Comparison of adsorption properties of Florisil and silica in high-performance liquid chromatography

I. Retention behaviour of monofunctional model solutes

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ABSTRACT

Earlier investigations demonstrated some special properties of Florisil and a greater selectivity than silica for the adsorption of some pairs of organic compounds. Differences in selectivity of the two adsorbents may be characterized by graphical correlations of retention parameters for these adsorbents. Consideration of relationship between $\log k'_{\text{Florisil}}$ and $\log k'_{\text{silica}}$ allows the interpretation of some factors that influence the adsorptive behaviour of organic compounds. The retention behaviour of several monofunctional aromatic compounds (quinoline bases, nitroarenes, primary and secondary aromatic amines and phenols) was therefore investigated by high-performance liquid chromatography in chromatographic systems using Florisil and silica and binary mobile phases consisting of heptane and a polar modifier (isopropanol, 1,4-dioxane or tetrahydrofuran).

INTRODUCTION

Florisil (magnesium silicate), produced mainly for thin-layer chromatography (TLC) or for classic column chromatography is frequently used in practical separations because of its special selectivity [1,2]. However only a single theoretical study of its properties has been published [3,4].

Soczewiński and co-workers [5–7] found that the molecular model of adsorption elaborated for silica can also be used for describing the adsorption behaviour of organic compounds on Florisil. Some information on the mechanism of adsorption from solution in polar solvents can be obtained from relationships between R_m ($\log k'$) and log (eluent composition).

Systematic studies of these relationships have been performed earlier for a number of model compounds belonging to different chemical groups [8,9] using TLC in sandwich tanks and Florisil as an adsorbent. These experiments indicated that steric and mesomeric effects have a significant influence on the chromatographic parameters of organic solutes. Although TLC in sandwich tanks operated in a quasi-column manner (continuous development, samples spotted behind the solvent front) [10] made it possible to obtain results close to those obtained in column chromatography [11], they were less accurate. Therefore, it was of interest to verify those observations using high-performance liquid chromatography (HPLC).

In this work, the retention behaviour of several monofunctional aromatic compounds (quinoline bases, primary and secondary aromatic amines, phenols) was investigated by HPLC in chromatographic systems using Florisil and binary mobile phases consisting of heptane and a polar modifier (tetrahydrofuran, 1,4-dioxane or isopropanol). These chromatographic data were compared with earlier results obtained for silica by HPLC [12,13].

EXPERIMENTAL

The chromatographic experiments for Florisil were performed at $19 \pm 1°C$ using a Type 302 liquid chromatograph (Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland) equipped with syringe pump and a UV detector (254 nm) at a flow-rate of 1.2 ml/min. Single solutes were injected in the eluent with the help of a 5-μl injection valve.

HPLC-grade 10-μm Florisil was prepared in the Institute of Inorganic Chemistry (Gliwice, Poland). Florisil (Fluka, Buchs, Switzerland) for TLC was milled in a Model 100 AFG counterflow-fluid mill produced by Alpine (Augsburg, Germany). Particle segregation of ground Florisil was made in several stages in a Model 100 MZR pneumatic separator (Alpine). Characteristics of this separator were obtained by a CILAS 715E laser granulometer (Alcatel, France). Separated material was analysed in a Model A 200 LS pneumatic apparatus (Alpine). The porosity parameters (determined using a Carlo Erba porosimeter) of the fraction used as a column packing were specific surface area (BET) 340 m^2/g and total porosity 46.2%.

The column (150 × 4 mm I.D.) was packed with 10-μm Florisil by the slurry method. It had an efficiency of about 3000 theoretical plates determined by the adsorption of diphenylamine or 1-nitronaphthalene using 2% tetrahydrofuran in n-heptane as the eluent. The void volume of the column was determined by injection of pure n-heptane. The experimental results represent the averages of three runs.

The chromatographic experiments with silica were performed using a Perkin-Elmer (Norwalk, CT, USA) Model 1210 liquid chromatograph with dual syringe pumps and a UV detector (254 nm). The column (125 × 4 mm I.D.) was packed with 10-μm LiChrosorb Si 60 (E. Merck, Darmstadt, Germany) with a declared surface area (BET) of 500 m^2 g. For further details see, refs. 12 and 13.

