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COADSORPTION EFFECTS IN LIQUID–SOLID SYSTEMS OF THE TYPE SILICA–HEPTANE + DIOXANE

II. CORRELATION OF RETENTION PARAMETERS OF AROMATIC COMPOUNDS IN DIOXANE AND TETRAHYDROFURAN SYSTEMS

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SUMMARY

Relationships between capacity factors, k', and the concentration of modifier [dioxane (diox) or tetrahydrofuran (THF) in heptane solutions] were determined; for polar aromatic compounds, log k' values were correlated for the two eluents at constant modifier concentrations. Different correlation lines (log k'_{diox} vs. log k'_{THF}) were obtained for various classes of compounds; as a rule, solutes having proton donor groups (–OH, =NH) were relatively more strongly retained in dioxane systems, which is interpreted in terms of an aditional adsorption on the monolayer of dioxane molecules on the adsorbent surface. The individual retention behaviour in dioxane systems can be utilized for the variation of selectivity, *e.g.*, by the use of mixed modifiers (dioxane + tetrahydrofuran).

INTRODUCTION

The optimization of liquid–solid chromatographic (LSC) systems is usually carried out in two stages. In the first stage the eluent strength is optimized by the choice of a suitable solvent from the eluotropic series, usually diluted to a suitable concentration in a less polar solvent. If the selectivity of the eluent is not satisfactory, another polar modifier is chosen on the basis of the equieluotropic series[1,2]. An advanced method, introduced by Bakalyar *et al.*[3] consists in the use of mixed modifiers, thus fine-tuning the selectivity of the system. The method was primarily used for reversed-phase systems of the type octadecyl silica–water + methanol + tetrahydrofuran. Further developments of the optimization technique for ternary and quaternary eluents have been reported[4,5].

In the optimization of selectivity it is essential to choose modifiers having marked differences in retention behaviour[3–6]. In a recent paper[7] we demonstrated that, for normal-phase systems, dioxane as modifier shows (in comparison to isopropanol) distinct differences in the sequence of zones for aromatic solutes with two to four polar groups; separate log k'_{diox} vs. log k'_{iPrOH} correlation lines were obtained

for various groups of compounds, depending first of all on the presence of proton-donor groups (OH, NH_2). These differences were interpreted as result of a dual adsorption mechanism for proton-donor solutes: competitive adsorption on the silica surface and non-competitive adsorption on the monolayer of dioxane molecules, due to the electron-donor character of the latter caused by exposed ether oxygen atoms. A mechanistic model of the adsorption equilibrium was presented in the preceding paper[8].

In the present study the properties of dioxane (diox) are compared to those of its close analogue tetrahydrofuran (THF), and the number of solutes is greatly extended, including monofunctional compounds whose adsorption behaviour should be simpler to interpret.

EXPERIMENTAL

Reagent-grade *n*-heptane, tetrahydrofuran and dioxane were used. The solvents were dried using wide-pore silica.

The capacity factors of the solutes were determined for various concentrations of the modifiers in *n*-heptane as a diluent. The chromatographic experiments were carried out at 20 ± 0.5°C using a Perkin-Elmer liquid chromatograph Model 1210 with dual syringe pumps, an UV detector set at 254 nm and a flow-rate of 0.85 ml/min. Samples (5 μl) containing single solutes were injected. The column (125 mm × 4 mm I.D., *ca.* 3000 theoretical plates) was packed with 10-μm LiChrosorb Si 60 (E. Merck, Darmstadt, F.R.G.); its void volume was determined by injection of pure heptane. The reproducibility was monitored by determination of the retention times of 2- and 4-nitroaniline.

The experimental results are represented as plots of log k', against log X_S, the mole fraction of the modifier, dioxane or tetrahydrofuran. Typical plots are illustrated in Fig. 1; they are usually slightly curved which is characteristic for displacement equilibria increasingly affected by solvation (and coadsorption, *cf.*, ref. 8, Fig. 2 and ref. 9, Fig. 1). The capacity factors were determined from the plots of constant modifier concentrations. This procedure is more reliable and accurate than measurements at a constant X_S value owing to the narrow range of k' values determinable with a satisfactory accuracy.

RESULTS AND DISCUSSION

Examples of log k'_{diox} *vs.* log k'_{THF} plots are given in Fig. 2 (solutes having a single polar group) and in Fig. 3 (di- and trifunctional solutes). The solutes were subclassified according to their chemical type or presence of electron-donor (B) or donor-acceptor (AB) groups, and this classification is taken into account in the symbols used in Figs. 2, 3.

