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RETARDATION BY PHASE SOAKING IN CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

"Phase soaking" is a solvent effect that occurs in the coated column beyond the flooded inlet section and may influence the shape and the retention of early eluting peaks. Solvent is retained by the regular stationary phase and increases the retention power of the system. The strength of a phase soaking effect depends primarily on this increase of the retention. "Retardation factors" were determined for some solutes by the temporary saturation of the carrier gas with vapours of some solvents and repeated injections of a component at known time intervals. The retardation factors varied between 1 and more than 10, *i.e.*, between no influence of the added solvent vapour and a more than a 10-fold slower migration in the soaked than in the pure stationary phase. Retardation factors depend on the solubility and the retention of the solvent in the stationary phase and on the polarity of the soaked compared with the pure stationary phase. They correlate reasonably well with the reconcentration of partially trapped components. Phase soaking with a retardation factor of at least 2 is needed in order to provide a considerable reconcentration effect and of at least 3 for complete reconcentration.

INTRODUCTION

Our studies on solvent effects in splitless and cold on-column sampling led to the conclusion that there are two processes to be considered separately. Condensed solvent in the column inlet (introduced directly on-column or via recondensation in splitless sampling) acts as a temporary stationary phase with a very thick film. Sample components are pre-chromatographed in this solvent layer, resulting in the phenomena called "solvent trapping effects"[1,2]. The commonest case is "full trapping", where a component is fully retained by the solvent until the solvent has evaporated. Full trapping releases a sharp solute band with an extra-retention time corresponding to the evaporation time of the solvent in the column inlet. In "partial trapping" a component evaporates together with the solvent and starts the chromatographic process as a broad band, often with a width that corresponds to the evaporation time of the solvent. "Non-trapping" is not considered in this paper; it is observed for components that are hardly retained by the solvent and released immediately after the injection.

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The solute band, as it leaves the condensed solvent layer in the inlet section, may be further modified by another solvent effect with completely different characteristics. Its origin is explained as follows. The carrier gas is saturated with solvent vapour as long as there is condensed solvent in the column inlet (which may last between a few seconds and a few minutes). At the column temperatures used for injections with a solvent effect (below the boiling point of the solvent), some of the solvent is retained by the regular stationary phase. Some stationary phases become overloaded to such an extent that their film thickness is increased several-fold, which we thought could be adequately described as "phase soaking". A soaked stationary phase has an increased retention power, due to an increased film thickness and a reduced viscosity or to an additional change in polarity.

In a previous paper[3] we described in detail the action of phase soaking on the band of *n*-octane injected (on-column) as a solution in *n*-heptane. *n*-Octane was partially trapped by *n*-heptane and left the inlet section as a band of width 2 min. It was reconcentrated by phase soaking to a band of width less than 1 sec between 2 and 5 m in the column. Two aspects contributed to this remarkable result. First, the stationary phase (OV-1) soaked with *n*-heptane slowed down the migration of the first *n*-octane material which had left the flooded inlet section. In this way, the front of the *n*-octane band migrated only a few metres into the column until the last portion of the *n*-octane started to be chromatographed (*i.e.*, until the solvent in the inlet was completely evaporated), instead of having already left the column at that time. However, the major reconcentration was due to the second mechanism involved: the solute band accelerated to the normal migration speed as soon as the solvent band had withdrawn and left the solute in the pure stationary phase. As the rear of the *n*-octane band accelerated first, it became more rapidly moving than the front of the band and reduced its delay to the advanced material, and thus reduced the band width.

The degree of reconcentration of a solute band by phase soaking depends on the difference in the migration speeds of the solute in the soaked and the pure stationary phase or, in other words, how much more slowly a solute migrates in the soaked than in the pure stationary phase.

