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RETENTION AND SELECTIVITY CHARACTERISTICS OF A NON-POLAR PERFLUORINATED STATIONARY PHASE FOR LIQUID CHROMATOGRAPHY

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SUMMARY

An experimental study has been made of the chromatographic characteristics of a perfluorinated chemically bonded stationary phase for reversed-phase liquid chromatography. It is demonstrated from the retention data that the perfluorinated material behaves as a less polar stationary phase than an octadecyl (RP-18) material. The gain in selectivity, however, is obscured by large specific effects towards both fluorinated solutes and certain classes of compounds not containing fluorine atoms. The specific fluorine–fluorine interaction can also occur in the mobile phase, when 2,2,2-trifluoroethanol is used as an organic modifier.

INTRODUCTION

In reversed-phase liquid chromatography (RPLC), a non-polar stationary phase is combined with a polar mobile phase. Most often, a chemically bonded hydrocarbon-type material is used. A high concentration of alkyl groups on a silica surface yields a non-polar stationary phase. Different alkyl chain lengths can be used and their mutual differences have been studied[1,2]. Moderately polar materials can be obtained by chemical bonding of alkylsilanes containing a functional group in the ω-position[3]. Such materials can be used for special separations, *e.g.*, the application of amino-type stationary phases for the analysis of sugars[4]. Also, stationary phases equipped with diol and cyano groups can occasionally be used advantageously[5,6]. However, materials with branched chains[7], alkenes[3] and phenyl groups[8,9] appear to be of limited interest in chromatographic practice.

Recently, we reported on the synthesis of highly fluorinated stationary phases for liquid chromatography[10]. These phases appeared to show a remarkably specific fluorine–fluorine interaction. Solutes containing fluorine atoms could be specifically retarded relative to the hydrogen-containing molecular analogues. Moreover, we have suggested elsewhere[11] that the extremely low polarity of the perfluorinated stationary phases could result in a higher overall selectivity, if these phases were used for common reversed-phase separations.

This paper describes a more detailed study of the chromatographic properties

of perfluorinated phases. Both specific effects and the general separation power will be considered. Mobile phases containing trifluoroethanol as the organic modifier are used to investigate the occurrence of specific fluorine–fluorine interactions.

THEORETICAL

Retention and selectivity

Elsewhere[11], we have discussed a simple model from which different LC phase systems can be evaluated and mutually compared. This model is based on the concept of polarity, and expressed in terms of the solubility parameter, δ. The resulting expression for the capacity factor, k, is

$$\ln k_i = (v_i/RT)(\delta_m + \delta_s - 2\delta_i)(\delta_m - \delta_s) + \ln(n_s/n_m) \tag{1}$$

in which v_i = molar volume (cm^3 mole^{-1}) of the solute, R = gas constant (= 1.9865 cal K^{-1} mole^{-1}), T = absolute temperature (°K), δ = solubility parameter (cal$^{\frac{1}{2}}$ cm$^{-3/2}$), n = the number of moles present in the column and the subscripts refer to solute (i), mobile (m) and stationary (s) phase.

Two conclusions can readily be drawn from this equation:

(1) Reasonable retention times can be obtained if the polarity (solubility parameter) of the solute is roughly intermediate between those of the two chromatographic phases, *i.e.*:

$$\delta_i \approx \tfrac{1}{2}(\delta_m + \delta_s) \tag{2}$$

(2) The general selectivity, ∇, of the chromatographic phase system can be defined as the absolute difference between the polarities of the two phases:

$$\nabla = |\delta_m - \delta_s| \tag{3}$$

∇ determines the separation power of the system towards a pair of solutes with equal molar volumes and a given difference in polarity.

Eqns. 2 and 3 give us the key to the development and operation of LC phase systems. In current high-performance liquid chromatography (HPLC), hydrocarbonaceous stationary phases are favoured, the polarity of which can be approximated by the common value for alkanes: $\delta = 7$ cal$^{\frac{1}{2}}$ cm$^{-3/2}$. Adequate general selectivity can then only be obtained with mobile phases of higher polarity, which means that (by definition) we are working with a reversed-phase system (RPLC). The maximum mobile phase polarity is obtained with pure water ($\delta = 25.5$; *cf.*, ref. 16) as the eluent. By using appropriate binary mixtures as mobile phase, all values of δ_m between 7 and 25.5 can be realized and hence, according to eqn. 2, all solutes with polarities between 7 and 16.25 can be eluted from a conventional RPLC column with reasonable retention times. The lower the solubility parameter of the solute, however, the lower that of the mobile phase should be, and hence, with δ_s = constant = 7, the lower the selectivity of the chromatographic system becomes (*cf.*, eqn. 3).

