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## THE EFFECT OF THE GEOMETRICAL STRUCTURE AND THE SURFACE CHEMISTRY OF SILICA GELS ON SEPARATIONS IN LIQUID-SOLID CHROMATOGRAPHY

N. P. LEBEDEVA, I. I. FROLOV AND YA. I. YASHIN

*Experimental Design Bureau Automatics, Sel'skokhosaistvennaya 20, Moscow (U.S.S.R.)*

## SUMMARY

The effect of the geometrical structure of silica gels on retention volumes, band broadening and separation has been investigated. The retention times of nitrobenzene, aniline, diphenylamine and nitronaphthalene on hydroxylated and dehydroxylated silica gels have been measured. It has been shown that, for analytical purposes and taking into account the analysis time, it is preferable to use temperature programming of the column.

## INTRODUCTION

Silica gels and alumina gels are widely used in liquid-solid chromatography<sup>1,2</sup>. The literature contains little information on the influence of geometrical structure and surface chemistry of hydroxylated and dehydroxylated silica gels on retention volumes and band broadening. The effect of the type of pores in the silica gels on the chromatographic separation of sterines was studied by KLEIN<sup>3</sup>. The influence of impurities in silica gels on retention volumes has been discussed by SPITZ<sup>4</sup>.

The present work involves a study of the effect of the geometrical structure and the surface chemistry of silica gel on retention volumes, peak broadening and resolution.

## EXPERIMENTAL

All measurements were made on equipment assembled in the laboratory. The detector was a UV spectrophotometer. Commercial silica gels were the adsorbents, the structural properties of which are given in Table I.

Hydroxylation of silica gels was carried out by boiling in distilled water for 2 days, and dehydroxylation by heating at 950° for 5-6 h. The particle sizes of the silica gels were 0.04-0.09 mm. *n*-Hexane was used as eluent. It was dried in a column filled with microporous silica gel.

TABLE I

STRUCTURAL PROPERTIES OF THE SILICA GELS USED

Silica gel	Specific surface area, $S$ ( $m^2/g$ )	Average pore radius ( $\text{Å}$ )
C-3	260	82
C-4	540	14.8
KCK-2	368	64
KCK-2, 5	340	56
KCC-3	560	29
KCC-4	660	18.8
KCM-5	650	16.3
Silochrom C-80	80	—

## RESULTS AND DISCUSSION

In order to study the effect of geometrical structure on retention volume ( $V_R$ ) the dependence of  $V_R$  on the specific surface area ( $S$ ) was obtained (Fig. 1). It can be seen from Fig. 1 that at surface areas greater than those specified, non-linear dependence of  $V_R$  on  $S$  is observed. The larger the molecules of adsorbate are the less is the deviation from linearity.

Nonlinearity of the dependence of  $V_R$  on  $S$  is connected with the "ultraporosity effect" as in gas chromatography<sup>5</sup>.

Fig. 2 shows the dependence of the selectivity criterion  $K_c$  (defined as the ratio of the difference of the corrected retention volumes to their sum for two neighbouring peaks) on the average pore radius. The selectivity of separation increases with