This retardation of solutes by phase soaking is the subject of this paper. The reconcentration effect also depends on the speed of the withdrawing solvent relative to the migration speed of the solute in the pure stationary phase. If the rear of the solvent band withdraws more slowly than the solute is able to migrate in the pure phase, the rear material of the solute band follows closely the rear of the solvent band and is enabled to catch the front of its band. If the solvent withdraws more rapidly, and hence if the liberated solute material lags behind, the reconcentration is only partial because the front of the solute band is liberated before the rear material reaches it. All this must be considered in the context that the rear of the solvent band accelerates its migration speed when proceeding through the column. This appears to be the reason why the two factors determining the degree of reconcentration by phase soaking are not really independent of each other.

If a solute elutes before the solvent peak, phase soaking has the opposit effect on the solute band. It retards the band and broadens it because the rear solute material is retained in the soaked zone for a longer time than its front ("reverse solvent effect"[4]).

We determined the retardation of solutes by phase soaking as "retardation

factors". A retardation factor is the ratio of the migration speeds of a solute in a pure and a soaked system whereby a system is soaked if the carrier gas is saturated with solvent vapour. Retardation factors depend first on the amount of solvent that is retained by the stationary phase and second on the change in the chromatographic properties (polarity) of the soaked in comparison with the pure stationary phase. Hence retardation factors depend on the stationary phase, the solvent and the solute, and are therefore complex. We determined a number of such factors to help to detail our picture of the phase soaking effect and also because a deeper understanding of the solvent effects facilitates the optimization of conditions for the analysis of components that tend to form distorted peaks (*i.e.*, most solvents). We would not be surprised, however, if such retardation factors could be exploited for other purposes.

We could not find any references in the literature that reported data corresponding to retardation factors. The idea of adding an active component to the carrier gas, primarily water vapour, ammonia, volatile amines or acids, has been reported many times for gas–solid chromatography or for gas–liquid chromatography to reduce adsorption phenomena[5–9]. Tsuda and co-workers[10,11] determined retention volumes with vapours of organic solvents as the carrier gas and compared them with retention volumes obtained with helium as the carrier gas. However, these data refer to column temperatures above the boiling point of the solvents; hence little solvent is retained by the stationary phase and phase soaking is not involved. Janak *et al.*[12] found that water vapour in the carrier gas did not change the retention volumes of a number of test components by more than 10% if chromatographed on Tenax. Two papers reported on the influence of trace amounts of water vapour in the carrier gas on the chromatographic properties of capillary columns[13,14]. Two papers that really deal with phase soaking concentrate on polarity shifts due to the presence of solvent vapour in the carrier gas (benzene[15] and water[16]).

EXPERIMENTAL

The determination of a retardation factor requires the measurement of the retention times of a solute when chromatographed using pure and solvent-vapour-saturated carrier gas. It would be desirable to detect the solute by a system that is specific for the solute and suppresses all the solvents of interest. However, we used a technically simpler method involving flame-ionization detection (FID).

The carrier gas was saturated with solvent vapour by a loop inserted between the pressure regulator and the injector. Two valves within this loop forced the carrier gas either to pass through a bottle containing solvent or to bypass this solvent. The experiments were carried out on a vapourising injector with a constant split flow-rate of 100 ml/min. The split flow ensured that dead volumes in the loop were rapidly purged and clean carrier gas reached the column when the supply of solvent vapour was cut off. The split mode also allowed small amounts of dissolved solute to be introduced into the column to minimize additional solvent effects. The whole system was operated at ambient temperature. The flow-rate through the columns was *ca.* 3 ml/min (hydrogen).

Instead of determining absolute retention times in separate runs, we injected the same solute several times at known time intervals within the same run. The column was soaked with carrier gas containing solvent vapour for a few minutes (time

was found not to be critical) before syringe needle volumes (0.8 μl) of a solute dissolved in *n*-pentane (1:1000) were injected three to five times at precisely determined intervals of 1–2 min. One minute after the last injection, the supply of solvent vapour was stopped and the solute bands eluted. Thus the solute bands passed through the major part of the column under non-soaked conditions. Fig. 1 shows the chromatogram obtained during such an experiment. To calculate the retardation factor the time between two subsequent injections was divided by the difference in the retention times of the corresponding neighbouring peaks.

