CHROM. 7286

PROBLEMS OF SELECTIVITY AND EFFICIENCY IN LIQUID–SOLID CHROMATOGRAPHY

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SUMMARY

The influence of the chemistry of adsorbent surfaces and of the nature of the eluent upon the selectivity of liquid–solid chromatographic systems was investigated by a few examples of the adsorption of some aromatic compounds from different solvents (*n*-hexane, chloroform and isopropanol). Macroporous silica (Silochrom) with hydroxylated, partly dehydroxylated, silanized, alkylamine-grafted and polymer (Melon) film coated surfaces, as well as the macroporous carbon black (Carbochrom), were used as adsorbents. The influence of the geometrical structure (specific surface area and porosity) of silica gels on the efficiency of chromatographic columns was also considered. For the system studied the optimal values of pore size and specific surface area were found, which allowed a more selective and effective separation of the mixtures.

INTRODUCTION

The basic conditions of separation with a given instrument are the values of the physicochemical parameters of the chromatography, that is (1) the chemical nature of the adsorbent surface, the geometrical structure of the adsorbent (specific surface area and pore sizes), the shape and size of the particles and the amount of adsorbent in the column, (2) the nature and concentration of the eluent, and (3) the temperature. In the case of gas chromatography we can usually neglect the adsorption of carrier gas, and selectivity depends mainly on the properties of the adsorbent. However, in the case of liquid–solid chromatography it is better to speak of the selectivity of the chromatographic system as a whole: adsorbent, solutes and eluent. As the solution is a condensed phase, adsorption from solution involves the mutual displacement of the molecules of solute substances and of the eluent (for reviews, see refs. 1–3). In this situation the value of Gibbs' adsorption is negative, at least for one component of the solution[4,5]. That is why selectivity in the case of liquid–solid chromatography depends not only on the chemical and geometrical structures of the adsorbent and the molecules to be separated, but also on the nature and concentration of the components of the eluent (see for example refs. 1, 2 and 6).

INFLUENCE OF THE CHEMISTRY OF THE ADSORBENT SURFACES AND THE NATURE OF THE ELUENT

The retention characteristics of different aromatic hydrocarbons and their derivatives have been studied when adsorbed from different eluents (*n*-hexane, chloroform and isopropanol) on samples of commercial macroporous silica, Silochrom[7]. These samples of silica have already been used in a different kind of LSC as reported in previous papers[3,6]. The surface of the Silochrom was either hydroxylated, partly dehydroxylated, silanized, alkylamine-grafted or covered by a thin film of polymer (Melon) which was insoluble in the eluents used.

Using *n*-hexane as the eluent the differences in the adsorption properties of these adsorbents can be observed. The lowest selectivity was found in the case of the silanized surface, which is close in chemical nature to a paraffin. The retention values relative to benzene, $\alpha = V_{R,t}/V_{R,C_6H_6}$, where $V_{R,t}$ is the net retention volume of the substances studied, are nearly the same for the different aromatic hydrocarbons and do not exceed unity to any large extent. Molecules having active functional groups (acetophenone, α-aminonaphthalene) are slightly more retained under the same experimental conditions (probably on account of the residual silanol groups on the adsorbent surface) but this phenomenon is still very weak. Also in this case the α values do not exceed 2.6. The selectivity of Silochrom towards specifically[3] adsorbing molecules increases as does the concentration of silanol groups on the surface (Table I). Thus, for the partly dehydroxylated Silochrom the increase of the retention volumes follows the sequence benzene < naphthalene < phenanthrene or benzene < diphenyl < terphenyl. This adsorbent very strongly retains molecules capable o specific adsorption, *e.g.* α-aminonaphthalene ($\alpha \simeq 40$). The specific character of adsorption from solutions in hexane is even more obvious in the case of a Silochrom with a hydroxylated surface. The V_g and α values for polynuclear aromatic hydrocarbons on hydroxylated Silochrom are considerably larger than the corresponding values for a Silochrom with partly dehydroxylated and (especially) silanized surfaces.

The Silochrom samples with the surfaces modified by the grafting of organoamine groups or by depositing a film of Melon (nitrogen-containing polymer) are also very specific. The selectivity of separation of aromatic hydrocarbons during adsorption from *n*-hexane eluent is produced by specific intermolecular interactions of surface functional groups with solute molecules, because the non-specific (mainly dispersion) interactions of the solute and solvent (eluent) molecules with the adsorbent are rather similar. Thus, α increases with the number of aromatic nuclei but practically does not change with the length of the saturated chain in alkylbenzenes (for all the adsorbents studied toluene, ethyl-, isopropyl- and butylbenzenes are retained in the column at nearly the same time). The α value for the aromatic hydrocarbons diminishes when the eluent is capable of forming specific intermolecular interactions with the molecules to be separated. For this reason when we used chloroform and isopropanol as eluents (see Table I) the retention volumes of aromatic hydrocarbons were so similar that we did not notice any difference between them. Thus these eluents are unsuitable for the separation of aromatic hydrocarbons on the adsorbents studied. But in the case of strong specifically adsorbing substances, for example in the case of aromatic amines, we must use an eluent capable of specific intermolecular interactions. The *ortho*, *meta* and *para* isomers of nitroaniline are so strongly adsorbed

TABLE I

SPECIFIC AND RELATIVE RETENTION VOLUMES OF AROMATIC COMPOUNDS ON SILOCHROMS OF DIFFERENT SURFACE CHEMISTRY

Eluents: (I) n-hexane, (II) chloroform, (III) isopropanol. Temperature, 25°. The specific retention volumes, V_g, are in ml/g (upper data); the relative retention volumes, $\alpha = V_g/V_{g,C_6H_6}$, are expressed with reference to benzene $= 1.00$ (lower data).