As mobile phases, n-heptane solutions of isopropanol (for HPLC, E. Merck), 1,4-dioxane (for HPLC, Romil Chemicals, Shepshed, UK) and tetrahydrofuran (for chromatography, redistilled, International Enzymes, Windsor, UK) were used.

RESULTS AND DISCUSSION

The experimental results for the solutes listed in Table I are illustrated graphically as plots of log k' (capacity factor) against log c (concentrations; %, v/v), where c is the concentration of the polar component of the solvent. Fig. 1 shows these relationships for monofunctional solutes (of class AB according to the Pimentel–McClellan classification [14]) in the system with Florisil and tetrahydrofuran–n-heptane as eluent. The plots obtained for Florisil are linear, in accordance with the Snyder–Soczewiński model of adsorption [15,16]. The slopes of the lines can be differentiated: for anilines the plots are slightly steeper than those for the phenols. This indicates stronger adsorption of aromatic amines than phenols on the acidic centres of the Florisil surface.

Fig. 2 shows correlation plots of log k' values obtained for monofunctional solutes adsorbed on Florisil against log k' values of these compounds

TABLE I

SOLUTES INVESTIGATED

| Solute	Abbreviation
Aniline	An
1-Aminonaphthalene	1AN
2-Aminonaphthalene	2AN
4-Methylaniline	4MAn
2,3-Dimethylaniline	23MAn
2,4-Dimethylaniline	24MAn
2,5-Dimethylaniline	25MAn
N-Benzylaniline	BylAn
Diphenylamine	diϕA
Phenol	P
3-Methylphenol	3MP
4-Methylphenol	4MP
2,3-Dimethylphenol	23MP
2,5-Dimethylphenol	25MP
Thymol	T
2-Napthol	2HN
Quinoline	Q
6-Methylquinoline	6MQ
7-Methylquinoline	7MQ
8-Methylquinoline	8MQ
3-Methylisoquinoline	3MiQ
5,6-Dimethylquinoline	26MQ
Benzophenone	Bf
1-Nitronaphthalene	1NtN
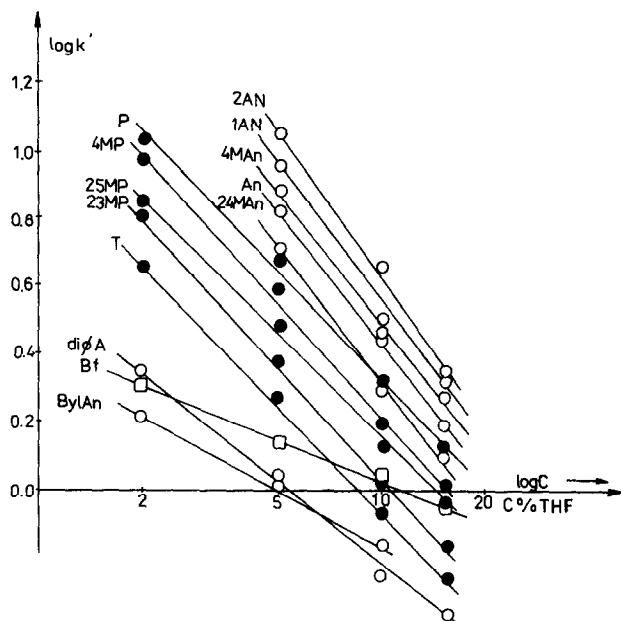
Fig. 1. Plots of log k' versus log (concentration of modifier in the mobile phase) (c, %, v/v) for monofunctional aromatic compounds. Active solid Florisil; mobile phase, tetrahydrofuran–n-heptane. For identification of solutes, see Table I.

adsorbed on silica in different eluent systems. These correlations illustrate the differences in adsorption on the Florisil and silica surfaces. In all three diagrams for three eluent systems, tetrahydrofuran–n-heptane, dioxane–n-heptane and isopropanol–n-heptane for phenols and for aniline derivatives (primary aromatic amines) respectively two correlation lines can be plotted. These lines can be expressed by the following equations:

