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

### III. COMPARISON OF DIOXANE WITH ETHYL ACETATE OR 2-PROPANOL AS MODIFIERS

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#### SUMMARY

The retention behaviour of several compound types (quinolines, nitroarenes, primary and secondary amines and phenols) was compared with dioxane (DX), ethyl acetate (EtOAc) and 2-propanol (iPrOH) as modifiers. As with tetrahydrofuran (THF), proton donor solutes were relatively more strongly retained by DX than by EtOAc, which can be explained by their additional adsorption on the adsorbed DX molecules. For iPrOH as modifier, some dispersion of points in the  $\log k'_{DX}$  vs.  $\log k'_{iPrOH}$  correlation diagrams was observed: the points for phenols and anilines were grouped along individual correlation lines, but the points for the remaining solutes were dispersed. This can be explained by specific solvation effects of the associated alcohol molecules and by differences in solute/modifier competitive adsorption equilibria. For mixed modifiers (DX + THF), linear  $k'$  vs.  $X_{DX}$  plots were obtained, which can be utilized for “fine tuning” of selectivity.

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#### INTRODUCTION

In preceding papers<sup>1,2</sup>, the retentions of several groups of polar aromatic compounds in systems of the type silica–heptane + dioxane (DX) were compared with the retentions in analogous systems containing monofunctional tetrahydrofuran (THF) as the modifier. Marked differences in selectivities were observed for the two system types. For electron-donor solutes (class B, according to the classification proposed by Pimentel and McClellan<sup>3</sup>), the predominant adsorption mechanism is competition for silanol groups between solute and modifier molecules; for proton-donor solutes (class AB), additional solvation effects contribute to the adsorption equilibrium for THF systems, and a third retention mechanism, coadsorption on the adsorbed modifier molecules, for DX. Differences in the molecular structure of the solutes result in variation in the three effects with corresponding differences in selectivity.

In this study, the investigations have been extended to two other modifiers,

TABLE I  
SOLUTES INVESTIGATED

No.	Solute	No.	Solute
1	1-Nitronaphthalene	24	2,3-Dimethylphenol
2	4-Nitrotoluene	25	2,5-Dimethylphenol
3	4-Nitrobiphenyl	26	3,4-Dimethylphenol
4	Benzophenone	27	Thymol
		28	2-Naphthol
11	Quinoline		
12	6-Methylquinoline	31	Aniline
13	7-Methylquinoline	32	4-Methylaniline
14	8-Methylquinoline	33	2,3-Dimethylaniline
15	2,6-Dimethylquinoline	34	2,4-Dimethylaniline
16	Isoquinoline	35	2,5-Dimethylaniline
17	3-Methylisoquinoline	36	1-Aminonaphthalene
18	5,6-Benzoquinoline	37	2-Aminonaphthalene
21	Phenol	41	N-Benzylamine
22	3-Methylphenol	42	Diphenylamine
23	4-Methylphenol	43	Indole

ethyl acetate (EtOAc) and 2-propanol (iPrOH) (the latter was investigated with a small group of compounds having two or three functional groups<sup>4</sup>).

#### EXPERIMENTAL

The capacity factors ( $k'$ ) of the solutes (for solutes investigated, see Table I) were determined for several concentrations of the modifiers in the eluent, and the results were plotted as  $\log k'$  vs.  $\log X_S$  ( $X_S$  = molar fraction of modifier). A Per-

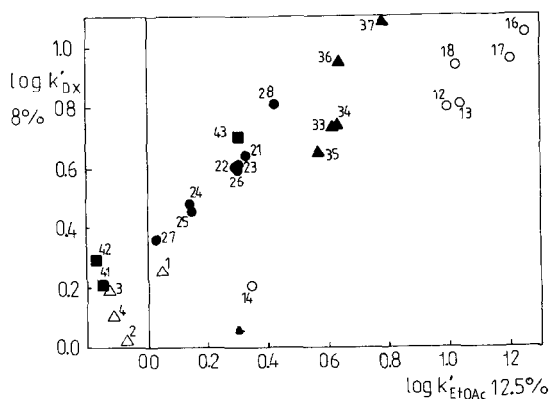


Fig. 1. Correlation between  $\log k'$  values for dioxane systems (8%, ordinate) and  $\log k'$  values for ethyl acetate systems (12.5%, abscissa) (all concentrations are in vol.-%). ○ = Quinolines; ● = phenols; ▲ = primary aromatic amines; ■ = secondary amines; △ = aromatic nitrocompounds. For notation of solutes, see Table I. Diluent: heptane.

