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PROPERTIES OF BINARY STATIONARY PHASES IN GAS-LIQUID PARTITION CHROMATOGRAPHY

II. INFLUENCE OF THE AMOUNT AND POLARITY OF STATIONARY PHASE ON THE OBSERVED RETENTION DATA

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SUMMARY

The retention mechanism of a group of aromatic hydrocarbons and of several polar oxygen-containing compounds on Polsorb B NAW has been investigated in the binary stationary phase bis(2-ethylhexyl) tetrachlorophthalate-squalane. The bulk partition coefficients and adsorption contributions to the observed retention data have been determined. The influences of the stationary phase polarity and temperature on the adsorption effects have been defined. In the investigated system, there exists a concentration of the polar component such that regardless of the amount of the stationary phase on the support, the measured retention data correspond to pure partition.

INTRODUCTION

The partition-adsorption mechanism of retention in gas chromatography, observed some 20 years ago by Martin¹, has not yet been quantitatively surveyed, despite the fact that changes in retention data, connected with the kind of support and the amount of stationary phase, are still troublesome to many chromatographers. Adsorption on the support surface^{1,2} and on the stationary phase surface^{3,4} hinders the determination of physico-chemical values from chromatographic data^{5,6} and changes the values of the best of the ways of expressing retention, *i.e.*, retention indices^{7,8}.

The magnitude of the adsorption contribution to the observed retention data depends on the kind of support, stationary phase polarity and on the polarity of the solutes^{1,4,9-11} and remains a function (in the case of typical diatomite supports) mainly of the amount of the stationary phase. However, it follows from recent and other numerous data^{6,9,11} that even a considerable loading of the support with the

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stationary phase (10–15%) does not always allow us to avoid adsorption. This is so, since even if the stationary phase blocks the active support sites, or if they are already blocked owing to deactivation, Gibbs adsorption may still occur on the stationary phase surface even when the differences in the polarities of stationary phases and solutes are small.

The equation of Conder *et al.*¹² for the retention volume has been successfully applied by many authors^{6,9,11,13–15} to the determination of the adsorption contributions to observed retention data. It is, however, most often used for defining one of its forms, either adsorption on the support⁶ or on the stationary phase surface^{13,16}, and in such chromatographic systems in which adsorption on the support or on the stationary phase surface may be neglected. In the present work, this equation is also used as the basis for determining the influence of stationary phase polarity and temperature on the contribution of adsorption effects to the retention data.

EXPERIMENTAL

Diatomite, non-silanized support Polsorb B NAW¹⁷ (white, non-acid treated), with specific surface area 0.5 m²/g, and the mixed binary stationary phase bis(2-ethylhexyl) tetrachlorophthalate (EHTCP)–squalane were used. The application of the mixed binary stationary phase, instead of a series of single solvents of different polarities, permitted continuous change of the polarity and did not complicate the overall picture with effects resulting from the introduction of a new kind of functional group. The increase in the stationary phase polarity was achieved by increasing the EHTCP concentration in squalane solution. The following substances were analysed: aromatic hydrocarbons (benzene, toluene, ethylbenzene); polar oxygen-containing compounds (butanol, diethyl ketone, isoamyl acetate), *i.e.*, compounds capable of specific interactions, either with an aromatic ring or with the carbonyl group of the stationary phase.

Chromatographic measurements were made using a Perkin-Elmer 116 E chromatograph equipped with a katharometer. Nitrogen was used as the carrier gas at a flow-rate of 60 ml/min. A silanized glass column (1 m × 4 mm I.D.) was used. Measurements were made at 67.6, 76.7, 83.4 and 95.6°C. The sample size was 0.1 μl. The Polsorb B NAW support had a particle-size of 0.2–0.3 mm and was dried for 4 h at 200°C. It was then coated with EHTCP and its mixtures with squalane in the proportions 3:1, 1:1 and 1:3 w/w using the fluidization method and in the amounts 3,

TABLE I

DENSITIES OF BIS(2-ETHYLHEXYL) TETRACHLOROPHTHALATE AND SQUALANE AT VARIOUS TEMPERATURES

Solvent	Density (g/cm ³)			
	67.6°C	76.7°C	83.4°C	95.6°C
Bis(2-ethylhexyl) tetrachlorophthalate	1.1495	1.1425	1.1367	1.1256
Squalane	0.7772	0.7722	0.7682	0.7612

6 and 10% (w/w). Columns were conditioned overnight at 120°C in a carrier gas flow. Column packings were prepared w/w and the stationary phase volume at the temperature of measurement was calculated on the basis of the previously measured densities of the liquids (Table I).