(a) for tetrahydrofuran as a modifier:
for phenols (upper line):

$$\log k'_{Florisil} = 1.29 \log k'_{silica} + 0.05; \quad r = 0.89 \ (n = 8)$$

for anilines (lower line):

$$\log k'_{Florisil} = 0.82 \log k'_{silica} - 0.28; \quad r = 0.84 \ (n = 6)$$

(b) for dioxane as a modifier:

for phenols (upper line):

$$\log k'_{Florisil} = 1.98 \log k'_{silica} - 0.19; \quad r = 0.98 \ (n = 7)$$

for anilines (lower line):

$$\log k'_{Florisil} = 1.33 \log k'_{silica} - 0.37; \quad r = 0.97 \ (n = 7)$$

(c) for isopropanol as a modifier:
for phenols (upper line):

$$\log k'_{Florisil} = 1.62 \log k'_{silica} + 0.08; \quad r = 0.88 \ (n = 7)$$

for anilines (lower line):

$$\log k'_{Florisil} = 1.50 \log k'_{silica} - 0.37; \quad r = 0.94 \ (n = 7)$$

For combined phenols and anilines much lower correlation coefficients (r) would be obtained.

The points for secondary amines (diphenylamine, N-benzylamine), nitronaphthalene and benzophenone are dispersed near these two lines. For all compounds, especially in systems with tetrahydrofuran and isopropanol, the correlation coefficients are lower, which is due to differences in selectivity between the two adsorbents. The correlation coefficients for dioxane are high and the lines are close to each other. It seems that dioxane (class B) modifies the Florisil and silica surfaces by ether oxygen. This leads to adsorption of solutes by displacement and solvation of molecules [12,17]. The adsorbed molecules of dioxane on the Florisil or silica surface can interact with the second ether oxygen with the chromatographed solutes. This leads to co-adsorption of class AB solutes on the monolayer of dioxane, which causes the differences in the surface properties of Florisil and silica in this system to decrease and therefore the adsorption of solutes is similar.