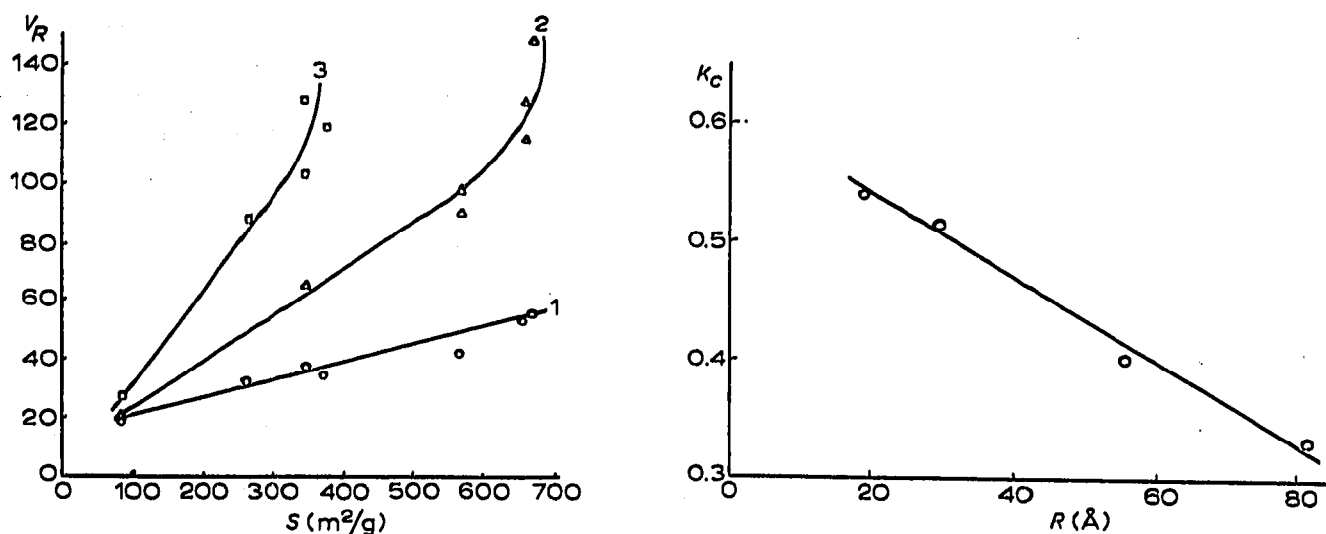


Fig. 1. Relation of retention volumes ( $V_R$ ) to specific surface area ( $S$ ) of silica gels. 1 = Benzene; 2 = naphthalene; 3 = phenanthrene. Temperature, 25°; column dimensions, 50 × 0.5 cm; flow rate of mobile phase (hexane), 0.85 ml/min.

Fig. 2. Relation of the selectivity criterion ( $K_c$ ) (between benzene and naphthalene) to average pore radius ( $R$ ). Conditions as in Fig. 1.

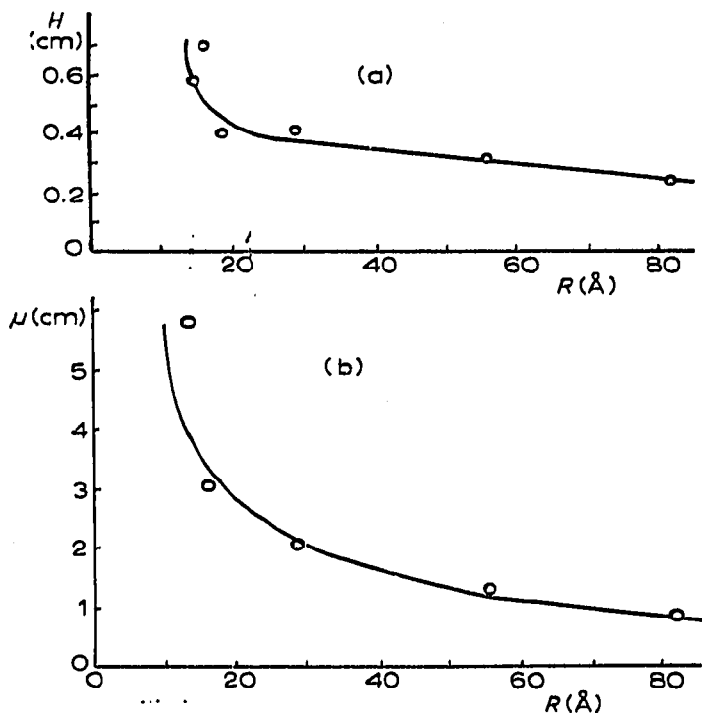


Fig. 3. Relation of: (a)  $H$  to  $R$  and (b) width of band ( $\mu$ ) to  $R$ . Conditions as in Fig. 1.

decrease of average pore radius. However with decreasing average pore radius the width of the band increases (Fig. 3).

The separation ability, estimated by analogy with gas chromatography<sup>6</sup> by the separation criterion  $K_1$ , depends on  $S$  to a smaller degree, since it is determined both by the effectivity and also by the selectivity of the separation (Fig. 4)<sup>7</sup>.