RESULTS AND DISCUSSION

The bulk partition coefficient was calculated from the equation of Conder *et al.*¹² in the form

$$V_N/V_L = K_L + (K_S A_S + K_L A_L)/V_L \quad (1)$$

where K_L is the bulk partition coefficient, K_S the coefficient of sorption on the support surface A_S and K_L , the coefficient of sorption on the stationary phase surface A_L . This expression enables us to calculate K_L from an extrapolation of observed partition coefficients, K_{obs} , at different coverages to the infinite volume of the stationary phase.

The dependences $V_N/V_L = f(1/V_L)$ and $V_N/V_L = K_{obs} = f(\text{percentage of the stationary phase})$ for various stationary phase compositions and temperatures take different courses for aromatic hydrocarbons and for polar oxygen-containing compounds. Retention data of the oxygen-containing compounds at all temperatures and at all stationary phase compositions decrease, when the amount of the stationary phase on the support is increased (Figs. 1a and 2a).

The way in which the retention of aromatic compounds changes is closely connected with the stationary phase polarity. With pure EHTCP and its solutions in

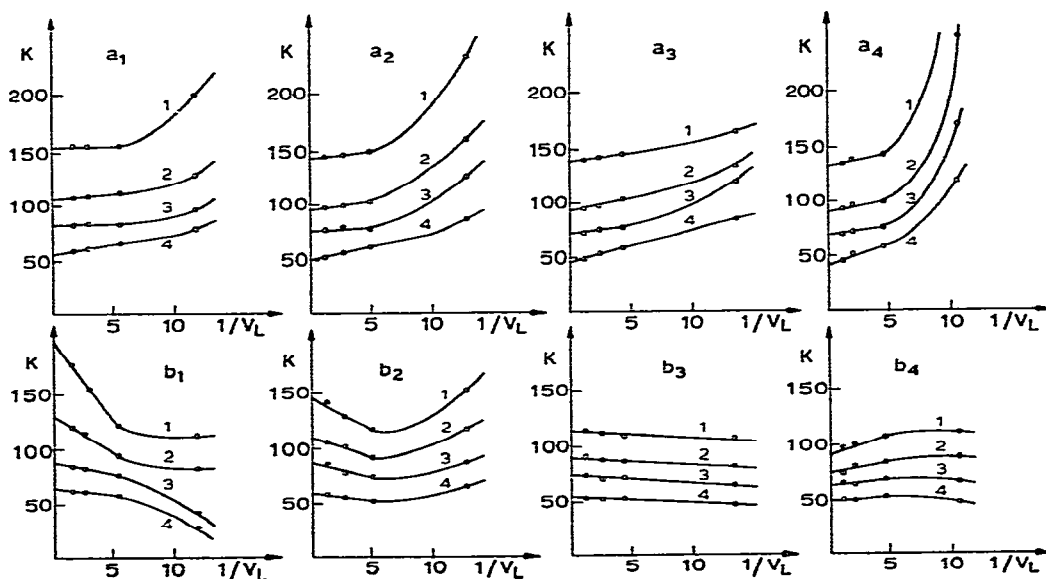


Fig. 1. Partition coefficient as a function of stationary phase volume at various temperatures and stationary phase compositions for *n*-butanol (a) and benzene (b). Stationary phases: EHTCP (a_1, b_1); EHTCP-squalane 3:1 (a_2, b_2); 1:1 (a_3, b_3); 1:3 (a_4, b_4). Curves: 1 = 67.6°C; 2 = 76.7°C; 3 = 83.4°C; 4 = 95.6°C.