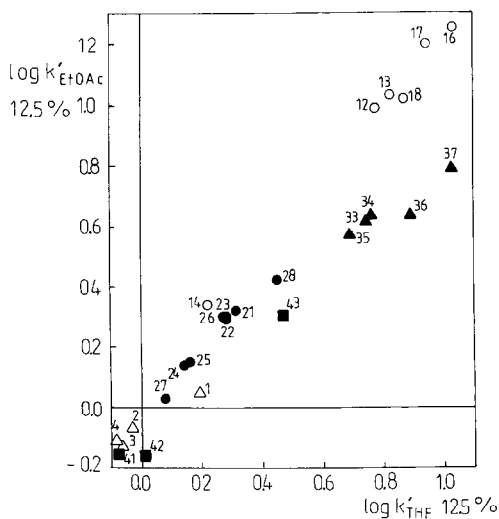


Fig. 2. As Fig. 1, correlation for ethyl acetate (12.5%) and THF (12.5%) as modifiers.

kin-Elmer Model 1210 liquid chromatograph with dual syringe pumps and a UV detector (254 nm) was used (Perkin-Elmer, Norwalk, CT, U.S.A.); the column (125  $\times$  4 mm I.D.) was packed with 10- $\mu$ m LiChrosorb Si 60 (E. Merck, Darmstadt, F.R.G.). The void volume was determined by injection of *n*-heptane. For further details, see ref. 2.

## RESULTS AND DISCUSSION

The  $\log k'_{DX}$  values determined for DX systems in the preceding study<sup>2</sup> are

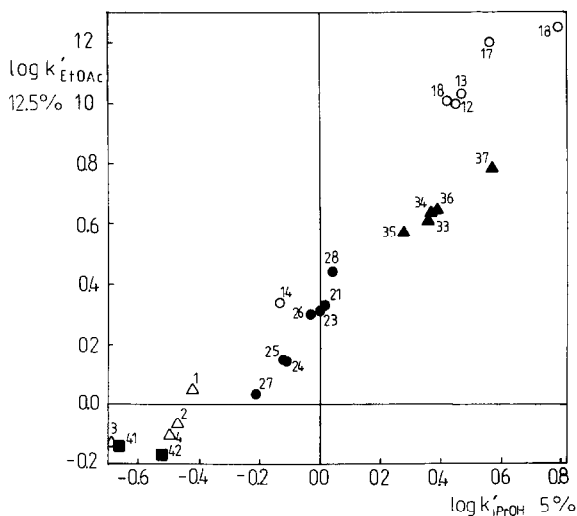
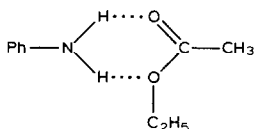


Fig. 3. As Fig. 1, correlation for ethyl acetate (12.5%) and 2-propanol (5%) as modifiers.

compared, in the form of correlation plots, with  $\log k'_{\text{EtOAc}}$  values determined for EtOAc systems (Fig. 1). As in correlations with THF systems (ref. 2, Figs. 2 and 3), the points for proton-donor solutes (class AB, closed circles) are above the correlation line of electron-donor solutes (quinolines and nitro compounds, open circles). This indicates relatively stronger retention of class AB solutes, consistent with the concept of their coadsorption on the monolayer of DX molecules. The points for class B solutes are dispersed; among the aromatic amines (closed triangles), the points for naphthylamines are closer to the correlation line of class AB solutes and shifted upwards relative to methylanilines.

In Figs. 2 and 3 the retention behaviour of the five groups of solutes is compared for pairs of monofunctional modifiers, EtOAc-THF (Fig. 2) and EtOAc-iPrOH (Fig. 3). It can be seen that the points for four groups of solutes (nitrocompounds, quinolines, secondary amines and phenols) are grouped about a single correlation line of slope approximately unity. On the other hand, anilines are less strongly adsorbed from EtOAc systems. The weaker adsorption of anilines can be explained by the formation of more stable cyclic solvates:



The anilines are solvated by both EtOAc and iPrOH; the autoassociation of the alcohol in the heptane medium only slightly decreases its solvation strength relative to class AB solutes, which can be included in the association chain<sup>5,6</sup>.

The  $\log k'$  values obtained for constant concentrations of DX (20%) and iPrOH (5%) are compared in Fig. 4 (*cf.*, Figs. 4 and 5 in ref. 2 for DX-THF). Solute with similar molecular structures tend to give parallel lines. However, even with isomers, some individual differences frequently occur.

The same data are represented in Fig. 5 as the  $\log k'_{\text{DX}}$  vs.  $\log k'_{\text{iPrOH}}$  correlation plot. It can be seen that quinolines and nitro compounds form dispersed clusters of points, whereas phenols and anilines form well defined individual correlation lines; the points of naphthylamines lie above those of the anilines, approximately parallel, which is equivalent to relatively weaker adsorption in iPrOH systems, probably for steric reasons.