The method described determines the migration speed of the first solute band of a pair of injections in the soaked system between its injection and the moment the second solute band is introduced. A strong phase soaking (linkage to a large retardation factor) allows the first band to migrate only a short distance during this interval. The second solute band serves as a marker. The two bands are assumed to be chromatographed under identical conditions. They migrate with a constant distance, first slowly in the soaked and later more rapidly in the pure stationary phase. The difference in their retention time still reflects the reduced distance the first solute band migrated until the second was introduced.

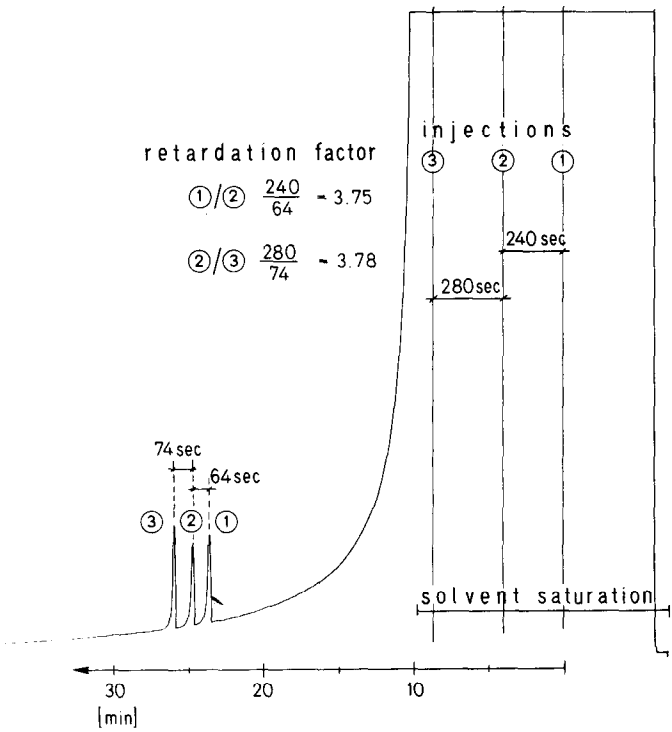

Fig. 1. Procedure for determining retardation factors. The carrier gas was saturated with solvent vapour (*n*-hexane), which gave full-scale deflection of the recorder after the dead time of the column. A few minutes afterwards, three injections (needle volumes, *n*-decane in pentane, 30:1 split) were made at precisely determined intervals. One minute after injection No. 3, the supply of solvent vapour was stopped and the peaks were eluted. The retardation factors were calculated by division of the time between two injections by the difference in the retention times of the corresponding peaks. Column, 15 m × 0.30 mm I.D.. glass capillary coated with 0.15 μm OV-1; carrier gas, 0.3 atm of hydrogen.

We paid special attention to two points. First, it was difficult to adjust the temperature of the solvent to saturate the carrier gas at the column temperature because the solvent was cooled by bubbling carrier gas through it. Further, the GC oven, even with an open door, was a few degrees above ambient temperature and hence the solvent had to be slightly warmed. If the solvent temperature was higher than the column temperature, it recondensed in the column and caused a strong increase in retention times due to solvent trapping. The use of a "milky" pre-column (length 1 m) allowed such recondensation to be excluded because condensed solvent is easily observed by turning the column transparent[17]. A deviation of the temperature to the opposite side was less dramatic: the retardation factors were only reduced by 10% when the column temperature increased 8°C above the solvent temperature.

The second point is concerned with a weakness of the concept, *viz.*, that the method cannot ensure that the solute bands of two subsequent injections are located in the soaked zone up to the exactly same moment. If the solvent band does not move rapidly compared with the solute bands, the second solute band is liberated considerably earlier than the first and reduces the distance to the first injected band. In fact, retardation factors were incorrectly high if the solutes eluted close to the solvent peak. This deficiency of the method forced us to use test compounds that eluted far beyond the solvent, *i.e.*, that became separated from the solvent at the beginning of the column within a short time. The error became particularly small if the time intervals between the injections were short.