It should be noticed that, for example, anilines are separated on Florisil using isopropanol (Fig. 2c) in the range of 0.5 log k' units and on silica only 0.3 log k' units, which means that the corresponding k' values are in the range of about 3.2 units on Florisil and 2 units on silica. A contrary effect can be observed for the same group of compounds using tetrahydrofuran as a modifier (Fig. 2a). In this instance the log k' values are in the range of about 0.25 units for Florisil and 0.35 units for silica and hence the separation of anilines on Florisil is worse. It seems that tetrahydrofuran binds to the Florisil surface, so that its specific polar properties decrease. Probably this results from the formation of a monolayer of tetrahydrofuran molecules. This film of adsorbed modifier molecules shields and deactivates particularly the surface of Florisil.
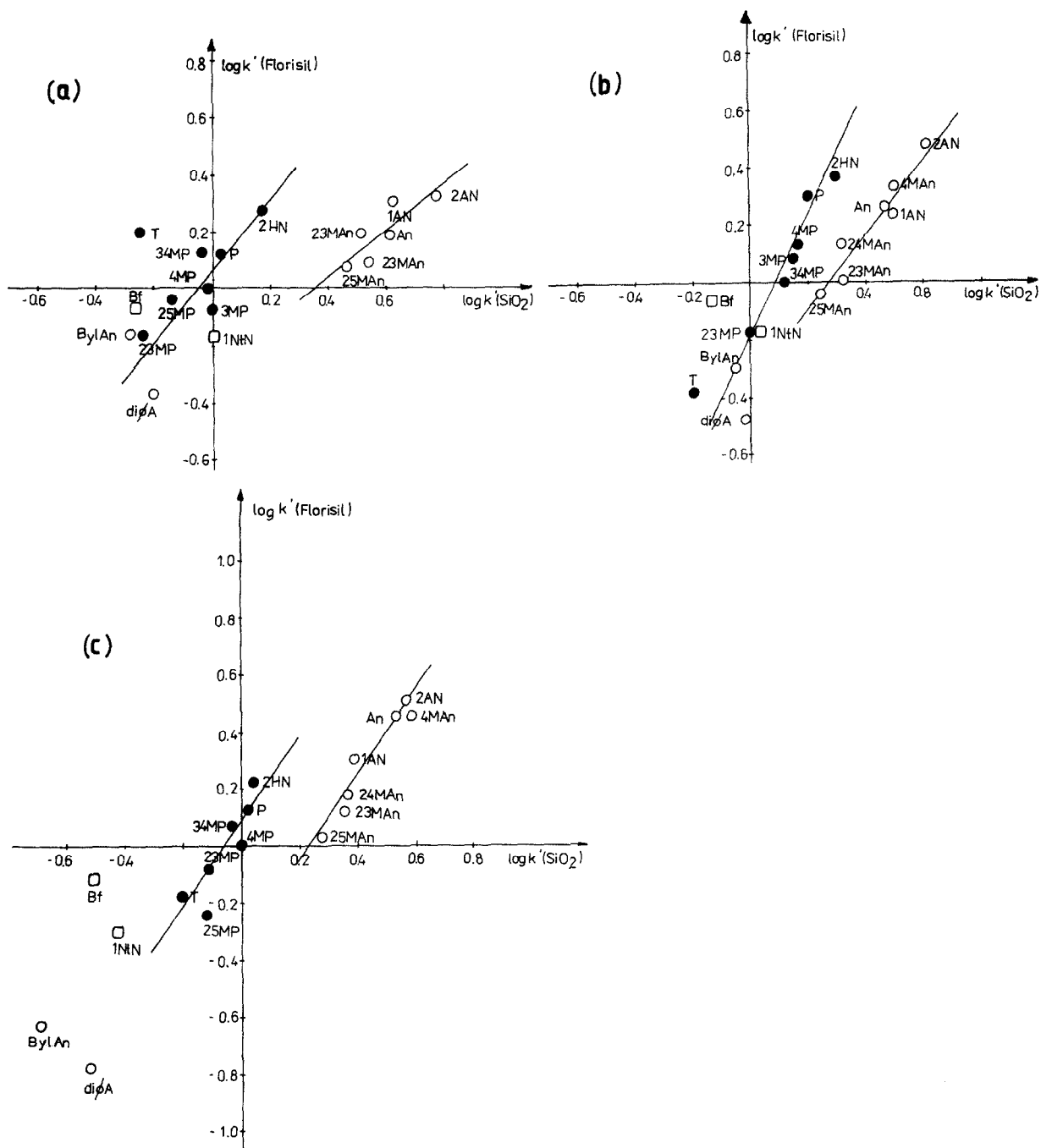
Fig. 2. Correlation between log k' values of monofunctional aromatic compounds on Florisil and silica. Solutes: (●) phenols; (○) anilines; (□) other compounds. Mobile phase: (a) tetrahydrofuran–n-heptane (15%, v/v, for Florisil and 20%, v/v, for silica); (b) dioxane–n-heptane (20%, v/v, for both adsorbents); (c) isopropanol–n-heptane (5%, v/v, for both adsorbents).
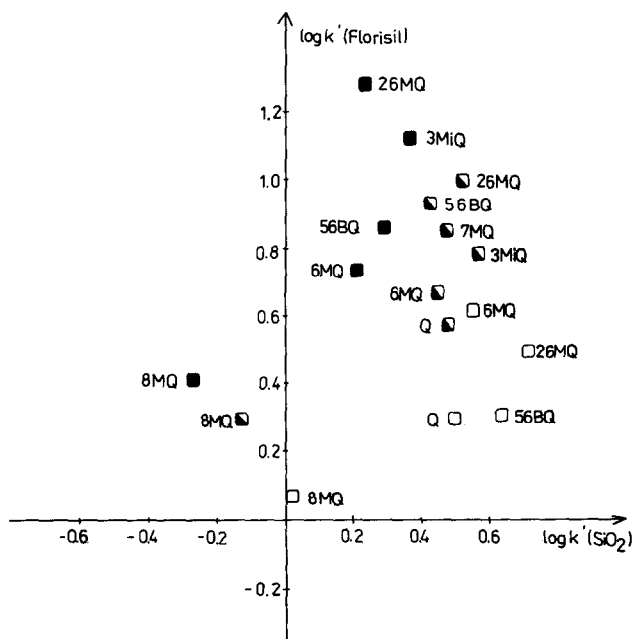
Fig. 3. Correlation between log k' values of monofunctional solutes (quinoline bases) on Florisil and silica using following systems: (□) tetrahydrofuran–n-heptane (40%, v/v, for Florisil and 20%, v/v, for silica); (◨) dioxane–n-heptane (50%, v/v for Florisil and 30%, v/v, for silica); (■) isopropanol–n-heptane (30%, v/v for Florisil and 5% v/v, for silica).