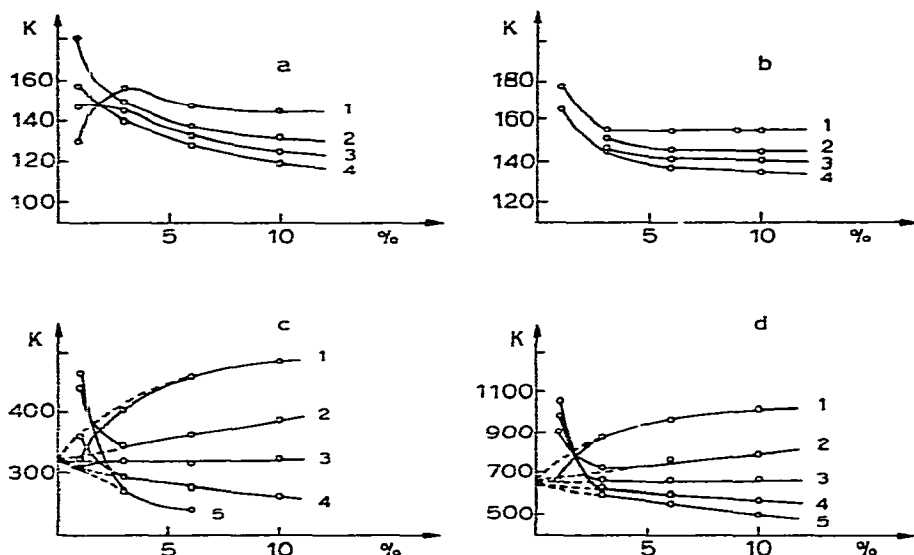


Fig. 2. Relationship between partition coefficient and stationary phase percentage at 67.6°C. for diethyl ketone (a), *n*-butanol (b), toluene (c) and ethylbenzene (d). Stationary phases: 1 = EHTCP; 2 = EHTCP-squalane (3:1); 3 = EHTCP-squalane (1:1); 4 = EHTCP-squalane (1:3); 5 = squalane.

squalane in the proportions 3:1 and 1:1 the retention increases with increasing amount of stationary phase (which becomes weaker, however, as it is being progressively diluted in squalane; Fig. 1b) but in the proportion 1:3 the retention begins to decrease when the support is covered mostly with the stationary phase (Figs. 1b and 2, curve 4). Fig. 2 shows clearly the diversification of the retention behaviour depending on the polarity of the stationary phase and the kind of solute. In Fig. 3, it is seen that a rise in temperature makes K_{obs} virtually independent of the amount of stationary phase and of its polarity in the case of aromatic hydrocarbons.

Retention data obtained at stationary phase concentrations less than 3% show a considerably higher contribution from adsorption and are less regular. An increase

TABLE II

BULK PARTITION COEFFICIENTS, K_L , FOR VARIOUS SOLUTES IN BIS(2-ETHYLHEXYL) TETRACHLOROPHTHALATE-SQUALANE AT VARIOUS CONCENTRATIONS OF EHTCP AND TEMPERATURES

Solute	2.14 mol/l				1.42 mol/l			
	95.6°C	83.4°C	76.7°C	67.6°C	95.6°C	83.4°C	76.7°C	67.6°C
Benzene	63.4	90.0	128.3	197.3	56.4	77.0	98.0	141.6
Toluene	153.5	228.3	312.5	508.8	137.6	197.6	270.1	404.3
Ethylbenzene	295.0	413.8	603.8	1042.3	266.9	318.7	536.8	817.0
<i>o</i> -Xylene	492.0	787.7	1057.9	1739.0	416.0	663.8	875.6	1292.2
<i>m</i> -Xylene	368.0	610.0	768.2	1370.2	326.0	525.0	625.4	1051.5
<i>n</i> -Butanol	56.4	81.9	107.0	155.0	50.9	77.0	103.0	144.0
Diethyl ketone	63.5	75.5	94.1	135.3	56.5	71.0	89.4	122.8
Isoamyl acetate	262.3	347.5	455.8	665.0	228.0	323.0	422.5	570.0

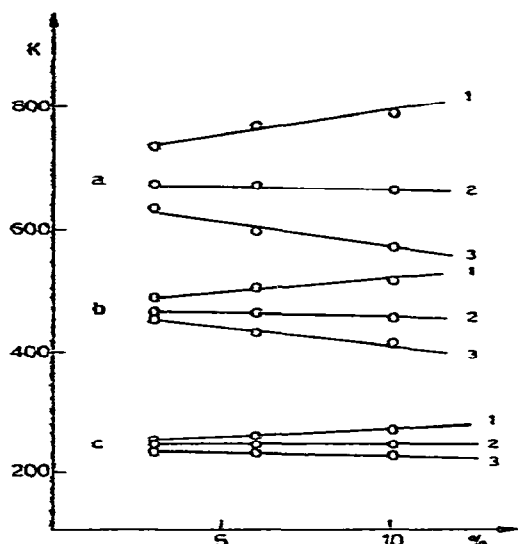


Fig. 3. Relationship between the partition coefficient of ethylbenzene and stationary phase percentage at 67.6°C (a), 76.7°C (b) and 95.6°C (c). Stationary phases: 1 = EHTCP-squalane (3:1); 2 = EHTCP-squalane (1:1); 3 = EHTCP-squalane (1:3).