For separation on silica gels with similar surface areas, but different average pore radii, larger retention times and better separations are observed with the more microporous silica gels (Fig. 5).

The dependence of the separation criterion  $K_1$  and of the height equivalent to a theoretical plate on the velocity of the eluent is of interest in connection with slow mass-transfer in liquid-solid chromatography (Fig. 6a, b).

Fig. 6 shows that the effectivity of a column increases (*i.e.* the value of  $H$  decreases) with decrease of velocity, and that broadening occurs in the main as a

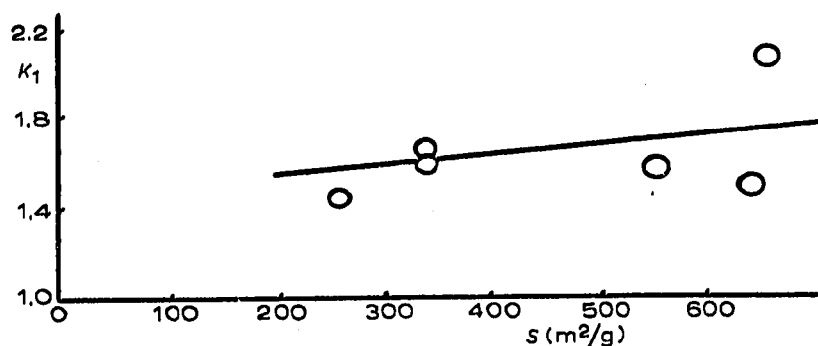


Fig. 4. Relation of the separation criterion ( $K_1$ ) to  $S$  (between benzene and naphthalene).