The correlation plots of log $k'_{Florisil}$ against log k'_{silica} (Fig. 2) allow a comparison of the selectivities of the systems. For instance, it can be seen that although anilines are less strongly adsorbed on the Florisil than on the silica surface, in most instances they can be better separated using Florisil than silica, especially when using isopropanol or dioxane as a modifier (see Fig. 2b and c). For example, isomers such as dimethylanilines (23MAn, 24MAn, 25MAn) and aminonaphthalenes (1AN, 2AN) are better separated on Florisil using isopropanol–n-heptane or dioxane–n-heptane as the eluents. However, the adsorption of phenols on Florisil and on silica is similar, although there are some individual differences in chromatographic behaviour (e.g., dimethylphenols). The isomers of xylenol are better separated on Florisil than on silica with all the eluent systems investigated (see Fig. 2). There are greater differences for Florisil than for silica in the retention of phenol and 2-naphthol and of phenol and 4-cresol with all three eluent systems.

The chromatographic properties of the above systems can also be compared by the retention of quinoline bases (class B). Quinolines are more strongly adsorbed on Florisil than on silica in all the systems investigated. The effect of shielding of the Florisil surface and its deactivation, especially by tetrahydrofuran molecules, can be observed (see Fig. 3). In all instances the compounds can be better separated using Florisil than silica. For example, in all eluent systems methylquinolines (7MQ or 6MQ) can be separated from dimethylquinoline (26MQ), and also from quinoline (Q).

Fig. 4 compares the selectivity of Florisil with different solvent systems as the log k' "spectrum" obtained for a constant concentration of a modifier (comparable solvent strength) for monofunctional solutes of class AB. The different slopes of the straight segments of lines indicate marked changes in selectivity; changes in the sequence of the elution of the compounds are also apparent. The effect of the individual substituents on retention can be
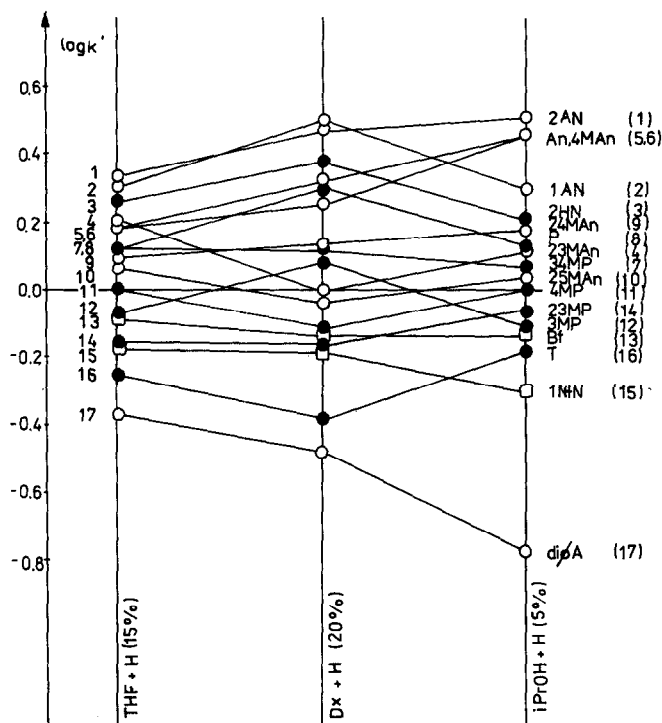