in the amount of squalane in the stationary phase causes a radical increase in the retention data of aromatic and oxygen-containing compounds (Figs. 1 and 2). This increase is not, however, proportional to the increase in stationary phase polarity since, for example, when the proportion of solvents is 1:1 the contribution from adsorption is the smallest. Adsorption of these substances is probably determined not only by the support activity itself and its wettability, but also by the way in which the stationary phase is placed on its surface, *i.e.*, by the orientation of particular liquid layers and the mutual positioning of EHTCP and squalane molecules which may be dependent on their relative amounts. A thorough interpretation of the retention mechanism in this range of coverages requires additional measurements.

Bulk partition coefficients, determined graphically from such dependences as

0.86 mol/l				0.40 mol/l			
95.6°C	83.4°C	76.7°C	67.6°C	95.6°C	83.6°C	76.7°C	67.6°C
50.9	66.5	83.0	115.2	45.7	56.2	69.7	94.8
122.4	170.4	227.6	320.5	105.5	153.2	192.0	258.8
242.9	349.8	468.9	644.6	219.9	315.9	408.9	543.8
363.2	549.4	708.1	1006.4	317.6	465.0	557.6	794.2
281.0	446.0	589.7	795.6	259.4	382.9	470.9	647.5
46.1	73.6	96.4	137.0	42.2	70.5	92.6	132.3
52.0	67.4	90.0	115.0	47.5	63.5	83.5	109.1
215.5	310.0	423.8	541.0	192.0	295.8	409.8	516.6

shown in Fig. 1, are given in Table II. In Fig. 4 they are shown as a function of the concentration of the polar component of the stationary phase (curves 4), expressed in mol/l. Also presented is an analogous dependence of the observed partition coefficients, K_{obs} , at a different stationary phase coverage. Completely different dependences for the aromatic (ethylbenzene) and oxygen-containing compounds (diethyl ketone) can be seen. For the ketone, the curves showing pure partition always lie, at all temperatures, below the curves for partition coverages (3, 6 and 10%), *i.e.*, in all cases adsorption increases the retention data (Fig. 4b).

The curves of ethylbenzene intersect at one point at all temperatures. There exists, then, a concentration of the polar component at which, regardless of the extent of coverage of the support with the stationary phase, the observed partition coefficient is the same as the bulk one ($K_{\text{obs}} = K_L$). Up to this concentration, the course of the dependences is of the same type as the one for diethyl ketone. Above this concentration the value of the bulk coefficient is higher than the value of the observed coefficient at a given coverage. In this case adsorption decreases the retention data, and probably occurs on the stationary phase surface. Ethylbenzene, which is less polar than the ketone, starts to accumulate (at a certain concentration of EHTCP) on the polar surface of the stationary phase. So beyond the point of the intersection of the curves, this is probably the only form of adsorption present. For diethyl ketone such a range would appear in solvents more polar than EHTCP, since all the curves drawn for this solute in the pure phthalate tend to converge.

In order to clarify the changes in the character of adsorption with the polarity of the stationary phase, and the polarity of the solutes, the adsorption contribution to the observed retention data has been calculated (percentage adsorption = $(K_{\text{obs}} - K_L)/K_{\text{obs}}$) and plotted as a function of the concentration of the polar component of the stationary phase, C_A , for different amounts of the stationary phase and various temperatures (Figs. 5 and 6). An increase in the amount of stationary phase at all temperatures results in a decrease in the adsorption effects on the retention of both aromatic and oxygen-containing compounds. The influence of temperature, however, varies. Benzene, whose K_{obs} is most distant from K_L , at 95.4°C and at 10% liquid phase loading exhibits an adsorption effect almost equal to that of oxygen-containing compounds (ketone, acetate; Figs. 5, curves 4 and 6). The retention data of the polar oxygen-containing compounds change in a variety of ways. At all degrees of support coverage at 67.6°C, diethyl ketone exhibits considerably higher adsorption contributions to the retention than butanol but at 95.4°C the opposite situation is observed (Fig. 5, curves 1 and 3).