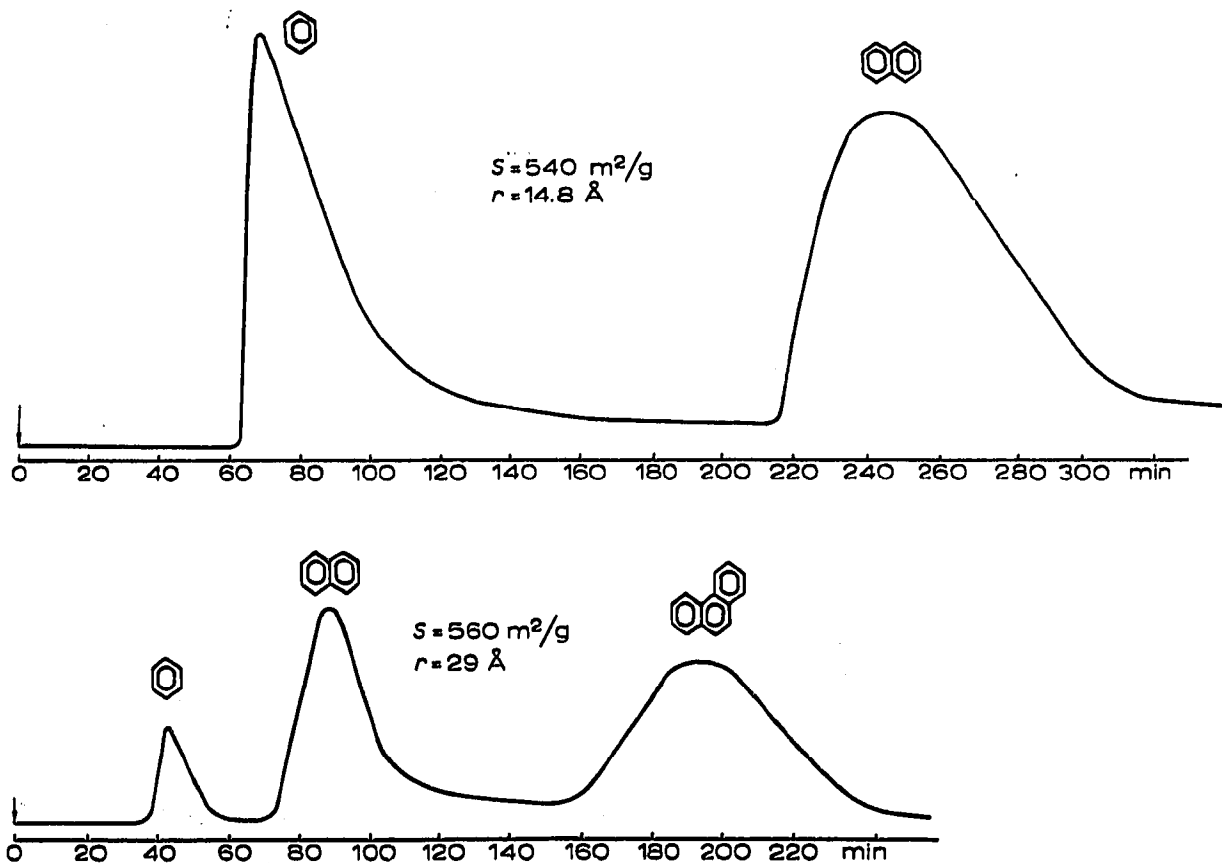


Fig. 5. Comparative chromatograms of benzene, naphthalene and phenanthrene obtained on silica gel column at equal specific surfaces and at various pore radius (shown on the chromatogram).

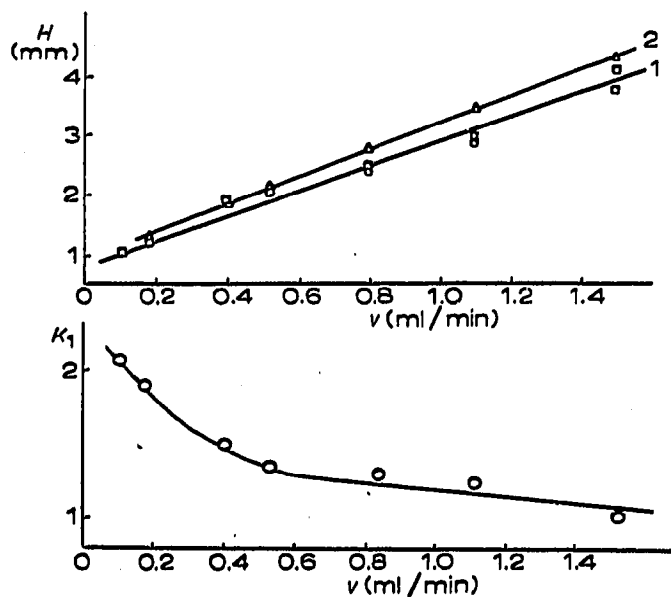


Fig. 6. (a) Relation of  $H$  to velocity of eluent; 1 = benzene; 2 = naphthalene. (b) Relation of the separation criterion ( $K_1$ ) between benzene and naphthalene to velocity of eluent.

TABLE II

COMPARISON OF RETENTION TIMES ON HYDROXYLATED AND DEHYDROXYLATED SILOCHROM C-80  
Eluent, hexane; flow rate, 0.85 ml/min.

Substances	Adsorbent	Temperature ( $^{\circ}\text{C}$ )				
		60	50	40	30	20
Nitrobenzene	Dehydroxylated	27.3	29	34	36.5	40
	Hydroxylated	48	56.4	67	70	81
Aniline	Dehydroxylated	41	58	78.5	89	139
	Hydroxylated	210	264	332	342	—
Diphenylamine	Dehydroxylated	23	27	31	34.5	41.5
	Hydroxylated	60	82.4	102	108	152
Nitronaphthalene	Dehydroxylated	29.2	34	38.5	43	54
	Hydroxylated	53	65	81	—	120

result of kinetic factors. The separation ability of a column (the value of  $K_1$ ) increases with decrease of velocity of the eluent (Fig. 6b). However, the decrease of velocity of the eluent leads to a great increase in analysis time. Taking the analysis time into account more macroporous silica gels are to be preferred for practical purposes. However, the nature of the substances to be analysed must always be taken into consideration.

