, 500, and 100 Å. Eluant, toluene.

sieve. This effect has found important applications in liquid chromatography of polymers and microbiological substances on macromolecular sieves.

In their usual form macromolecular sieves are cross-linked polymers (*e.g.* Sephadex). Good results have been obtained with cross-linked copolymers of vinyl acetate in separating oligophenylenes and polystyrene into fractions of different molecular weights¹⁰⁰. However, organic polymers in liquid media often swell to

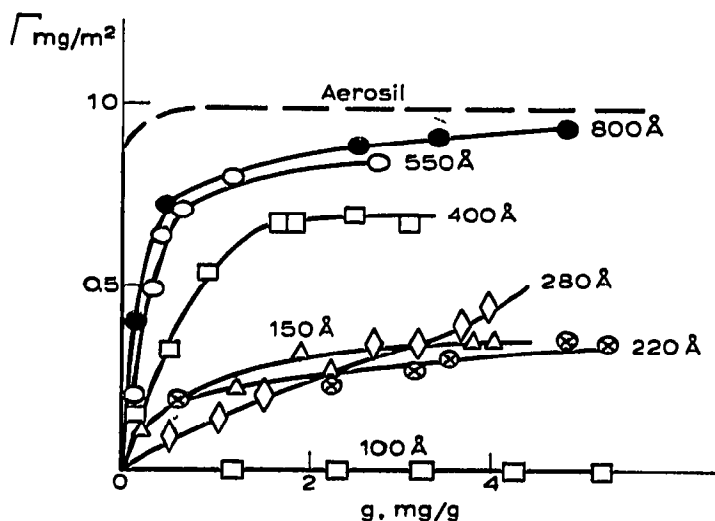


Fig. 34. Adsorption isotherms for polystyrene (mol. wt. $\approx 300\,000$) from CCl_4 solutions on aerosil (dotted line) and macroporous silica gel with different effective pore diameters as indicated.

various degrees, depending on the solvent system. Therefore in addition to this type of sieve, the macromolecular sieves that are rigid and do not swell are of great interest. Such sieves should possess the maximum possible homogeneous distribution of pores according to their size. They should have a sufficiently large total volume of pores and a definite chemical composition of the surface and should readily undergo regeneration. These problems are now being solved on the basis of macroporous glass¹⁰⁷⁻¹⁰⁹, macroporous silica gels^{110,111} and macroporous aerosilgels (Silocroms)³⁴. Some results obtained by KISELEV *et al.*¹¹² are given below.

In Fig. 32, chromatograms are shown of the separation of polystyrene solutions in toluene on an aerosilogel with an effective pore diameter $d \approx 1500 \text{ \AA}$. The highest molecular weight fraction of the polymer passes through a column without hindrance. Macromolecules with the lowest molecular weight diffuse into the pores and return to the eluant flow somewhat later. The corresponding dependence of the retention volumes as a function of the molecular weights of the polystyrenes separated on silica gels having pore sizes of approx. 1500, 500, and 100 \AA is shown in Fig. 33. In the case of silica gel having the large pore size ($d \approx 1500 \text{ \AA}$), the best results were obtained for polystyrene having molecular weights in the range of one million to several hundred thousands. Silica gel with a $d \approx 500 \text{ \AA}$ gives the best fractionation for samples with molecular weights in the range of several hundred thousands to tens

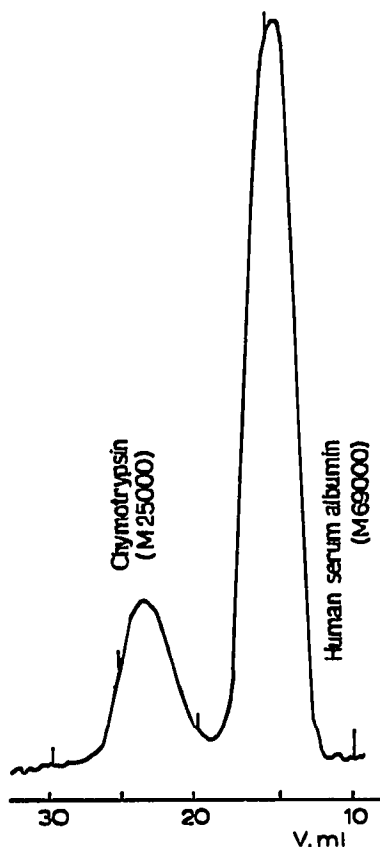


Fig. 35. Chromatograms for human serum albumin (mol. wt. = 69 000) and chymotrypsin (mol. wt. = 25 000) in 0.1 *M* acetic acid on silica gel with $d \approx 280 \text{ \AA}$. Column size, $4.5 \times 0.8 \text{ cm}$; flow rate, $\approx 0.5 \text{ ml/min}$.

of thousands. The adsorbent with the small pore size ($d \approx 100 \text{ \AA}$) effectively separates only relatively low molecular weight fractions of polystyrene.