Substance	Dehydroxylated			Hydroxylated			Alkylamine grafted		Melon film coated		
	I	II	III	I	II	III	I	II	I	II	III
Benzene	0.52	0.83	0.91	0.82	0.68	0.57	0.96	1.01	0.58	0.70	0.49
	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Naphthalene	0.67	0.83	0.91	1.19	0.68	0.57	1.28	1.08	1.06	0.60	0.49
	1.29	1.00	1.00	1.45	1.00	1.00	1.33	1.07	1.83	0.86	1.00
Phenanthrene	0.80	—	0.91	1.75	0.68	0.57	2.26	0.83	1.67	0.60	0.49
	1.54	—	1.00	2.13	1.00	1.00	2.36	0.82	2.88	0.86	1.00
Diphenyl	0.67	—	0.91	1.36	0.68	0.61	1.20	0.93	1.46	0.70	0.49
	1.29	—	1.00	1.66	1.00	1.07	1.25	0.92	2.52	1.00	1.00
p-Terphenyl	1.40	—	0.91	2.97	0.68	0.61	3.71	0.93	2.00	0.60	0.49
	2.70	—	1.00	3.63	1.00	1.07	3.87	0.92	3.47	0.86	1.00
Nitrobenzene	3.82	0.97	0.56	7.82	0.73	0.61	6.72	1.00	6.00	0.80	0.65
	7.35	1.17	0.62	9.55	1.07	1.07	7.00	0.99	10.35	1.14	1.33
Acetophenone	—	0.97	0.56	*	0.70	0.69	22.0	0.88	—	0.80	0.73
	—	1.17	0.62		1.03	1.21	22.9	0.87	—	1.14	1.49
α-Aminonaphthalene	20.5	0.97	—	*	1.73	0.77	*	1.38	*	1.10	0.99
	39.5	1.17	—		2.54	1.35		1.37		1.57	2.02

* Very strong retention, not detected.

from hexane on hydroxylated, alkylamine-grafted or Melon-coated Silochrom surfaces that they are not detected at the outlet of the corresponding columns. However, if chloroform is used as eluent a difference is observed in the retention of these isomers. From the columns packed with these specific adsorbents o-nitroaniline emerges first, but the *meta* and *para* isomers are eluted together (*e.g.* in the case of Silochrom modified by Melon the α values are, respectively, 1.01, 2.13 and 2.13, and with hydroxylated Silochrom the corresponding α values are 1.07, 2.04 and 2.04). However the α values of these isomers are very different from one another when Silochrom is modified with 10% of $AgNO_3$ (1.07, 1.93 and 3.34, respectively) (see Fig. 1). On the contrary, if a more polar eluent (isopropanol) is used, the selectivity of these adsorbents diminishes (*e.g.* the α values of these isomers with hydroxylated Silochrom are 1.1, 1.49 and 1.49, respectively). From the column packed with $AgNO_3$-modified Silochrom all these isomers are eluted by isopropanol quickly and simultaneously.

When eluted by hexane the aromatic hydrocarbons are retained on the hydroxylated Silochrom surface more strongly than on the partly dehydroxylated surface. The opposite phenomenon is observed when these compounds are eluted by isopropanol. A reverse retention order for aromatic hydrocarbons and their derivatives containing active functional groups is observed in the case of partly dehydroxylated
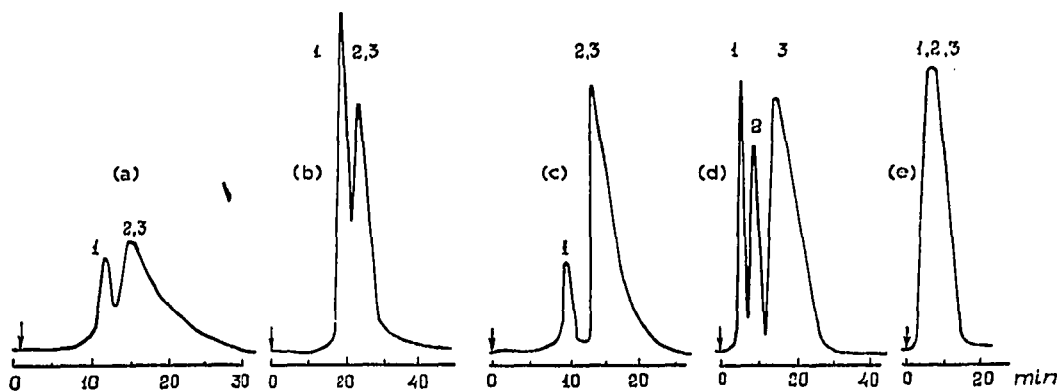
Fig. 1. Chromatograms of (1) *o*-, (2) *m*- and (3) *p*-nitroanilines on Silochroms with surfaces treated by different methods. (a) Alkylamine-grafted; eluent, chloroform; flow-rate of eluent, 0.36 ml/min; column, 37 cm × 0.35 cm. (b) Coated by a Melon polymer layer; eluent, chloroform; flow-rate of eluent, 0.20 ml/min; column, 50 cm × 0.35 cm. (c) Hydroxylated; eluent, chloroform; flow-rate of eluent, 0.50 ml/min; column, 50 cm × 0.35 cm. (d) Modified by $AgNO_3$; eluent, chloroform; flow-rate of eluent, 0.58 ml/min; column, 10 cm × 0.35 cm. (e) Modified by $AgNO_3$; eluent, isopropanol; flow-rate of eluent, 0.58 ml/min; column, 10 cm × 0.35 cm. A UV detector at 20° was used.