These observations, as well as the behaviour of the aromatic hydrocarbons [Fig. 6, the curves $A = f(C_A)$ intersect the x axis at increasingly higher EHTCP concentrations], can, most probably, be accounted for by changes in the orientations of the stationary phase molecules at the liquid-gas and liquid-solid interphases. On the one hand, the binding between the polar groups of the stationary phase and the surface groups of the support probably weakens or even disappears (the active sites of the support are released) and, on the other hand, the structure of the surface layers changes. The liquid surface becomes less polar, since we observe a decrease in the adsorption of benzene above the point of intersection of the curves $A = f(C_A)$ (Figs. 5 and 6) and an increase in the adsorption of butanol. The latter phenomenon may also be caused by the adsorption of butanol on the unblocked active sites of the support.

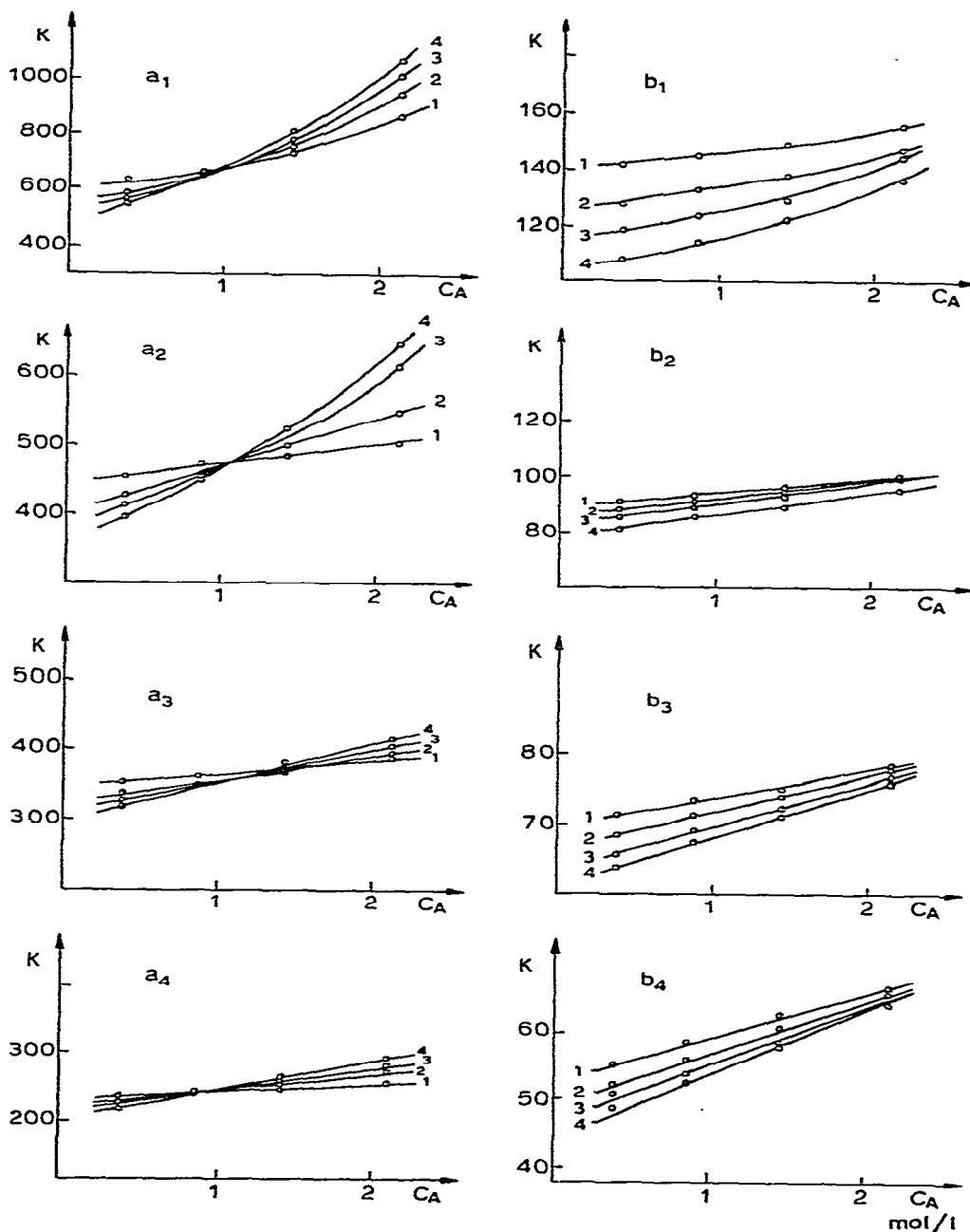


Fig. 4. Observed and bulk partition coefficients as a function of the concentration of the polar stationary phase component for ethylbenzene (a) and diethyl ketone (b) at 67.6°C (a₁, b₁), 76.7°C (a₂, b₂), 83.4°C (a₃, b₃) and 95.6°C (a₄, b₄). Curves: 1 = 3% loading; 2 = 6% loading; 3 = 10% loading; 4 = bulk partition coefficients.