Perfluorinated hydrocarbons are materials of extremely low polarity, even lower than that of alkanes[12]. A value of $\delta = 5$ can be taken as an estimate of their solubility parameter. Hence, a stationary phase containing perfluorinated carbon

chains instead of the conventional alkyl groups can be expected to behave as one of extremely low polarity. If the mobile phase polarity is kept constant, replacement of the conventional RP column ($\delta_s \approx 7$) by a perfluorinated RPF column ($\delta_s \approx 5$) will lead to a decrease in retention. This can easily be seen by differentiation of ln k (eqn. 1) with respect to δ_s:

$$\partial \ln k / \partial \delta_s = (2v_i/RT)\, (\delta_i - \delta_s) \tag{1a}$$

Hence, ln k will decrease with decreasing δ_s, as long as $\delta_i > \delta_s$. This, of course, will always be true in reversed-phase liquid chromatography, and has been observed in practice[10]. The familiar remedy is to increase the water content (and hence the polarity) of the mobile phase. This can also be explained in terms of eqn. 2. If the polarity of the stationary phase is decreased, an increase of the mobile phase polarity is needed to fulfil eqn. 2 or, in other words, to maintain optimal retention times.

    If we now look at eqn. 3, we see that the combination of a decrease in δ_s and an increase in δ_m should lead to an increase in selectivity in RPLC. Hence, perfluorinated stationary phases might prove to be superior in RPLC.

Iso-eluotropic systems

    Previously, we introduced the term iso-eluotropic for mobile phases of different composition that yield (on the average) equal retention times on a given RPLC stationary phase[13]. For example, on RP-18, aqueous solvents containing 36 % acetonitrile (ACN) or 33 % tetrahydrofuran (THF) are mutually iso-eluotropic, and also with a reference mixture of 50 % methanol in water. As a result, the eluotropic strength of such mixtures can be expressed as the volume fraction of the corresponding binary mixture of methanol in water, ϕ_M^*.

    When another stationary phase is used the retention will change. However, this effect can be nullified by adapting the mobile phase composition. Let us consider the capacity factor of $k = 5.1$ obtained for chlorobenzene in a binary mixture of 50 % methanol and 50 % water ($\phi_M^* = 0.5$) on a (reference) RP-18 column. Using a RPF-10 perfluorinated stationary phase, the same retention is obtained with a mobile phase of 34 % methanol and 66 % water ($\phi_M^F = 0.34$). The value of ϕ_M^* that corresponds to ϕ_M^* = 0.50 will be different for different solutes. However, if the variations in ϕ_M^F are small, we can take the average over a large number of solutes, $\overline{\phi_M^F}$. The RPLC systems RP-18/methanol (ϕ_M^*)–water and RPF-10/methanol (ϕ_M^F)–water can then be referred to as iso-eluotropic systems. An arbitrary solute is then expected to yield similar capacity factors in both systems.

The specific effect

    Since the mobile phase compositions of iso-eluotropic systems are defined as an average over a large number of solutes, few solutes will actually show identical retention times. When a reference RP-18 system is replaced by an iso-eluotropic RPF system, some solutes will be specifically retarded by the stationary phase, while others will be more rapidly eluted. These variations in retention for solutes eluted from iso-eluotropic systems will be referred to as specific effects or specificity[14].

    Quantitatively, we can define the specificity for solute i eluted in a particular system relative to the iso-eluotropic system RP-18/methanol–water as
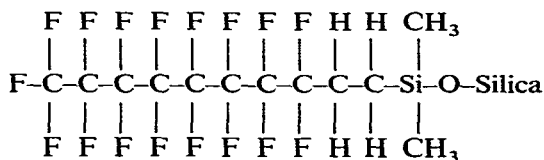
$$S_i = \ln k_i - \ln k_i^* \tag{4}$$

where k_i^* is the capacity factor in the reference system and k_i is the capacity factor in the phase system under consideration. It should be noted that this definition complements the one used to define specific effects induced by the application of different mobile phases[14]. Eqn. 4 leads to a positive specificity when a solute is specifically retarded by an RPF stationary phase.