RESULTS

Retardation factors

Table I shows some retardation factors determined on a 15 m × 0.30 mm I.D. glass capillary coated with 0.07 μm of SE-52. A retardation factor of unity indicates that the peaks of two injections eluted with the same time interval as they were injected or that the band introduced by the first injection was not retarded by phase soaking.

Retardation factors were close to unity for methanol as a soaking solvent and apolar to medium-polar solutes because this polar solvent was hardly retained by the apolar stationary phase. However, 1-octanol was considerably retarded because the small amounts of methanol retained in SE-52 increased the polarity of the stationary

TABLE I

RETARDATION FACTORS ON A 15 m × 0.30 mm I.D. SE-52 COLUMN (0.07 μm FILM THICKNESS)

Column temperature, 27°C.

Soaking solvent	*Solute injected*		
	n-Decane	*2-Chlorotoluene*	*1-Octanol*
n-Hexane	3.5	2.0	2.2
Dichloromethane	2.5	4.0	8.3
Acetone	1.4	1.7	6.6
Methanol	1.1	1.2	3.3

phase. The less polar acetone retarded 1-octanol more strongly than methanol. The retardation factors in Table I show that even apolar solutes are retarded by acetone soaking. As polarity decreases the retention of *n*-decane, it may be concluded that a considerable amount of acetone is retained by SE-52, retarding primarily by an increase in film thickness. This larger amount of retained acetone is also responsible for the more pronounced increase in the polarity of the stationary phase than is observed for methanol.

A non-polar solvent such as *n*-hexane on SE-52 as the stationary phase caused extra-retention primarily by an increase in film thickness, which is reflected by the fact that the retardation factors were similar for all three solutes tested. The retardation factor for *n*-decane was identical with that calculated for *n*-octane (solute) and *n*-heptane (solvent) by an independent method[3].

Dichloromethane gave high retardation factors for all three stationary phases tested (SE-52, Table I; Carbowax 400, Table II; and Pluronic L 61, Table III). Its retardation effect is due to an increase in film thickness (*n*-decane on SE-52) as to its function in helping to dissolve solutes in stationary phases of different polarity. The latter effect is exemplified by the large retardation factors for 1-octanol on SE-52 and *n*-undecane on Carbowax 400 (Table II). The retardation factor for *n*-undecane on Carbowax 400 could not be determined because the two peaks resulting from two injections with a 5-min interval co-eluted; it must have exceeded 30. *n*-Hexane on Carbowax 400 as methanol on SE-52 retarded exclusively by adjusting the polarity of the stationary phase. Methanol very strongly retarded lower alcohols. However, it would be more surprising if methanol would retard alkanes even by factors exceeding 5, as the experiment indicated. But preliminary experiments have shown that Carbowax 400 and the even more polar methanol create reversed-phase phenomena which are misinterpreted by our experiment.

Table III shows the retardation factors for Pluronic L 61, (90% polypropylene glycol), our preferred stationary liquid for the analysis of solvents. As solvents and other volatile components are notorious for partial solvent trapping, reconcentration by phase soaking is of particular interest. The retardation factors on Pluronic L 61 are situated between the values with SE-52 and Carbowax 400.

Retardation factors are nearly independent of the volatility of the solute, as we found by a comparison of *n*-octane and *n*-nonane on a thick-filmed OV-73 column as well as of *n*-nonane and *n*-decane on a thin-filmed SE-52 and a Pluronic L 61 column.

TABLE II

RETARDATION FACTORS ON A 25 m × 0.31 mm I.D. CARBOWAX 400 COLUMN

Soaking solvent	*Solute injected*			
	n-Undecane	*Chlorobenzene*	*n-Butanol*	*n-Propanol*
n-Hexane	1.4	1.1	1.0	1.0
Dichloromethane	>30	12	4.6	3.5
Acetone	7	2.4	2.7	2.6
Methanol	5.3 (?)	2.7	10	12