Silochrom when the eluent is changed from hexane to propanol. Thus, for naphthalene and nitrobenzene the α values are 1.3 and 7.35, respectively, when the compounds are eluted by hexane and 1.0 and 0.6, respectively, when the eluent is propanol.

An analogous influence of the eluent nature on the retention order of molecules of different structure can be observed in the case of a weakly specific polymer adsorbent of the third type[8], Polysorb[9].

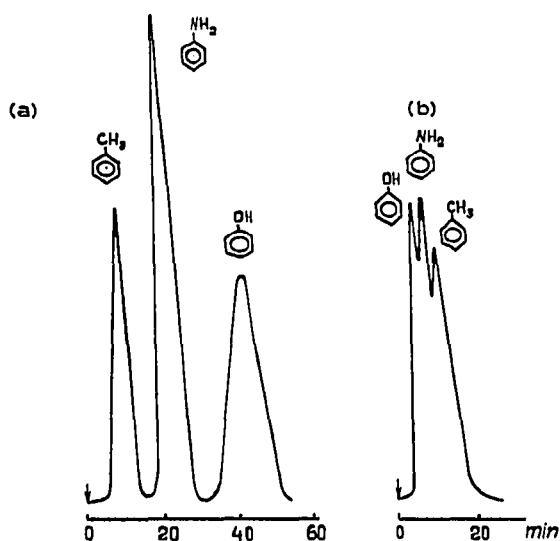Fig. 2 shows that if pentane is used as eluent the retention sequence is phenol >

Fig. 2. Chromatograms of toluene, aniline and phenol on Polysorb-1. (a) Column, 50 cm × 0.5 cm; eluent, *n*-pentane; flow-rate of eluent, 0.68 ml/min. (b) Column, 50 cm × 0.5 cm; eluent, *n*-propanol; flow-rate of eluent, 1.3 ml/min. A UV detector at 20° was used.
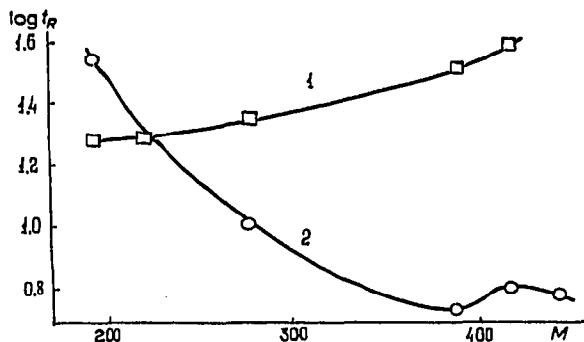
Fig. 3. Dependence of log t_R of phthalates on their molecular weight, M. (1) Adsorbent, Carbochrom; eluent, n-hexane; flow-rate of eluent, 2 ml/min; column, 67 cm × 0.7 cm. (2) Adsorbent, Silochrom; eluent, n-hexane; flow-rate of eluent, 2 ml/min; column, 67 cm × 0.4 cm. Dielectric capacity detectors were used.

aniline > toluene, but if propanol is used as eluent the retention sequence changes to the reverse order of toluene > aniline > phenol.

A change in the retention order can also occur with a given eluent by using adsorbents which are very different in their chemical natures. Figs. 3 and 4 show that with a column packed with Carbochrom[10] the retention volumes of phthalates increase with their molecular weight and the reverse is observed on a water-containing silica gel adsorbent. Figs. 5 and 6 show that from the silica gel column some ethers and esters are also eluted by hexane in a sequence of decreasing molecular weight (with the exception of ethyl formate, in which molecular association can occur).
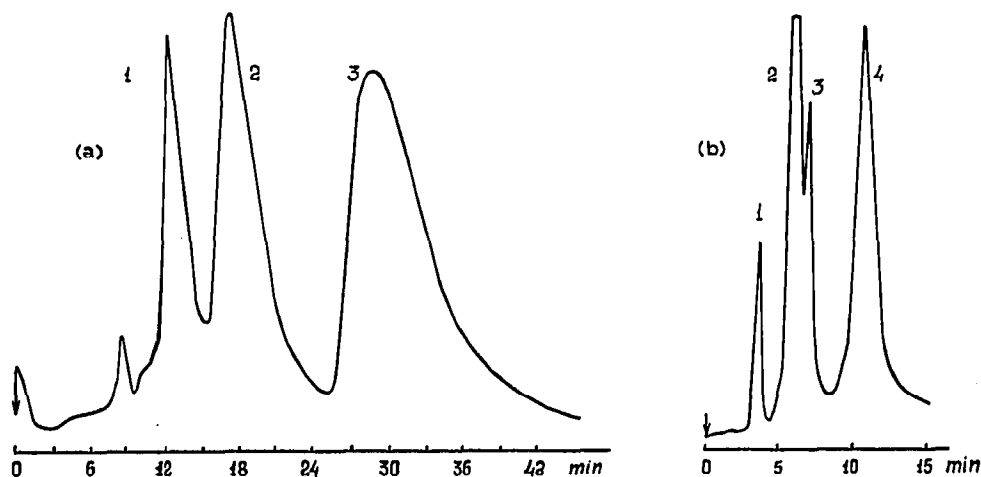