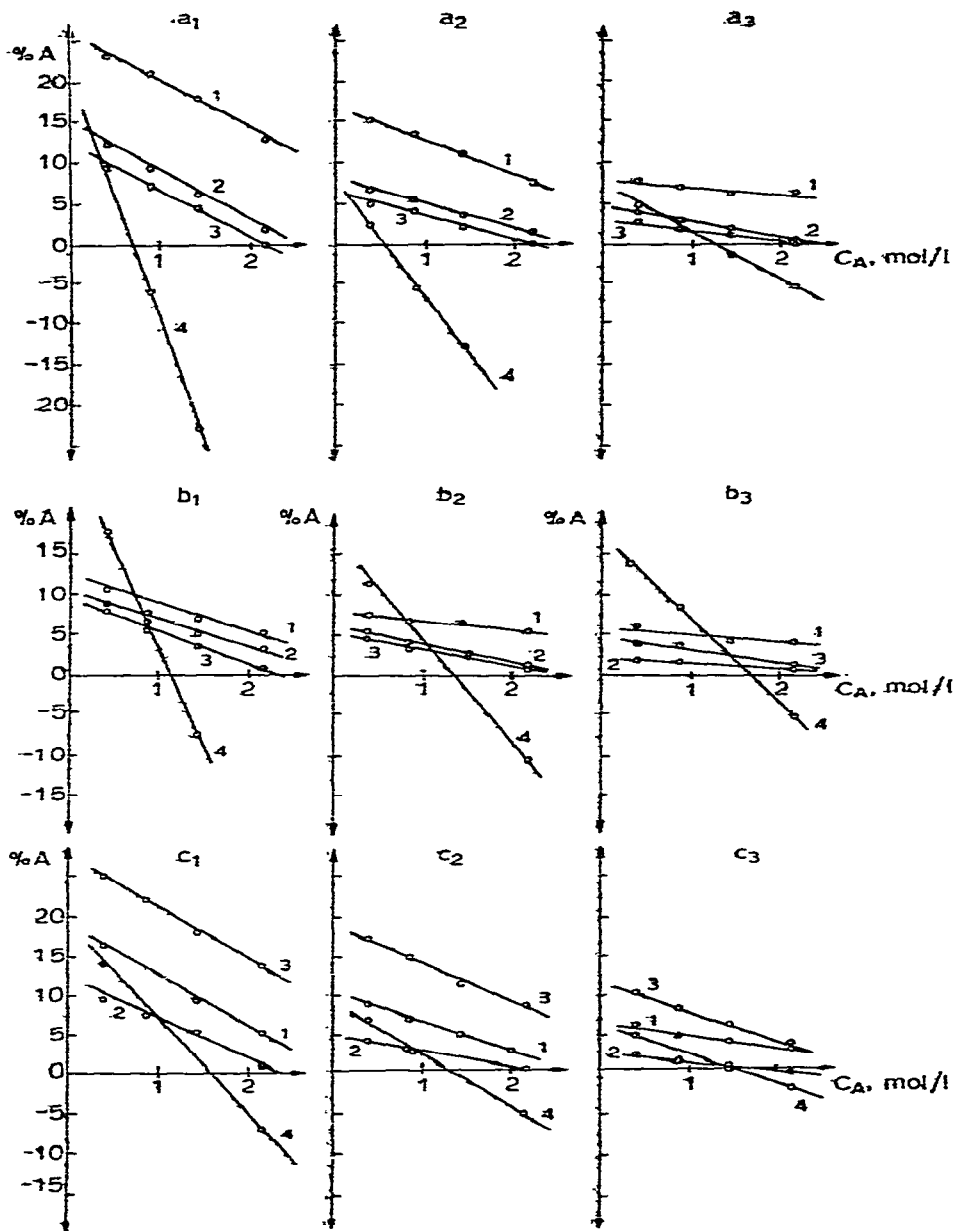


Fig. 5. Adsorption contributions to the observed retention data as a function of the concentration of the polar component of the stationary phase at various amounts of stationary phase on the support (3% a_1, b_1, c_1 ; 6% a_2, b_2, c_2 ; 10% a_3, b_3, c_3) and at 67.6°C (a), 76.7°C (b) and 95.6°C (c). Curves: 1 = diethyl ketone; 2 = isoamyl acetate; 3 = *n*-butanol; 4 = benzene.

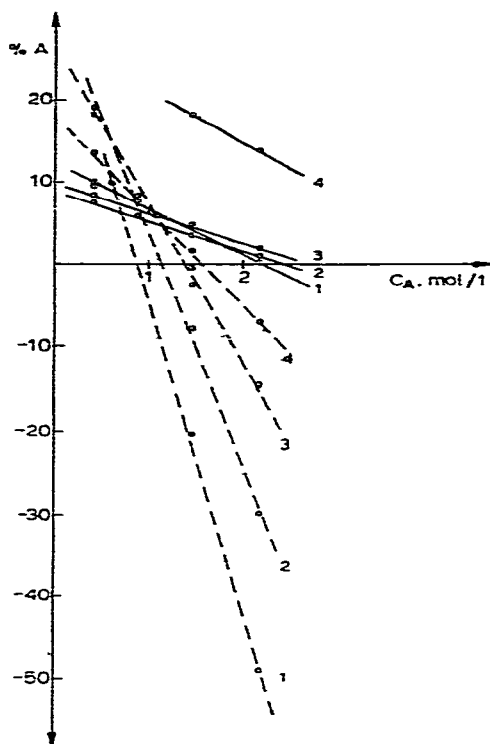


Fig. 6. Influence of temperature on the adsorption contributions to the observed retention data of *n*-butanol (—) and benzene (---) as a function of the concentration of the polar component of the stationary phase at 3% coverage. Curves: 1 = 67.6°C; 2 = 76.7°C; 3 = 83.4°C; 4 = 95.6°C.

The ketone group is less polar than the alcohol one, and a decrease in the polarity of the stationary phase surface for the former is advantageous for dissolution (Fig. 5a,b,c; curves 1).

It is worth noting that the dependences of K_{obs} on the extent of support coverage, in the range of 3–10%, and for different mixed stationary phase compositions (Fig. 2c,d) converge on the y axis, at a point such that the value of the partition coefficient corresponds to the point of intersection of the curves $K = f(C_A)$ in Fig. 4. This value of the partition coefficient in turn corresponds to the concentration of the polar solvent which blocks adsorptive interactions on the support surface, and could be regarded as "critical" for the given chromatographic system. The corresponding stationary phase polarity is that which counterbalances the specific interactions of both the support and the solute. The courses of the adsorption contributions to the retention data of benzene as a function of the concentration of the polar component of the mixed