TABLE III

RETARDATION FACTORS ON A 20 m × 0.30 mm I.D. PLURONIC L 61 COLUMN

Soaking solvent	*Solute injected*					
	n-Nonane	*n-Decane*	*Ethyl-benzene*	*Chloro-benzene*	*Dioxane*	*Isobutanol*
n-Hexane	2.4	2.6	1.6	1.4	1.35	1.25
Dichloromethane	7		5	3.45	9.1	2.5
Acetone	2.1		2.4			2.7
Methanol	1.1	1.15		1.5		
Water	1.0		1.07			

Table IV shows that the film thickness of the stationary phase does not have an important influence on retardation factors. A column coated with a 0.07 μm film of SE-52 was compared with one coated with 25 times more of the same type of stationary phase (OV-73). Alkanes were used as solutes to avoid polarity changes when adjusting the volatility of the solutes to the retention power of the two columns. This result suggests that in the thick-filmed column about 25 times as much solvent is accumulated in the (accordingly shortened) soaked zone than in the thin-filmed column. It also means that the amount of solvent retained is determined by the saturation of the stationary (not of the mobile) phase (phase soaking as an overload phenomenon of the liquid phase according to Yabumoto *et al.*[18]).

The results in Table V indicate that retardation factors are weakly dependent on the volatility of the solvent. On the one hand, a solvent with an increased boiling point is expected to be more retained by the stationary phase than a volatile one. On the other hand, saturation of the carrier gas occurs at a lower partial vapour pressure, which causes more dilute vapours to enter the coated column. The two (not really independent) factors appear nearly to balance each other.

Reconcentration effects

Phase soaking (and retardation factors) are of interest in relation to a number of phenomena. We concentrated on the reconcentration of partially solvent trapped bands, because such bands are often very broad and their width at the beginning of the chromatographic process is relatively easy to determine.

Is there a direct correlation between the reconcentration effect of phase soaking

TABLE IV

DEPENDENCE OF RETARDATION FACTORS ON THE FILM THICKNESS OF THE STATIONARY PHASE

Soaking solvent	*0.07 μm SE-52, n-decane*	*1.75 μm OV-73, n-octane*
n-Hexane	3.5	4.8
Dichloromethane	2.5	2.4
Acetone	1.4	1.4

TABLE V

DEPENDENCE OF RETARDATION FACTORS ON THE VOLATILITY OF THE SOLVENT

Column	*Solvent*	*Solute*		
		n-Nonane	*n-Hexyl nitrile*	*Ethylbenzene*
OV-1	*n*-Pentane	2.4	1.6	
	n-Hexane	3.1	1.8	
	n-Heptane	4.3	2.3	
Pluronic L 61	*n*-Hexane	2.4		1.6
	n-Heptane	3.1		1.85

and the retardation factor, and what is the minimum retardation factor required to achieve full reconcentration? From the experiment described in ref. 3 we know that a retardation factor of 3.5 gave a reconcentration effect that reduced a band of width 2 min to less than 1 sec.

In order to determine reconcentration effects by phase soaking, the band width of partially trapped solute at the end of the pre-column was divided by the residual