Fig. 4. Chromatograms of the separation of phthalates on different adsorbents. (a) Carbochrom at 60°; eluent, n-hexane; flow-rate of eluent, 1.3 ml/min; column, 67 cm × 0.4 cm. 1 = Dimethylphthalate; 2 = dioctylphthalate; 3 = dinonylphthalate. (b) Silochrom at 50°; eluent, n-hexane; flow-rate of eluent, 1.2 ml/min; column, 67 cm × 0.4 cm. 1 = Squalane; 2 = dioctylphthalate; 3 = dinonylphthalate; 4 = dibutylphthalate. Dielectric capacity detectors were used.
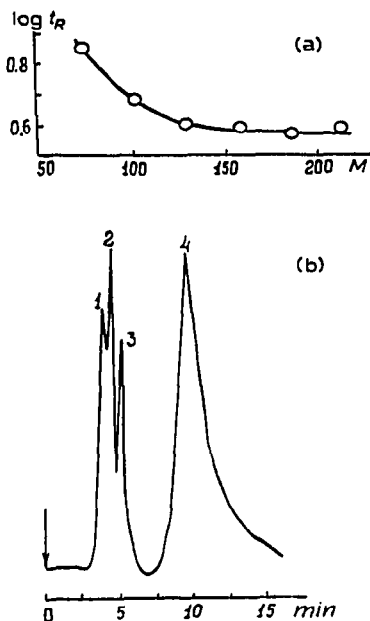
Fig. 5. Dependence of log t_R of ethers on their molecular weight M (a) and chromatogram of the ether mixture (b). Adsorbent, silica gel; eluent, n-hexane; flow-rate of eluent, 1.2 ml/min; temperature, 50°; column, 67 cm × 0.4 cm. 1 = Dihexyl, 2 = dibutyl, 3 = dipropyl, and 4 = diethyl ether. A dielectric capacity detector was used.

Thus by changing the chemical composition of the adsorbent surface and the nature of the eluent it is possible to regulate the selectivity of the liquid–solid chromatographic system and to optimize the choice of adsorbent and eluent for the separation of different mixtures.
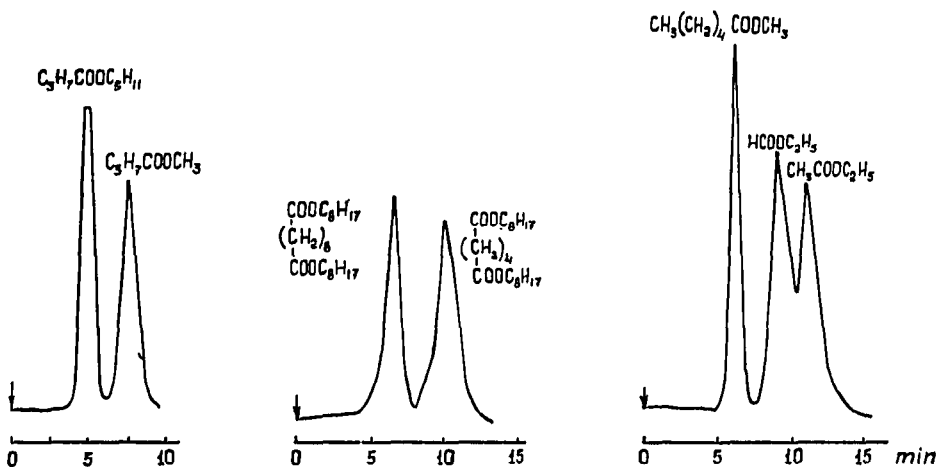

Fig. 6. Chromatogram of the separation of esters on silica gels at 24°. Further conditions are the same as in Fig. 5.

EFFECT OF THE PORE STRUCTURES OF SEVERAL ADSORBENTS ON THE LIQUID CHROMATOGRAPHY OF SOME MODEL MIXTURES

A thermodynamically possible separation can, however, be realized only partially because in liquid chromatography the diffusion is a very slow process. Thus, to obtain the best selectivity for a given system (eluate, eluent and adsorbent) it is necessary to optimize the efficiency of the column, *i.e.* to find the most suitable values of flow-rate, grain size and shape, and internal geometrical structure of the adsorbent used (specific surface area, s, pore size, d, and pore volume, v). The effect of grain size on separation in liquid chromatography has been investigated[11,12]. It was shown that the efficiency of columns characterized by the height equivalent to a theoretical plate, H, and component resolution are improved with a decrease in the size of spherical particles. However, the effect of the geometrical structure of the adsorbents themselves (the effect of s, d and v values) on chromatographic features has as yet received little attention. This aspect will now be considered.

Separation of quinoline and quinaldine eluted by diethyl ether
To study the effect of pore structure, different samples of silica adsorbents —silica gels KCM-6 and KCK-2.5 (ref. 13) and Silochrom C-3 (ref. 14)— having d and s values differing by one order of magnitude (Table II) were investigated. These adsorbents contain impurities, mainly Al and Fe, which essentially change the specificity of adsorption[15]. To find out the effect of the impurity content of silica gel fairly pure macroporous Silochrom C-80 (ref. 7) (similar in porous structure to Silochrom C-3) and alumina ("for chromatography" grade) have been investigated. The structures of the adsorbents were determined from the adsorption isotherms of benzene and krypton vapours[16] and the data are given in Table II.