In order to investigate the effect of the nature of the silica gel surface, retention volumes on hydroxylated and dehydroxylated silica gels were measured (Table II). All the substances given in Table II have considerably greater retention volumes on hydroxylated silica gels.

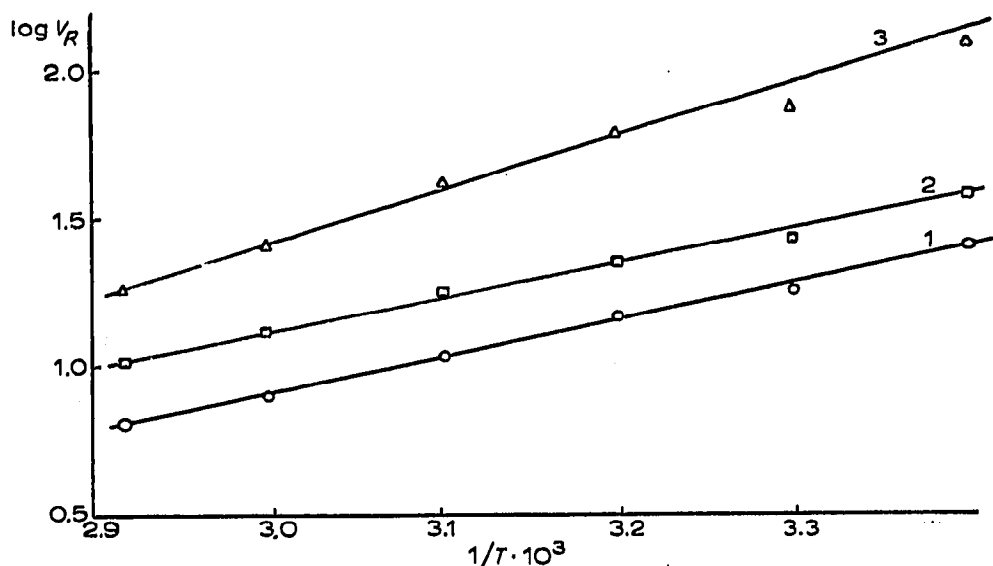


Fig. 7. Relation of  $\log V_R$  to reciprocal of absolute temperature on a column containing dehydroxylated Silica Gel CX-80. 1 = diphenylamine; 2 = nitronaphthalene; 3 = aniline.