Correlation lines were drawn by the least squares method choosing points lying near to a given line. For monofunctional solutes two distinct families of points were obtained (Fig. 2); the correlation lines can be expressed by the following equations:

Quinolines, anilines (lower line)
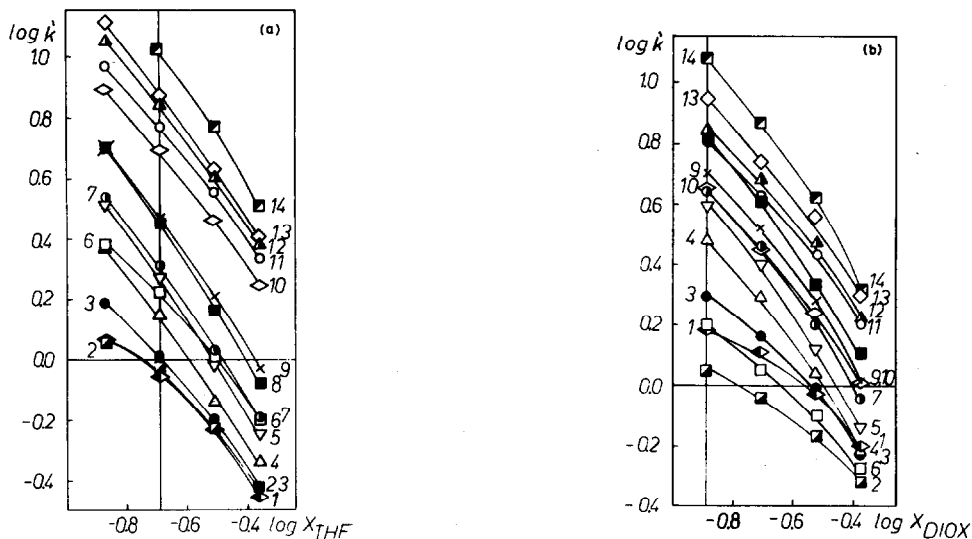log k'_{diox} = 1.047 log k'_{THF} − 0.036; r = 0.978

Fig. 1. Plots of log k' vs. log x_S for monofunctional aromatic solutes. Modifiers, S: (a) tetrahydrofuran; (b) dioxane. 1 = 4-Nitrobiphenyl; 2 = 4-nitrotoluene; 3 = diphenylamine; 4 = 2,3-dimethylphenol; 5 = 3,4-dimethylphenol; 6 = 8-methylquinoline; 7 = phenol; 8 = 2-naphthol; 9 = indole; 10 = 2,5-dimethylaniline; 11 = 6-methylquinoline; 12 = aniline; 13 = 5,6-benzoquinoline; 14 = 2-naphthylamine.

Phenols, secondary amines (upper line)

$$\log k'_{diox} = 0.853 \log k'_{THF} + 0.292; \quad r = 0.981$$

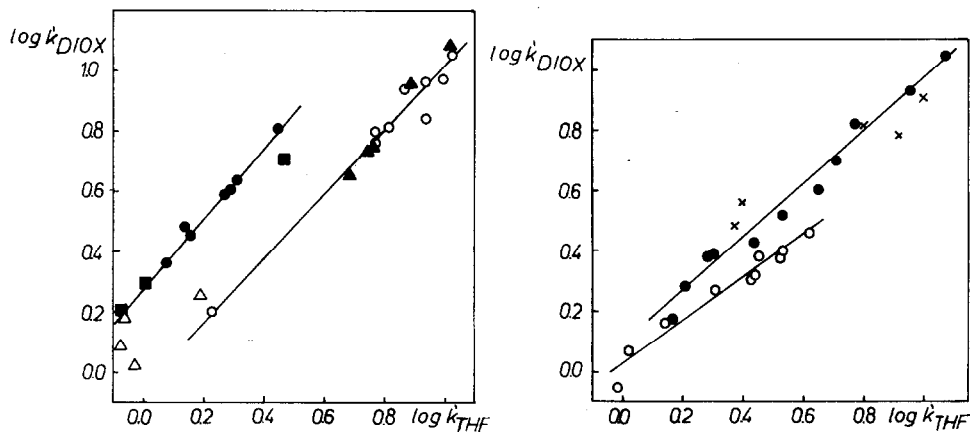The points for weakly retained nitro compounds and benzophenone (empty triangles) are dispersed between the two lines.