TABLE II

GEOMETRICAL STRUCTURE CHARACTERISTICS OF ADSORBENTS

Adsorbent	Bulk density, δ (g/ml)	Specific surface area, s (sq. m/g)	Pore volume, v (ml/g)	Effective (Kelvin) pore diameter, d (Å)	Total surface area of adsorbent in column, A = ms (sq.m)
KCM-6	0.98	550	0.19	20	3450
KCK-2.5	0.48	295	0.90	95	650
C-3	0.31	75	1.38	680	150
C-80	0.33	85	1.30	560	170
Al_2O_3	0.92	120	0.30	90	700

A liquid chromatograph with a dielectric capacity detector[17] was used. Eluent (diethyl ether) was fed by a pulseless pump into a glass column filled with adsorbent (43 cm in length and 0.4 cm in diameter) under 2.5 atm pressure. The flow-rate was about 0.8–0.9 ml/min. Quinoline and quinaldine, having a lone electron pair on the nitrogen atom (in conjugation with π electrons of nuclei), were taken as model substances. On the hydroxylated surface of silica gel the Gibbs adsorption of these
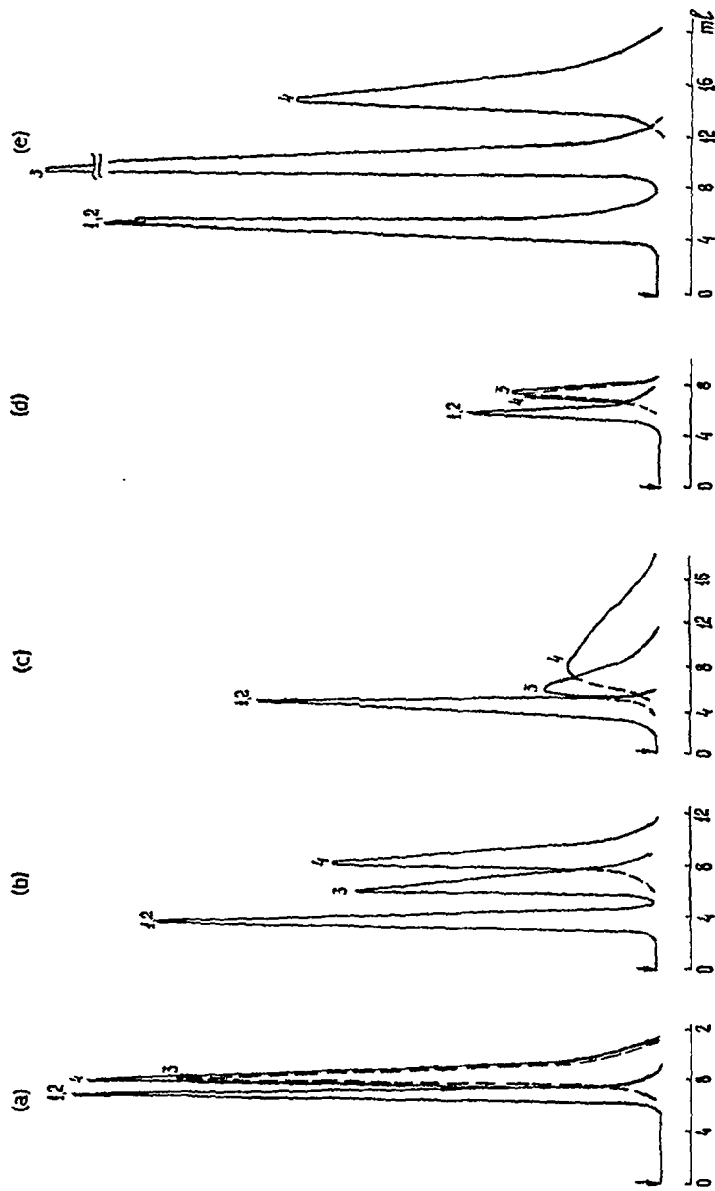
Fig. 7. Comparison of chromatograms of (1) n-hexane, (2) benzene, (3) quinaldine and (4) quinoline on porous silica adsorbents and alumina. Eluent, diethyl ether; flow-rate of eluent, $\approx$ 0.9 ml/min; column, 43 cm $\times$ 0.4 cm. (a) C-3; $d = 680$ Å; $s = 75$ sq.m/g; (b) KCK-2.5; $d = 95$ Å; $s = 295$ sq. m/g; (c) KCM-6; $d = 20$ Å; $s = 550$ sq.m/g; (d) C-80; $d = 560$ Å; $s = 85$ sq.m/g; (e) Al$_2$O$_3$; $d = 90$ Å; $s = 120$ sq.m/g. A dielectric capacity detector was used.

bases from solution in ether is positive. However, the presence of a methyl group near the nitrogen atom of the quinaldine molecule exerts a steric hindrance of optimal orientation of these molecules on the surface, in the case of adsorption from solutions. This reduces the adsorption of quinaldine on silica. Therefore, a more specific adsorbent (alumina) was chosen. Using ether as eluent we obtained the chromatograms of quinoline and quinaldine and also those of hexane and benzene, for which the Gibbs adsorption on the silica surface from ether solutions has a negative value[4,5].