In our first investigation into the behaviour of perfluorinated stationary phases we observed a remarkable positive specificity for molecules containing fluorine atoms. In this paper, we study in more detail the specific effects shown by the RPF column, using a variety of fluorinated solutes, as well as solutes containing other functional groups.

EXPERIMENTAL

The synthesis of the RPF-10 stationary phase has been described by Berendsen *et al.*[10]. The starting material 1H, 1H, 2H-perfluorodecene-(1) was purchased from Riedel-de Haën (Seelze-Hannover, G.F.R.) (Code no. 61016). Berendsen *et al.* reported a yield of 60% for the synthesis of the corresponding heptadecafluorodecyl(dimethyl)chlorosilane, *i.e.*, 0.6 moles of silane were obtained from each mole of the starting material. Using a slightly more laborious approach, we have succeeded in obtaining a yield of 80%. The structure of the bonded phase is:

```
    F  F  F  F  F  F  F  F  H  H  CH₃
    |  |  |  |  |  |  |  |  |  |   |
F–C–C–C–C–C–C–C–C–C–C–Si–O–Silica
    |  |  |  |  |  |  |  |  |  |   |
    F  F  F  F  F  F  F  F  H  H  CH₃
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The chromatographic apparatus consisted of a Waters M 6000 pump, a Waters M 440 single-wavelength absorbance detector and a Varian 8050 autosampler equipped with a pneumatic Valco injector. RP-18 columns (300 × 4.6 mm) were packed with a Shandon HPLC packing pump (Cat. no. 628 × 51). The RPF-10 column was packed according to the procedure described in ref. 10. The extremely low polarity of the perfluorocarbon bonded phase has consequences for its wetting properties. To maintain optimum column performance at low modifier content, a pressure restrictor must be included after the detector (or column). Methanol (J. T. Baker, Phillipsburgh, NJ, U.S.A.) and 2,2,2-trifluoroethanol (Aldrich-Europe, Beerse, Belgium) mixed with water were used as mobile phases. The flow-rate was set at 1.5 ml/min and was measured at regular intervals. All measured retention times were corrected for variations in the flow-rate and for the residence time outside the column. For both columns, we assumed a uniform t_0 value of 125 sec (at 1.50 ml/min) (*cf.*, the discussion in ref. 14). All solutes were of the highest purity available and diluted with methanol.

RESULTS AND DISCUSSION

Retention data for nineteen solutes were obtained on two columns, one filled

TABLE I

SUMMARY OF RETENTION DATA OBTAINED ON THE REFERENCE RP-18 AND ON THE PERFLUORINATED RPF-10 COLUMN

The values of ln k_0 and S were obtained from eqn. 5; standard deviations are those from the straight line of eqn. 5 for capacity factors between 1 and 10.

Solute	RP-18			RPF-10		
	ln k_0	S	S.D. 1–10	ln k_0	S	S.D. 1–10
Acetophenone	4.54	6.68	0.01	3.95	6.79	0.08
Benzene	4.87	6.05	0.01	3.23	4.90	0.04
Chlorobenzene	6.38	7.53	0.01	4.60	6.69	0.03
o-Difluorobenzene	5.68	7.15	0.02	4.53	6.43	0.03
Dimethyl phthalate	5.24	7.96	0.01	4.73	8.23	0.03
2,4-Dinitrofluorobenzene	4.08	5.85	0.01	3.27	5.72	0.02
Phenol	3.31	5.96	0.01	2.01	5.37	0.01
Fluorobenzene	5.23	6.58	0.01	3.82	5.59	0.02