Fig. 4. Graphical comparison of log k' values obtained for Florisil. Mobile phases: tetrahydrofuran (15%), dioxane (20%) and isopropanol (5%) in n-heptane (H).
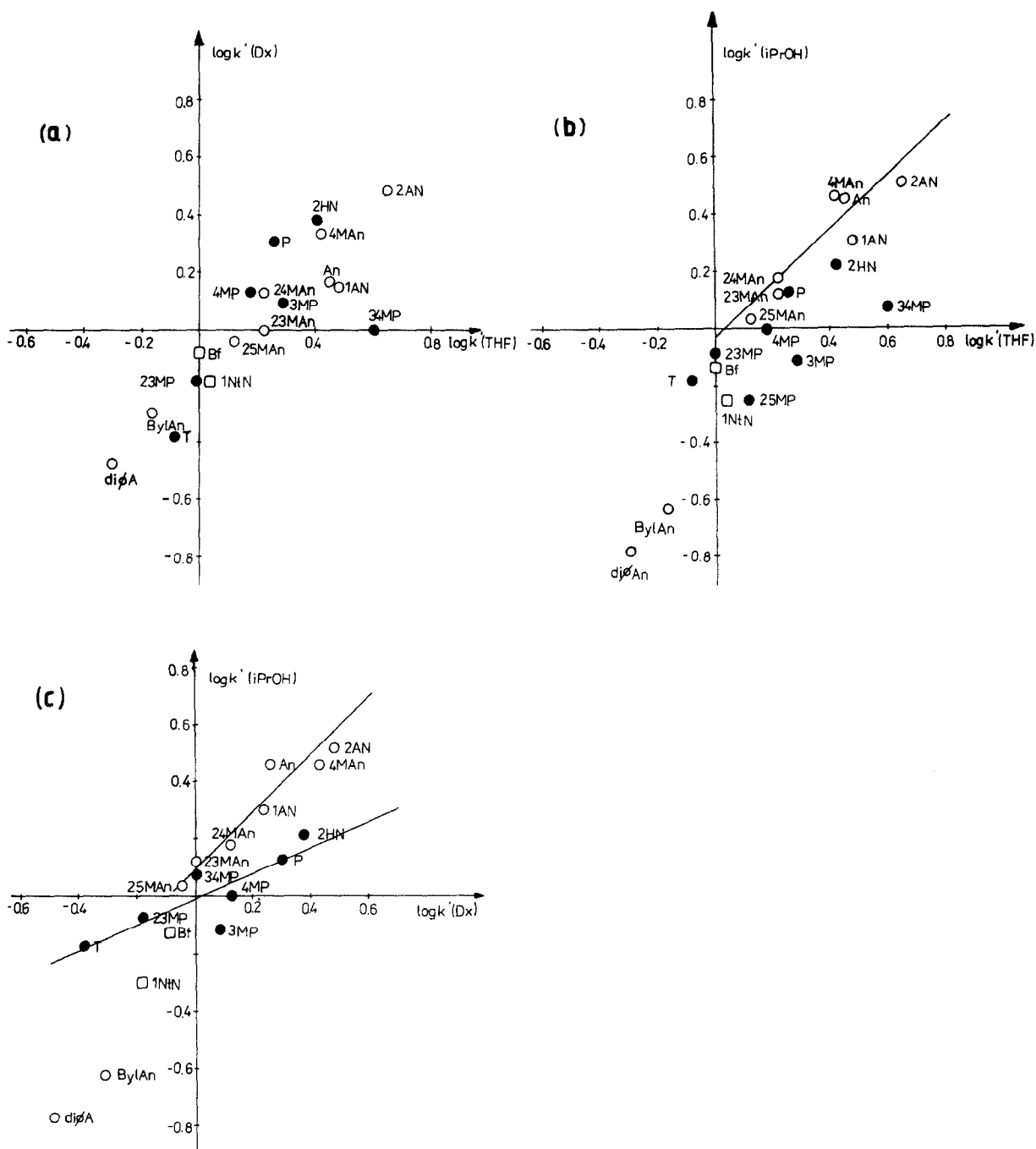
Fig. 5. (a) Correlation of log k' values for 20% (v/v) of dioxane (Dx) in n-heptane against log k' values for 10% (v/v) of tetrahydrofuran (THF) in n-heptane. Active solid, Florisil. (b) Correlation of log k' values for 5% (v/v) of isopropanol (iPrOH) in n-heptane against log k' values for 10% (v/v) of tetrahydrofuran in n-heptane. Active solid, Florisil; correlation line plotted for primary anilines. (c) Correlation of log k' values for 5% (v/v) of isopropanol in n-heptane against log k' values for 20% (v/v) of dioxane in n-heptane. Active solid, Florisil.

quantified by direct estimation from these diagrams.