From these chromatograms the value of plate height, $H = L/N$, characterizing the efficiency of an adsorbent, was calculated, where L is column length, $N = 16[(V_R + V_0)/\Delta v]^2$ is the number of theoretical plates, V_R and V_0 are the retention volumes of component and of non-adsorbed hexane and Δv is peak width at its base. The separation ability of the adsorbents is determined by the resolution factor, $R = (V_{R_2} - V_{R_1})/0.5(\Delta v_2 + \Delta v_1)$, where V_{R_2} and V_{R_1} and Δv_2 and Δv_1 are the retention volumes and band widths, respectively, for quinoline and quinaldine. The selectivity, $\alpha = V_{R_2}/V_{R_1}$, was also calculated. Retention volumes for quinoline and quinaldine per unit surface area of the adsorbent were calculated according to $V_s = V_R/ms$, where m is the amount of adsorbent in the column. At the same time the column capacity factor is obtained, which characterizes the amount of stationary phase used, $k' = V_R/V_0 = ms V_s/V_0$. If we assume that V_0 is the volume of liquid in the column, then k' is proportional to the whole adsorbent surface in the column, $A = ms$.

Table II illustrates the difference in the d, s and v values for the adsorbents used. The smaller the pore volume v of the adsorbent, the higher its bulk density, δ, and the larger the mass of adsorbent, m, that can be put into a given column. Microporous silica gel KCM-6 has the largest s and δ values. Macroporous Silochrom C-3 has the lowest s and δ values. Due to this difference in pore structure, the total surface area of the adsorbent is twenty times higher for the column packed with the KCM-6 sample than for the same column packed with the C-3 sample. Silica gel KCK-2.5 and alumina have similar d values ($\simeq 100$ Å). As the KCK-2.5 sample has a larger s value but a smaller δ value than alumina, the A values are almost equal for both samples.

Fig. 7 shows the chromatograms of hexane, benzene, quinaldine and quinoline and Table III lists the chromatographic characteristics calculated for hexane and benzene eluted with diethyl ether from the columns packed with silica gels and Silochrom. These compounds are eluted with narrow and almost symmetrical peaks. Hexane and benzene have nearly the same retention on all the silica samples. Alumina retains benzene more strongly than hexane, due to the ability of the benzene molecule to form weak specific interaction with the strong electron-acceptor centres of the alumina surface, while the hexane molecule exhibits only non-specific adsorption[18]. Quinaldine and quinoline, positively adsorbed from ether solutions on the surface of all these adsorbents, are eluted with symmetrical peaks on the macroporous silicas C-3, C-80, and KCK-2.5, and on alumina. With the microporous silica gel KCM-6, however, it is observed that the elution peaks are broad and asymmetrical for quinoline and even for quinaldine.

The efficiency of the columns measured from the chromatographic peaks of hexane and benzene is nearly independent of the pore size of the adsorbent. The H values increase from 1 to 2 mm when changing from macroporous samples of C-3, C-80 and KCK-2.5 to a microporous sample of KCM-6 (Table III). A sharp decrease

TABLE III

CHROMATOGRAPHIC CHARACTERISTICS OF ADSORBENTS

Adsorbent	n-Hexane		Benzene		Quinaldine				Quinoline				Quinoline/quinaldine	
	H (mm)	V_0 (ml)	H (mm)	V_R (ml)	H (mm)	V_R (ml)	$V_s \cdot 10^2$ (ml/sq.m)	k'	H (mm)	V_R (ml)	$V_s \cdot 10^2$ (ml/sq.m)	k'	α	R
KCM-6	1.9	4.0	2.0	0.2	17.7	2.1	0.06	0.51	48.5	4.6	0.13	1.10	2.1	0.26
KCK-2.5	1.3	4.3	0.8	0.0	1.3	3.2	0.49	0.76	1.7	5.0	0.78	1.2	1.56	0.80
C-3	1.2	6.7	1.1	0.1	1.1	1.1	0.74	0.16	1.1	1.7	1.15	0.24	1.49	0.27
C-80	1.2	6.7	1.4	0.1	1.7	1.2	0.67	0.18	1.5	1.1	0.62	0.17	0.93	0.13
Al$_2$O$_3$	1.8	4.3	1.6	1.1	1.9	3.6	0.51	0.83	2.7	7.2	1.02	1.7	2.0	0.91

in the efficiency of columns for quinaldine and quinoline occurs when changing from samples having $d \geqslant 100$ Å to samples having $d \simeq 20$ Å. In this last case the H values are ten times higher. It is observed that the nature of the adsorbent has almost no effect on the efficiency of the samples having $d \geqslant 100$ Å. The H values are similar for all the adsorbents used. On the most microporous sample of KCM-6 the stronger the adsorption of a given adsorbate, the larger was the H value (1.9, 18 and 48 for hexane, quinaldine and quinoline, respectively). It should be emphasized that the large values of H (1–2 mm), even for macroporous adsorbents, are due to the low eluent pressures used in the chromatograph. In connection with this, a fairly large adsorbent particle size (0.08–0.25 mm) had to be used, which further decreases the efficiency. V_R and k' values for quinoline and quinaldine are strongly affected when changing from the macroporous structure to the microporous one in the series of porous silica samples C-3, KCK-2.5 and KCM-6. The decrease in d from about 680 to 95 Å and the corresponding increase in s from 75 to 295 sq.m/g results in increases in V_R and k'. A further decrease in pore size up to $d \simeq 20$ Å and a considerable increase in s up to 550 sq.m/g leads, on the contrary, to some decreases in the V_R and k' values. In the case of the most microporous silica gel with the strongly adsorbing large molecules of quinoline and quinaldine a high resistance to mass transfer caused by slow internal diffusion and by molecular sieve effects may occur. So the large portion of the microporous surface takes no part in the chromatographic process. When comparing the retention volume values defined per unit surface area one can see, however, that this value for quinaldine on KCM-6 is eight and twelve times less than that on the wide-pore KCK-2.5 and on the macroporous C-3 samples, respectively.