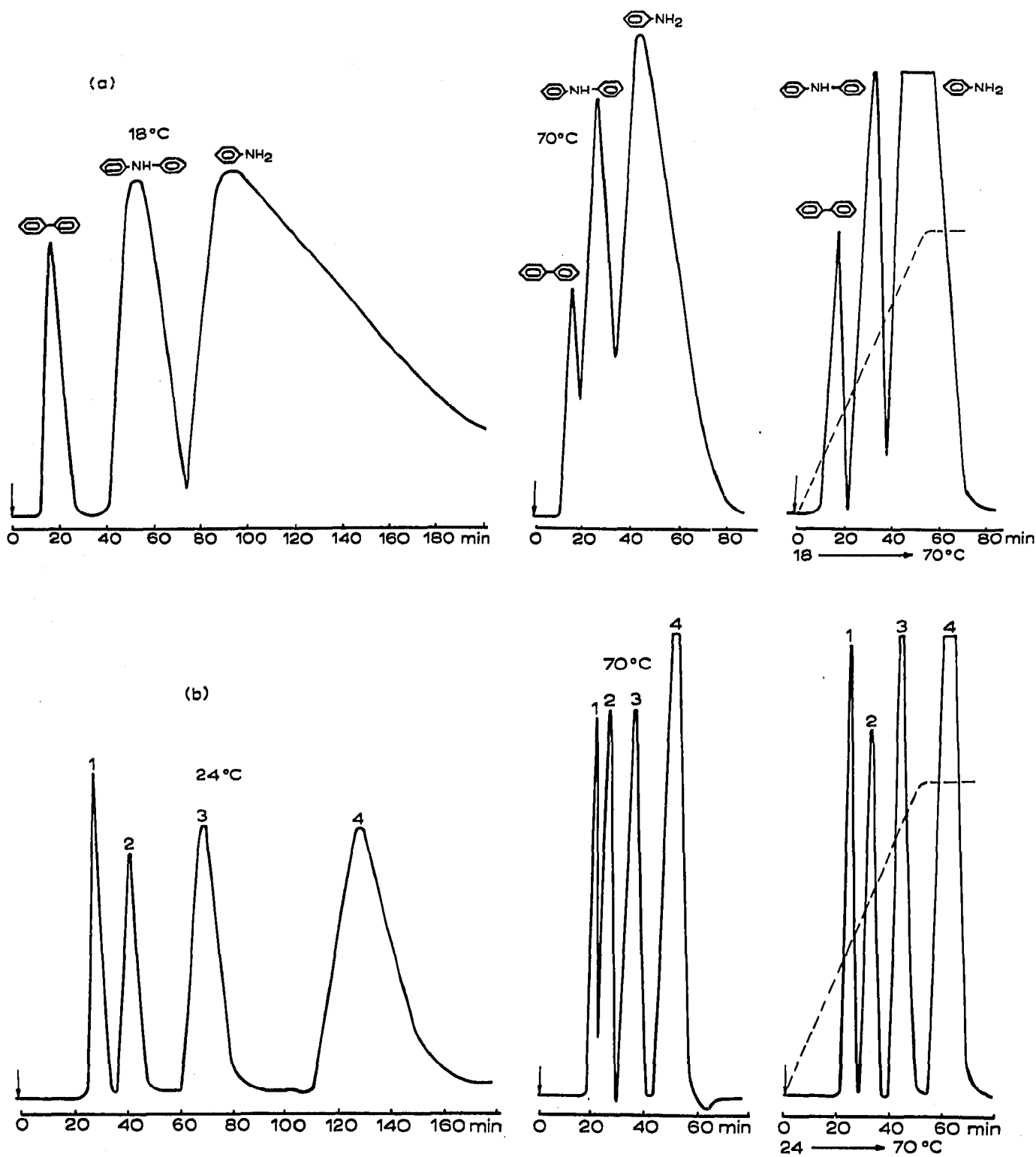


Fig. 8. Comparative separation. (a) Diphenyl, diphenylamine and aniline. Column dimensions,  $50 \times 0.5$  cm; adsorbent, Silochrom G-80 + 5% KCl; flow rate of mobile phase (hexane), 0.85 ml/min. (b) 1 = benzene; 2 = naphthalene; 3 = phenanthrene; 4 = 1,2-benzanthracene. Temperature as shown on the chromatograms. Column dimensions,  $50 \times 0.5$  cm; adsorbent, Silica Gel C-3; flow rate of mobile phase (hexane), 0.85 ml/min.

Fig. 7 shows the dependence of the logarithm of the retention volume on the reciprocal of the absolute temperature on dehydroxylated silica gel for a series of strongly polar substances. As in gas chromatography<sup>5</sup> this dependence is linear. From the slope of the lines, and by analogy with gas chromatographic measurements, it is possible to evaluate the energy of adsorption from solution (hexane). The energies of adsorption obtained from the diagrams are 8.6 kcal/mole for aniline, 6.0 kcal/mole for nitrobenzene and 5.7 kcal/mole for diphenylamine, respectively.

Fig. 7 shows that the retention volumes are very dependent on temperature and therefore programmed temperature of the column during the process of separation will be effective just as in gas chromatography.

The time of separation in liquid chromatography is longer and therefore the application of temperature programming means a considerable reduction in the time of separation and is of paramount significance (Fig. 8).

## CONCLUSIONS

The effect of the geometrical structure and surface chemistry of silica gels on the degree of broadening and on the degree of separation in liquid chromatography has been investigated. From the results obtained it may be concluded that for analytical purposes, and taking into account the analysis time, it is preferable to use more macroporous silica gels (with  $S \sim 80\text{--}300 \text{ m}^2/\text{g}$  and with average pore radius more than  $80 \text{ \AA}$ ).

Hydroxylation of the surface of silica gels leads to a large increase of retention volumes of polar substances, especially the amines.

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