Another method for comparison of the investigated eluent systems is to plot the log k' versus log k' relationships obtained using Florisil as an active solid and different modifiers in the mobile phase for all the investigated monofunctional solutes of class AB.

Comparison of dioxane–n-heptane and tetrahydrofuran–n-heptane eluent systems shows a common correlation line for all the compounds investigated (see Fig. 5a). However, there is a wide spread of points within each group; moreover, it is advantageous from the viewpoint of differences in selectivity between these modifiers (i.e., there are no separate parallel correlation lines for phenols and anilines as when using silica [12]).

Fig. 5b illustrates the correlations between the eluents isopropanol–n-heptane and tetrahydrofuran–n-heptane. The points for aromatic primary amines form the upper line, which can be expressed by the following equation:

$$\log k'_{iPrOH} = 0.93 \log k'_{THF} - 0.04; \quad r = 0.91 \ (n = 7)$$

The points for phenols are dispersed below this line.

Fig. 5c presents a correlation of isopropanol–n-heptane and dioxane–n-heptane systems. The points form two crossing lines. The upper line for anilines can be expressed by the following equation:

$$\log k'_{iPrOH} = 0.98 \log k'_{Dx} + 0.10; \quad r = 0.95 \ (n = 7)$$

For the lower line for phenols the equation is

$$\log k'_{iPrOH} = 0.43 \log k'_{Dx} - 0.02; \quad r = 0.83 \ (n = 7)$$

These relationships show the specific properties of dioxane as a modifier and indicate that phenols are strongly adsorbed on the Florisil surface modified by dioxane molecules forming a film with ether oxygen–electrodonor atoms opposing the bulk phase.

CONCLUSIONS

In spite of a number of analogies between adsorption on Florisil and on silica, especially for AB class compounds, distinct differences in the acidity of the adsorption centres and their distribution were observed (e.g., stronger adsorption of quinolines of class B and capability for separation of isomers). Either Florisil or silica may be used as a complementary adsorbent for some particular separations.

Modifiers such as isopropanol and dioxane are very interesting from the viewpoint of selectivity, especially the dioxane system, where an additional co-adsorption mechanism is observed.

REFERENCES

1 T. Wawrzynowicz, M. Waksmundzka-Hajnos and M. L. Bieganowska, Chromatographia, 28 (1989) 161.
2 M. Waksmundzka-Hajnos and T. Wawrzynowicz, J. Planar Chromatogr., 3 (1990) 439.
3 L. R. Snyder, Principles of Adsorption Chromatography, Marcel Dekker, New York, 1968.
4 L. R. Snyder, J. Chromatogr., 12 (1963) 488.
5 E. Soczewínski, T. Dzido and W. Golkiewicz, Chromatographia, 10 (1977) 298.
6 E. Soczewínski, W. Golkiewicz and T. Dzido, Chromatographia, 10 (1977) 221.
7 E. Soczewínski, J. Kuczmierczyk and T. Wawrzynowicz, Chem. Anal. (Warsaw), 29 (1964) 527.
8 M. Waksmundzka-Hajnos, Chem. Anal. (Warsaw), in press.
9 M. Waksmundzka-Hajnos, J. Planar Chromatogr., 4 (1991) 127.
10 T. Wawrzynowicz, E. Soczewínski and K. L. Czapińska, Chromatographia, 20 (1985) 223.
11 T. Dzido and T. Wawrzynowicz, Chem. Anal. (Warsaw), 24 (1979) 953.
12 T. Dzido and E. Soczewínski, J. Chromatogr., 388 (1987) 99.
13 T. Dzido and E. Soczewínski, J. Chromatogr., 395 (1987) 489.
14 G. C. Pimentel and A. L. McClellan, The Hydrogen Bond, Freeman, San Francisco, 1960.
15 E. Soczewínski, Anal. Chem., 41 (1969) 179.
16 L. R. Snyder in Cs. Horváth (Editor), High Performance Liquid Chromatography, Vol. 3, Academic Press, New York, 1983.
17 E. Soczewínski, J. Chromatogr., 388 (1987) 91.