The separation ability of an adsorbent depends on its selectivity and on its efficiency as well as on the capacity of the column. The resolution factor can be expressed as[10]

$$R = \frac{1}{4} \sqrt{\frac{L}{H}} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{k'}{k' + 1} \right) \tag{1}$$

which shows that for adsorbents with equal selectivity α and equal column length the separation is better when the capacity of the adsorbent and the efficiency of the

column are higher, *i.e.* at lower H values. Therefore, in spite of a somewhat lower efficiency, silica gel KCK-2.5 when compared with the macroporous C-3 sample provides a better separation of quinoline and quinaldine because of its larger capacity factor. The macroporous C-3 sample has much smaller k' and A values. Considering now the case of the extremely microporous silica gel KCM-6, a lower resolution is observed (in spite of an increase in a), mainly due to a sharp increase in H. Slow mass transfer in fine micropores results in a broadening of the quinoline and quinaldine peaks (Fig. 7). Therefore, of the commercial porous silica adsorbents considered, silica gel KCK-2.5 presents an optimal structure to separate quinoline and quinaldine under the experimental condition used (flow-rate, grain size and temperature).

As already mentioned above, the effect of the selectivity factor, a, depending on the nature of adsorbent surface, is of great importance for the separation ability of the column. The commercial porous silica containing strong electron-acceptor admixture centres (Al and others) retains quinoline more strongly than quinaldine (the order of their elution is the same as for alumina). However, in the case of a column of pure Silochrom C-80 quinoline is eluted by ether earlier than quinaldine ($a \simeq 0.94$). Therefore, the hydroxylated surface of pure silica provides insufficient selectivity for quinoline and quinaldine separation. As the value of a approaches unity, the resolution factor R for a column filled with Silochrom C-80 is extremely small. It is considerably smaller than that obtained with a column of Silochrom C-3, which has a similar pore structure but contains electron-acceptor centres.

A column filled with macroporous alumina is extremely selective. Moreover, the capacity and efficiency in this case are sufficiently high. As can be seen from Fig. 7 and Table III this adsorbent provides a better separation of quinoline and quinaldine than does silica.

Separation of aromatic hydrocarbon mixtures eluted by hexane
The separation of a benzene, naphthalene and phenanthrene mixture dissolved in *n*-hexane has been investigated on different commercial silica gels with pore sizes from 20 to 280 Å and specific surface areas from 900 to 120 sq.m/g. There is an optimal pore structure of the adsorbent which provides the best component separation (Fig. 8) under given experimental conditions (pore size, eluent flow-rate and
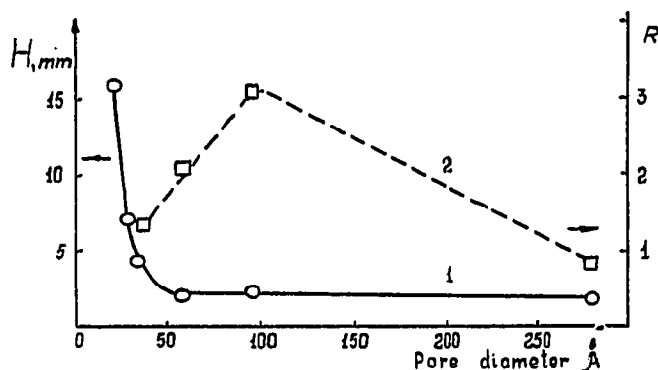

Fig. 8. Dependence of HETP, H, for benzene (1) and resolution factor, R, for phenanthrene/naphthalene (2) on the effective pore diameter of silicas. Eluent, *n*-hexane.
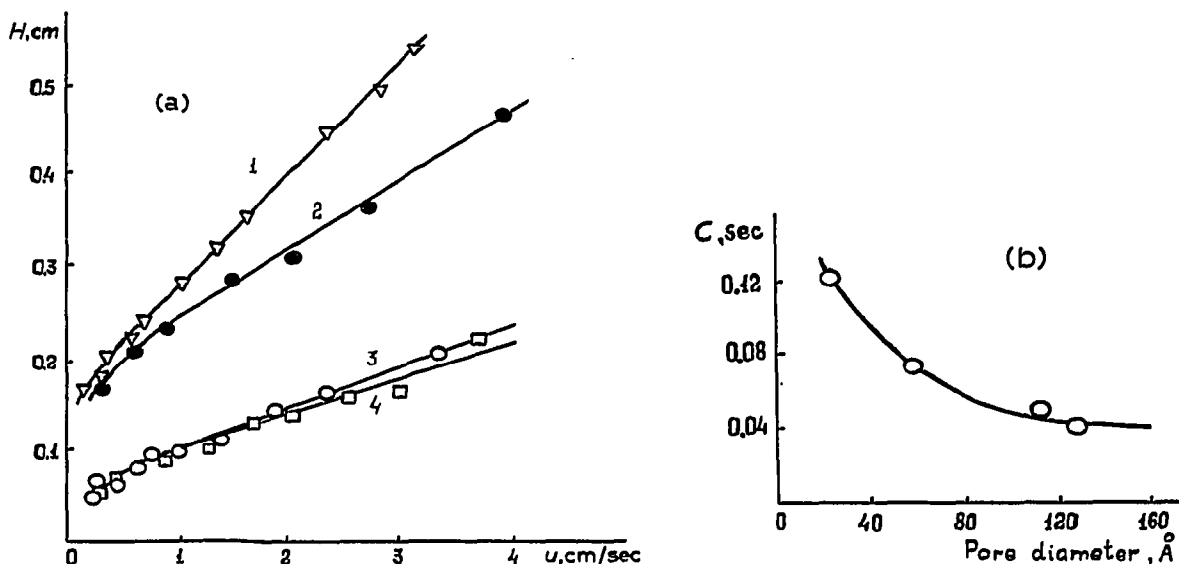
Fig. 9. (a) Dependence of HETP, H, for naphthalene on the linear velocity of the eluent (n-hexane), u, for silicas with different mean pore diameters. (1) $d = 25$ Å; (2) $d = 60$ Å; (3) $d = 110$ Å; and (4) $d = 130$ Å. (b) Dependence of the mass transfer coefficient, C, for naphthalene on the mean pore diameter of silica. Eluent, n-hexane.