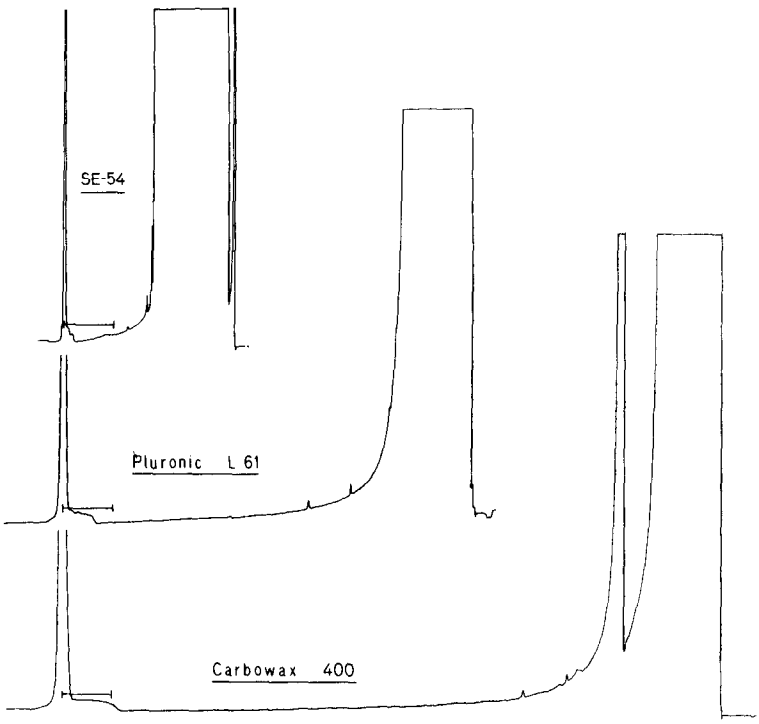

Fig. 2. Phase soaking effects by *n*-hexane on partially trapped chlorobenzene. Sample volume 4 μl, on-column injection, giving an evaporation time of the solvent in the column inlet of 130 sec (marked on the chromatograms on the peaks of chlorobenzene). There is an increasing reconcentration effect on chlorobenzene from the very polar Carbowax 400 to the apolar SE-54 which correlates with the increasing retardation factor.

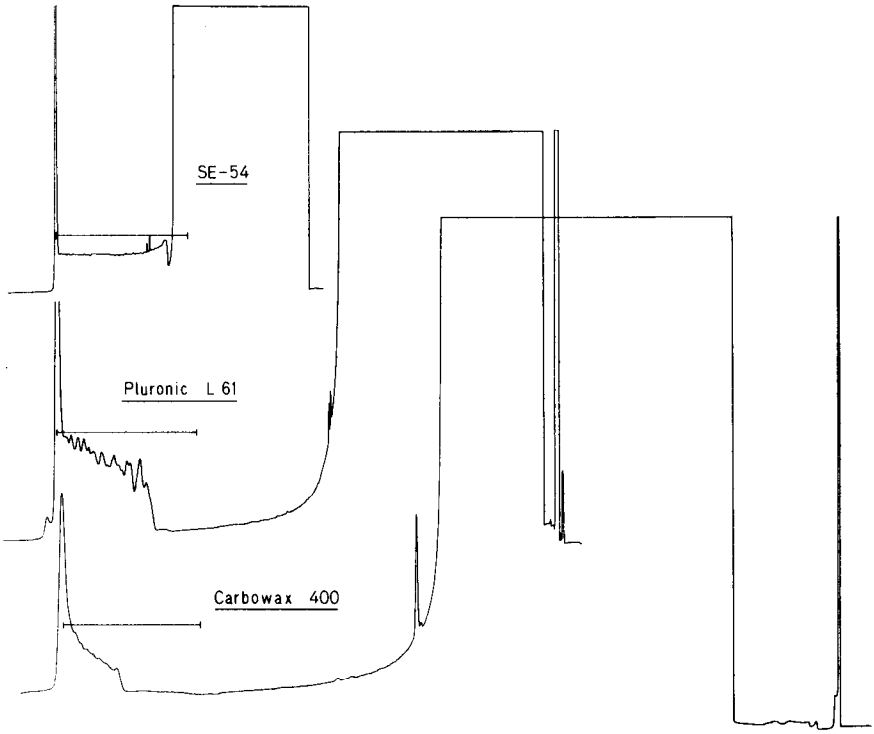

Fig. 3. Phase soaking effect by methanol, reconcentrating the chlorobenzene band. Sample volume 2.2 μl, on-column injection, giving an evaporation time of 6 min (indicated on the peaks of chlorobenzene). The solute started to elute from the methanol layer 55 sec after the injection, producing an initial band width of 305 sec. The polar solvent gives no significant reconcentration on the apolar phase and increasing effect on the more polar stationary phase.

band width observed for the eluted peak. The band widths of the partially trapped components are often close to the evaporation time of the solvent in the column inlet, which was measured by the use of a "milky" pre-column[2]. There remains the possibility that a solute leaves the solvent layer only some time after the injection. This was tested by disconnecting and purging the pre-column at various times to check which material had already been transferred at that time[2,3]. The residual band width due to the partial solvent trapping on the eluted peak was calculated by subtracting the peak width due to normal chromatography from the base width of the peak observed.