Fig. 2. Correlation between log k' values for dioxane systems (8%, v/v) and log k' values for tetrahydrofuran systems (12.5%, v/v) solutes: O, quinolines; ●, phenols; ▲, anilines; ■, those with = NH group; △, aromatic nitrocompounds and benzophenone.

Fig. 3. Plots as in Fig. 2 for di- and trifunctional solutes of classes B + B (O), B + AB and B + B + AB (●) and AB + AB (×). Concentrations of modifiers in the eluent: 30%, v/v.

The upper line is higher by about 0.3 log k' units which means that the corresponding k' values are about double (separation factor $\alpha = 2$) those corresponding to the lower line at the same abscissa. This difference is quite significant.

It is not clear why anilines (class AB) lie on the same corelation line as quinolines (class B). This behaviour may be explained by the fact that anilines, as bases having a small primary amino group, are strongly adsorbed by the displacement mechanism (*cf.*, the upper theoretical line in ref. 8, Fig. 2 where the three lines merge in the case of strong adsorption). Secondary amines are much less strongly adsorbed in the first adsorption layer because they need more space among the adsorbed modifier molecules; on the other hand, adsorption in the second layer (on the monolayer of dioxane molecules) is non-competitive and the steric effect of the second non-polar substituent is less pronounced, so that the behaviour of secondary amines is similar to that of phenols.

The differences are less pronounced for bi- and trifunctional solutes (Fig. 3), however the points for compounds having proton donor (AB) groups are distinctly shifted in the direction of higher k' values in dioxane systems. The regression equa-
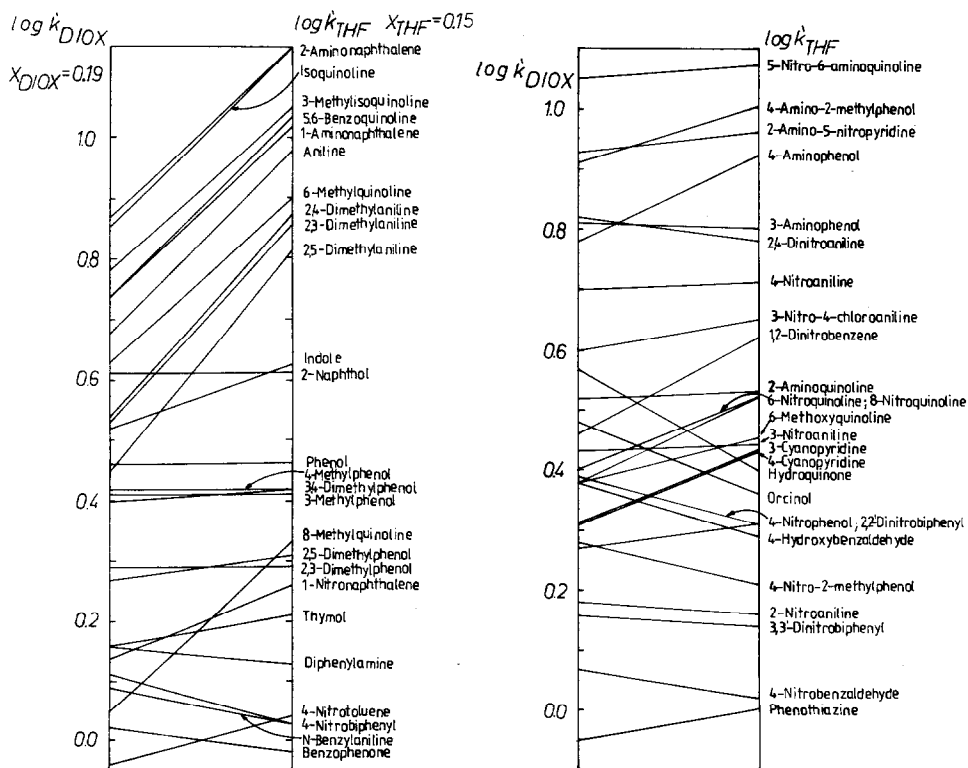
Fig. 4. Graphical comparisons of log k' values for the dioxane system ($x_{\text{diox}} = 0.19$) and for the tetrahydrofuran system ($x_{\text{THF}} = 0.15$). The eluent compositions are chosen so that identical k' values are obtained for the reference solute, phenol.