temperature). This occurs for the sample of silica gel having $d \simeq 95$ Å and $s \simeq 400$ sq.m/g. A decrease in the pore size leads to poor separation as a result of broad chromatographic peaks caused by a slower mass transfer in the fine micropores and slower diffusion of adsorbate molecules in these pores.

Fig. 9a shows the dependence of H on the linear velocity of the eluent, u and Fig. 9b shows the dependence of the mass transfer coefficient, C (estimated from the slope of the linear parts of the curves shown in Fig. 9a), on the pore size, d. A decrease in the separation on wide-pore silica gel having $d \simeq 280$ Å, in spite of similar H values, is the result of a decrease in the column capacity ($s = 120$ sq.m/g).

The effect of the geometrical structure of the adsorbents is shown in Fig. 10. It can be seen from this figure that the silica gel KCM-5, having a rather large s value and a small pore size, d, is extremely selective towards aromatic hydrocarbons. However, a decrease in d results in considerable peak broadening. The analysis time is also too long in spite of a rather high elution rate. When considering silica gel C-5, with a value of s about half that of KCM-5, we obtain much lower retentions (Fig. 10). However, the pore diameter of silica gel C-5 is even smaller than that of silica gel KCM-5 (Fig. 10a). Therefore in this case peak broadening as well as poor separation are observed; for example, whereas the H value for benzene on silica gel KCM-5 is nearly 7 mm, the H value on silica gel C-5 is almost twice that size. However, an increase in pore size, keeping s constant, results in a marked increase in the separation efficiency (Fig. 10). It is also important to take into consideration the dependence of optimal specific surface area and pore size values on the grain size of the adsorbent (the decrease in the grain size can somewhat displace the optimum pore size value to the region of lower d).
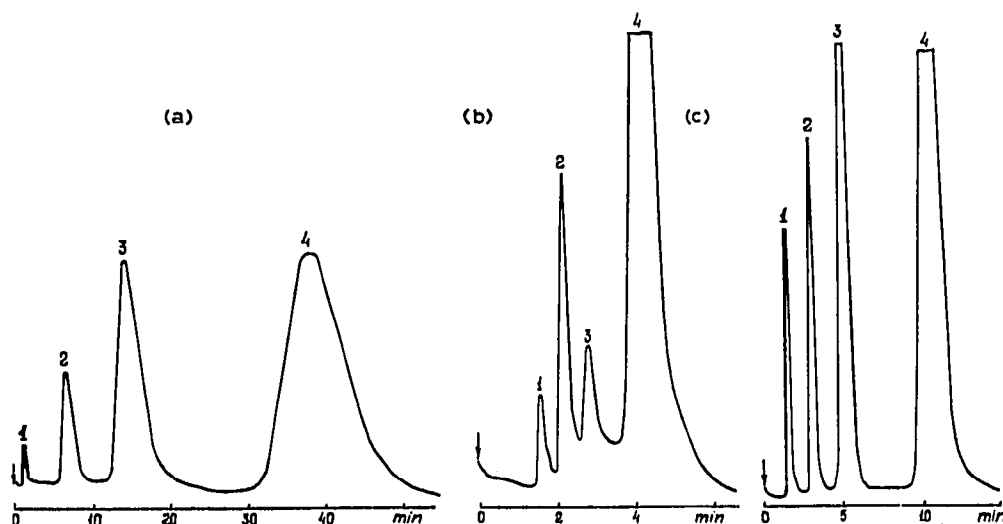
Fig. 10. Chromatograms of (1) carbon tetrachloride, (2) benzene, (3) naphthalene and (4) phenanthrene on silicas with different pore diameters, d. Column, 100 cm × 0.2 cm; detector, UV; temperature, 22°; eluent, n-hexane. (a) Silica gel KCM-5; $d = 28$ Å; flow-rate, $w = 1.8$ ml/min; $s = 800$ sq.m/g; (b) silica gel C-5; $d = 20$ Å; $w = 1.62$ ml/min; $s = 410$ sq.m/g; (c) silica gel C-6; $d = 95$ Å; $w = 1.66$ ml/min; $s = 400$ sq.m/g.

CONCLUSIONS

It is possible to find an optimal chemical composition of the adsorbent surface, as well as optimal values of specific surface area and pore size, for the separation of a given mixture. It is important to study the dependence of these factors on the nature and size of the molecules to be separated (for separation of larger-size molecules we have to use adsorbents with larger d and smaller s values, e.g. Silochrom C-80 was used for the separation of steroids[20]).

Further, we can note that it is necessary to investigate in each case the effect of modifications of the chemical and geometrical characteristics of the surfaces and pores of porous silica, alumina and other adsorbents in liquid–solid chromatography.

ACKNOWLEDGEMENTS

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