stationary phase at different temperatures (Fig. 6) support this conclusion. A rise of temperature is followed by a shift of the "critical" concentration towards higher polarities of the stationary phase. Thus, temperature constitutes a factor which opposes the effects resulting from the polarity of the components of the system.

CONCLUSIONS

The present mixed binary stationary phase is a very convenient system for measuring the retention mechanism, since it permits the estimation of adsorption effects under continuous changes of the stationary phase polarity. Hence, for a given compound or even for a group of compounds, one can clearly determine the stationary phase polarity at which, regardless of its amount, the observed partition coefficient will constitute the bulk coefficient.

This also suggests that there exist other chromatographic systems in which adsorption, even at stationary phase amounts higher than 10%, will always contribute to the retention data.

The value of the partition coefficient corresponding to the "critical" concentration of the compound or of a group of compounds of different polarities could, similarly to McReynolds¹⁸ constants, characterize the polarity of chromatographic packings, and thus determine their analytical usefulness.

An increase of the amount of the stationary phase on the support and of the temperature of the measurement generally results in a decrease in the adsorption contribution to the retention mechanism. In every case, however, the influence of both these factors is determined by the interrelation of the polarity of the stationary phase and of the solute. For example, in the above system an increase in temperature radically increases adsorption of the higher polar solute (butanol).

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