p-Fluorophenol	3.82	6.42	0.01	2.57	5.63	0.01
o-Fluoronitrobenzene	4.60	5.79	0.05	3.67	5.99	0.02
m-Fluoronitrobenzene	4.94	6.39	0.01	3.83	5.62	0.01
p-Fluoronitrobenzene	4.51	6.11	0.01	3.85	5.96	0.02
Hexafluorobenzene	6.77	7.76	0.06	6.86	7.71	0.01
Nitrobenzene	4.57	6.05	0.01	3.58	5.73	0.02
p-Nitrophenol	4.00	6.30	0.00	2.78	5.94	0.01
Pentafluorobenzene	6.65	8.07	0.01	6.28	7.49	0.01
1,2,4-Trifluorobenzene	5.67	7.20	0.02	4.96	6.79	0.02
x,x,x-Trifluorotoluene	7.25	8.79	0.01	6.53	8.59	0.03
Toluene	6.15	7.19	0.01	4.43	6.27	0.01

with RP-18 reference material and the other with the RPF-10 perfluorinated stationary phase, using mixtures of methanol and water at 10 % composition intervals as the mobile phase. In Table I these data are presented in a condensed form, using a linear equation to relate ln k with mobile phase composition, ϕ:

$$\ln k = \ln k_0 - S\phi \qquad (5)$$

The validity of this equation is limited to capacity factors between 1 and 10 (ref. 15). The parameters ln k_0 and S were obtained from least squares approximation of the generally convex ln k vs. ϕ curve by a straight line over this particular interval. This procedure has been described before[15]. Together with the parameters ln k_0 and S, Table I gives the standard deviation of ln k from the straight line for k values between 1 and 10. Note that a standard deviation of 0.01 for ln k corresponds to a deviation of 1 % in k, so that it can be concluded that eqn. 5 describes retention within a few percent.

It is seen from Table I that the values obtained for ln k_0 on the RPF-10 column are considerably smaller than those obtained with RP-18. This illustrates that, with the same mobile phase, retention will be weaker on the RPF-10 material. This is in agreement with the prediction from simplified solubility parameter theory that a decrease in δ_s will result in a decrease in retention (cf., eqn. 1a). To compensate
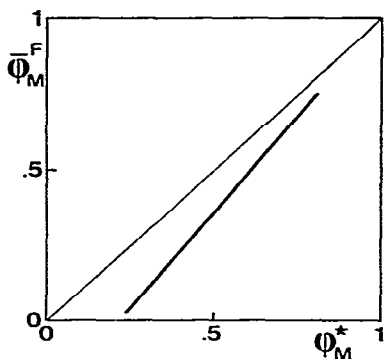
Fig. 1. Iso-eluotropic compositions of methanol–water mixtures on the RPF-10 column, as a function of the methanol–water composition on the reference RP-18 column. Compositions estimated from data on the nineteen solutes listed in Table I.
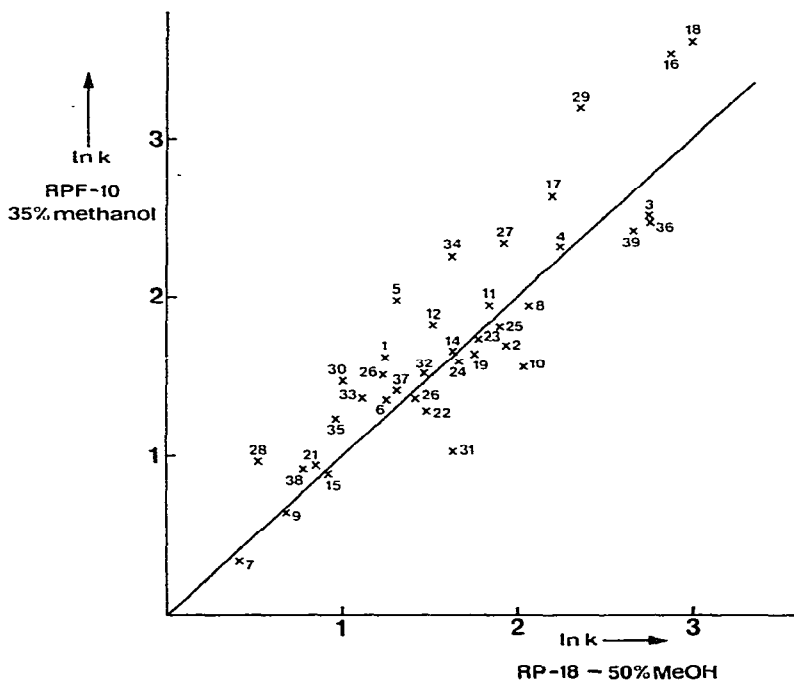

Fig. 2. Logarithmic plot of the capacity factors obtained on the RPF-10 column using a methanol–water (35:65) mobile phase *vs.* the capacity factors on the iso-eluotropic reference RP-18 system with a methanol–water (50:50) mobile phase. The straight line represents $\ln k_F = \ln k_{18}^*$. Deviations from this line are defined as specific effects (specificity) of the RPF-10 column. Solutes: 1–19, as in Table I; 20 = *p*-nitroacetophenone; 21 = 2-phenylethanol; 22 = *p*-chlorophenol; 23 = 2,4-dimethylphenol; 24 = 2,3-dimethylphenol; 25 = anisole; 26 = *o*-nitrophenol; 27 = methyl benzoate; 28 = *p*-chlorobenzaldehyde; 29 = dimethyl phthalate; 30 = benzonitrile; 31 = *p*-methylbenzaldehyde; 32 = 3-phenylpropanol; 33 = *p*-dinitrobenzene; 34 = 3,4-dinitrotoluene; 35 = benzaldehyde; 36 = *p*-phenylphenol; 37 = *o*-dinitrobenzene; 38 = *p*-nitrobenzaldehyde; 39 = 2,5-dimethylphenol.