Fig. 5. Graphical comparison of log k' values for di- and trifunctional solutes in 30% (v/v) dioxane and 30% (v/v) tetrahydrofuran.

tions are as follows: solutes of class B + B (two electron-donor groups), log k'_{diox} = 0.708 log k'_{THF} + 0.024, r = 0.976; class B + AB and B + B + AB, log k'_{diox} = 0.883 log k'_{THF} + 0.074, r = 0.988; class AB + AB, log k'_{diox} = 0.585 log k'_{THF} + 0.298, r = 0.968.

As in the case of monofunctional solutes (Fig. 2) there is some spread of points within each class, which is advantageous from the viewpoint of differences in selectivity between the two modifiers.

For all compounds with AB groups (classes B + AB, B + B + AB and AB + AB) the correlation coefficient is still high

$$\log k'_{diox} = 0.813 \log k'_{THF} + 0.121; \ r = 0.973$$

and the correlation line is significantly higher than that of solutes of class B + B. On the other hand, the correlation is distinctly less significant for all points in Fig. 3:

$$\log k'_{diox} = 0.887 \log k'_{THF} + 0.033; \ r = 0.956$$

Another method of comparison of the two systems is to plot the log k' values for constant concentrations of dioxane and THF on parallel ordinates and to connect the points for individual compounds with straight lines (Fig. 4 for monofunctional solutes and Fig. 5 for more complex compounds). The group behaviour is reflected here by parallel lines. The different slopes of the straight lines show marked changes in selectivities, with frequent changes in the sequence of the zones.

The changes in selectivity and sequence are additionally illustrated in Fig. 6 by actual chromatograms for an artificial ten-component mixture of aromatic compounds.
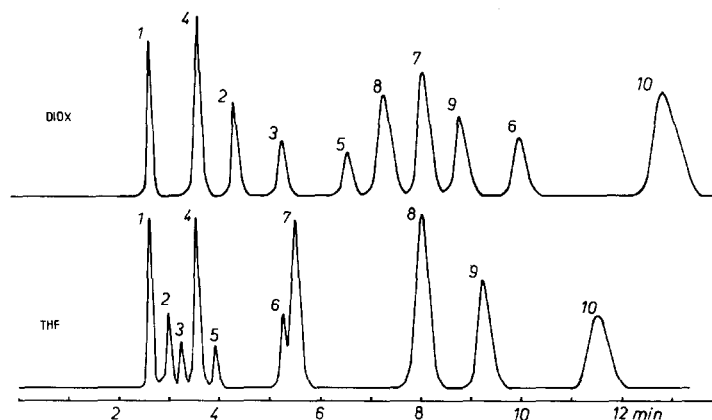

Fig. 6. Comparison of chromatograms of a ten-component mixture, obtained with 8% (v/v) dioxane and 12.5% (v/v) tetrahydrofuran (heptane as diluent). Solutes: 1 = 4-nitrotoluene; 2 = thymol; 3 = 2,3-dimethylphenol; 4 = 1-nitronaphthalene; 5 = 3,4-dimethylphenol; 6 = 2-naphthol; 7 = indole; 8 = 2,5-dimethylaniline; 9 = 2,4-dimethylaniline; 10 = 5,6-benzoquinoline.

CONCLUSIONS

Pairs of modifiers like tetrahydrofuran and dioxane are very interesting from the viewpoint of selectivity control. The different selectivities and sequences are due to the varying contributions from at least three molecular mechanisms. For solutes of class B (electron donors) the simple displacement mechanism predominates (k'_d, cf., discussion in ref. 8). For proton-donor solutes (class AB), displacement and competitive solvation mechanisms are observed for THF systems and an additional coadsorption mechanism for dioxane systems. The differences in behaviour between solutes of class B and class AB are not clear cut because the net effect depends on the relative values of K, K_{ZS} and K_{ASZ}, i.e., the equilibrium constants for displacement, solvation and coadsorption[8], which in turn depend on steric effects, electronic and mesomeric effects in the solute and modifier molecules in the bulk and adsorbed phases, delocalization of solute and solvent molecules on the surface, etc. All these effects are difficult to interpret so that their quantitative prediction is impossible.

However, the practical value for analytical chromatography is apparent from the experimental data. The correlations can also serve as a source of information on the molecular structure type, although for polyfunctional compounds the differences are somewhat less distinct.

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