The (uncoated) pre-column (length 1 m) remained the same for all experiments, *i.e.*, it was coupled to the various columns used. The carrier gas flow-rates were adjusted to give the same evaporation time for the solvents (an accurate method of reproducing flow-rates). Accordingly, it was assumed that the first solvent effect, the solvent trapping, was the same for all determinations and that variations of the residual band widths were caused by phase soaking.

Figs. 2 and 3 show the peaks of chlorobenzene partially trapped in *n*-hexane (Fig. 2) and methanol (Fig. 3). The evaporation time of *n*-hexane (4 μl injected on-column at 27°C) was 130 sec, and the first chlorobenzene left the solvent layer

about 10 sec after the injection. This initial band width of 2 min was hardly altered after a passage through the Carbowax 400 column (Fig. 2). The retardation factor of this configuration was 1.1 (Table II). On the Pluronic L 61 column a noticeable, although not strong, reconcentration was observed (retardation factor 1.4), whereas on the SE-54 column the reconcentration was nearly complete (retardation factor 2.0, determined for 2-chlorotoluene).

The results shown in Fig. 2 were reversed if methanol was used as the solvent (Fig. 3). A 2.2-μl volume of the methanol solution was injected on-column under the same conditions as for Fig. 2. The evaporation time of methanol was 6 min; chlorobenzene started to elute from the solvent layer into the analytical part of the column 55 sec after the injection. On the SE-54 column the chlorobenzene peak showed no significant reconcentration, whereas on Carbowax 400 the residual band width was about one third of the initial band width.

Table VI shows a comparison of reconcentration factors obtained by phase soaking with retardation factors, including the results in Figs. 2 and 3. There appears to be a reasonable correlation with the exception of the pair chlorobenzene-methanol on Carbowax 400, where some reversed-phase effects might have contributed (by a smaller extent than for the alkanes). A retardation factor of 2 produced a considerable reconcentration effect. The minimum retardation factor for creating full reconcentration might be closer to 2 than to the 3.5 known to be sufficient from ref. 3.

CONCLUSION

Figs. 2 and 3 and Table VI show that the choice of the stationary phase and the solvent may strongly influence the peak shape of partially trapped sample components. However, it should be borne in mind that first of all the solvent should be selected so as to create full solvent trapping. With chlorobenzene this should generally be easy because all solvents of intermediate polarity fully retain it. Hence the optimization of phase soaking will be of practical value only if there is no solvent giving full trapping or if sample preparation restricts the choice to one giving rise to partial solvent trapping, and there are still many of these cases.

TABLE VI

COMPARISON OF SOME RECONCENTRATION FACTORS OBTAINED BY PHASE SOAKING WITH THE RETARDATION FACTORS FROM TABLES I–III

Stationary phase	*Solvent*	*Solute*	*Reconcentration factor*	*Retardation factor*
SE-54	*n*-Hexane	Chlorobenzene	5.9	2
	Methanol	Chlorobenzene	1.2	1.2
	Methanol	*n*-Nonane	1	1.1
Pluronic L 61	*n*-Heptane	Toluene	2	1.85
	n-Hexane	Chlorobenzene	1.8	1.4
	Acetone	*n*-Nonane	3	2
	Methanol	Chlorobenzene	1.6	1.6
		n-Decane	1.1	1.1
Carbowax 400	*n*-Hexane	Chlorobenzene	1	1.1
	Methanol	Chlorobenzene	3	2.7

Our data suggest the following rules: if strong phase soaking should be obtained, a solvent should be selected that is not only well retained by the stationary phase but also serves as a good mediator to dissolve the components in the stationary phase (*e.g.*, dichloromethane). The choice of the stationary phase that is similar in polarity to the solvent may be useful. However, the resolution of volatile components from the solvent often requires opposite solutions.

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