Presumably owing to the dispersion of points of class B solutes, there is no distinct difference in Fig. 5 between solutes of classes B and AB (in contrast to Fig. 1 for EtOAc systems), which apparently form a single correlation line with a marked spread of the points, except for phenols and anilines, for which separate correlation lines can be drawn. Within these groups, the gain in selectivity on replacement of DX by iPrOH is limited or non-existent. However, for compounds belonging to various groups or having certain structural differences (*e.g.*, *ortho* isomers or for pairs of the type alkyylaniline-naphthylamine) the differences are greater.

The experiments with iPrOH systems show that the specific properties of DX as a modifier are exhibited distinctly only relative to certain modifiers, *e.g.*, THF or EtOAc. For monofunctional solutes (Fig. 5), only a limited spread of points was observed for the pair of modifiers DX-iPrOH. However, for the same pair, bi- and

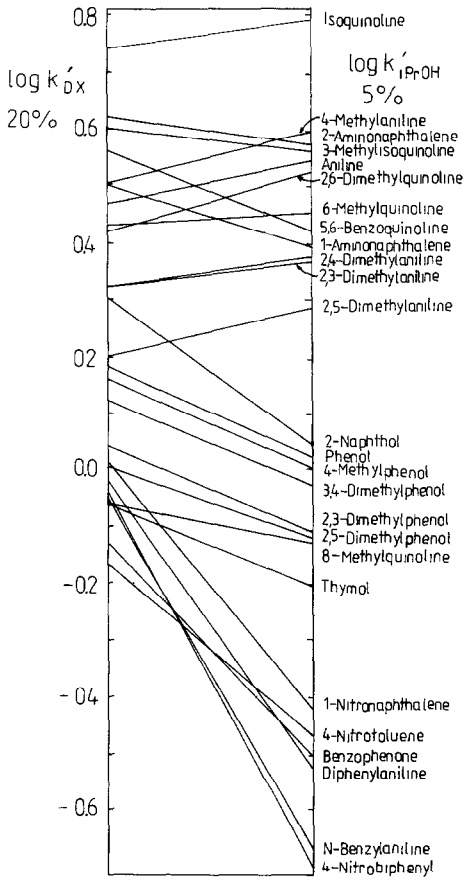


Fig. 4. Graphical comparison of  $\log k'$  values for dioxane (20%) and 2-propanol (5%).

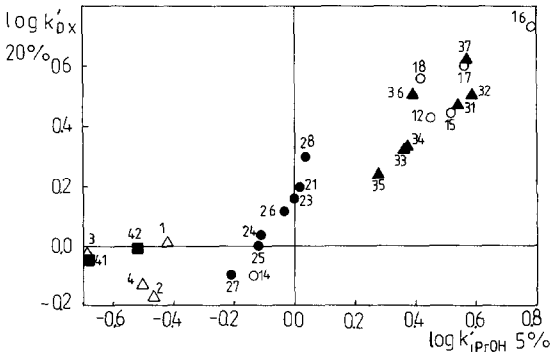


Fig. 5. As Fig. 1, correlation for dioxane (20%) and 2-propanol (5%).

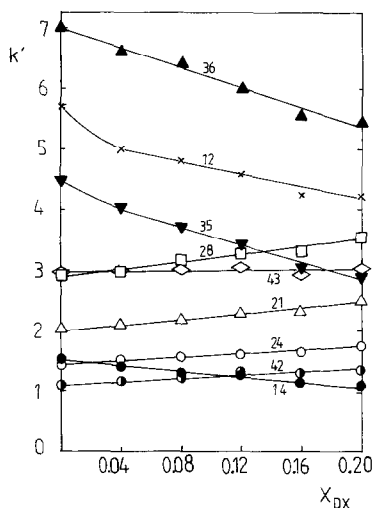


Fig. 6.  $k'$  values of several solutes plotted as a function of dioxane concentration in the ternary eluent ( $X_{DX} + X_{THF} = 0.2$ ;  $X_{heptane} = 0.8$ ).

trifunctional solutes show a more distinct dispersion of points and coadsorption effects<sup>4</sup>.

Intermediate selectivities can be obtained by the use of mixed modifiers. In Fig. 6, the  $k'$  values of nine solutes are plotted against the molar fraction of DX. The ordinate on the left corresponds to  $X_{THF} = 0.2$  and that on the right to  $X_{DX} = 0.2$ , the molar fraction of heptane being equal to 0.8 in all instances (*i.e.*,  $X_{DX} + X_{THF} = 0.2$ ). The  $k'$  values vary approximately linearly with the concentration of DX in the binary modifier, so that plots like Fig. 4 (and Figs. 4 and 5 in ref. 2) but with  $k'$  (and not  $\log k'$ ) values on the ordinate can be used for the "fine tuning" of selectivity by the use of mixed modifiers and the window diagram method.

The experimental results and conclusions are in agreement with the principles of the classification of solvent selectivity discussed by Snyder and Kirkland<sup>7</sup>.

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