However, the residence time of the polystyrene macromolecules in the macropores of the silica gel is related not only to the direct and reverse diffusion of the polystyrene molecules inside the pores but also to their adsorption. In Fig. 34, adsorption isotherms are shown for polystyrene, with a molecular weight $\approx 300,000$ in CCl_4 solution, on non-porous aerosil and on a number of macroporous silica gels with gradually decreasing pore size (from 800 to 110 \AA), as calculated per unit surface area of these adsorbents¹¹³. The values of the limiting adsorption of polystyrene on the surface of macroporous silica gels with effective pore size ranging from 500 to 1000 \AA practically coincide with each other and are close to the corresponding values for the adsorption on non-porous aerosil (0.9 mg/m²). This value corresponds approximately to the dense monolayer of polystyrene macromolecules spread over the adsorbent surface. A molecular sieve effect is only apparent with a pore size up to $\approx 200 \text{ \AA}$. However, under the dynamic conditions of liquid chromatography, one should take into account the slowness of the diffusion and adsorption processes. The time required for attaining equilibrium in the cases shown in Fig. 34 was 1 h for the aerosil adsorbent, 2 h for macroporous silica gel having pore size of *ca.* 800 \AA ; no equilibrium was attained after several days for silica gel having a pore size of *ca.* 280 \AA . The usual time required for carrying out a separation on a liquid chromatographic column is about 1 h. Thus the adsorption equilibrium for the above-mentioned silica gels will

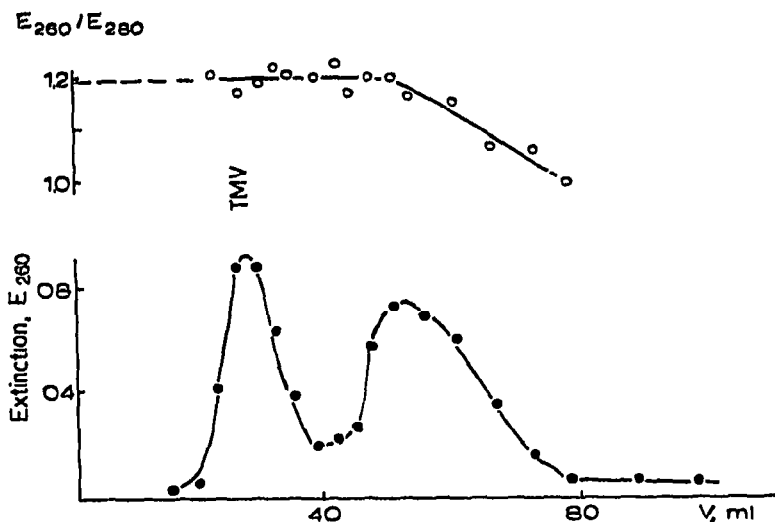


Fig. 36. Separation of tobacco mosaic virus on Silochrom with $d \approx 1500 \text{ \AA}$ in 0.01 M phosphate buffer solution, pH = 7.7. Column size 60 \times 1.0 cm; flow rate: $\approx 0.5 \text{ ml/min}$.

not be achieved. Nevertheless, the adsorption of polystyrene in the macropores does take place to a certain extent. Thus in the case of molecular sieve liquid chromatography, the retention of polystyrene in the column is due entirely to the molecular sieve effect (macromolecules of the largest size cannot enter the pore at all) and to parallel processes of diffusion and adsorption occurring on the most accessible parts of the surface.

Separation of proteins and purification of viruses

Data in Fig. 35 illustrate the separation of proteins on a macroporous silica gel. The pore size of the silica gel is *ca.* 280 Å. Serum albumin ($M = 69,000$) passes through the column without hindrance, as albumin hardly enters the pores of the silica gel. Chymotrypsin ($M = 2500$) enters the pores and is thus delayed in the column. It should be noted that in this case the adsorption of the macromolecules takes place both on the grain surface and in the macropores; this is indicated by the irreversible adsorption of the first parts of the protein sample and by the gradual decrease in the working macropore volume.

A pure molecular-sieve effect is of special importance in the fractionation of biopolymers of higher molecular weight such as viruses. Fig. 36 shows the molecular sieve chromatogram of a tobacco mosaic virus extract fractionated on macroporous silica gel with $d \approx 500$ Å. The particles of the virus (3000×500 Å) do not pass into the pores and leave the column without retention. The ratio of optical densities $E_{260}/E_{280} = 1.2$ shown in the figure is characteristic of this virus. The proteins and pigments contained in the virus sample do enter the pores or become adsorbed.

Thus macroporous silica can be used in liquid molecular sieve chromatography in the fractionation of polymers and other high molecular weight compounds.

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