for this effect, more polar mobile phases should be used with the RPF-10 column than with the RP-18 one.

The correspondence is expressed by the thick solid line in Fig. 1. In order to elute a solute from the RPF-10 column with the same capacity factor as observed on the RP-18 column, a mobile phase must be used that contains less methanol and, hence, more water. Consequently, the RPF-10 material behaves as an even less polar stationary phase, and hence shows less affinity towards the average solute than the common hydrocarbon material.

This effect is definitely due to the fluorination, and not to the shorter chain length of the RPF-10 material (10 rather than 18), as becomes obvious from the following two considerations. First, for the small solutes used in the present study, retention does not increase markedly when the chain length of the hydrocarbon stationary phases is increased from 10 to 18[1]. Secondly, an earlier comparison[10] between RPF-10 and a decyl (RP-10) bonded stationary phase confirms the lower polarity of the former.

Having determined the mobile phase composition that allows a fair comparison between RPF-10 and RP-18, we will examine the prediction of improved selectivity provided by the former column. We compared the capacity factors for 38 solutes, obtained with a mixture of 35% methanol and 65% water on the RPF-10 column (ln k_F) with those obtained in the iso-eluotropic system (cf., Fig. 1) applying a methanol–water (50:50) mixture and an RP-18 column (ln k_{18}). The results are shown in Fig. 2. A systematic increase in selectivity on the RPF-10 column would be manifested by a ln k_F vs. ln k_{18} plot with a slope of larger than unity. Least squares analysis of the data in Fig. 2 yields a straight line, expressed by ln $k_F = -0.3 + 1.3$ ln k_{18}. Hence, the slope of the line is indeed greater than unity. In this case the intercept must be negative because the two systems are iso-eluotropic. However, the scatter of the data points about the line is such that the correlation coefficient is only 0.77. Therefore, we conclude that although the RPF-10 appears to provide a slight gain in selectivity this is overshadowed by large specific effects.

According to eqn. 4, specific effects are defined as deviations from the line ln k_F = ln k_{18} in Fig. 2. Solutes that fall above this line show a specific retardation, when RPF-10 is substituted for RP-18. Such solutes can be said to undergo a specific interaction with the RPF-10 phase. Previously, we have observed such a specific interaction between the fluorinated stationary phase and fluorinated solute molecules[10]. This observation is confirmed by the data in Fig. 2, e.g., solutes 16 and 18. However, specific effects are not limited to fluorinated solutes. Dimethyl phthalate (5) and diethyl phthalate (29) are good examples of solutes that show a similar specific retardation on RPF-10.

A clear illustration of the specific effects occurring in the RPF-10 system is provided by the chromatograms in Fig. 3. These chromatograms have been constructed using the experimental retention times from Fig. 2. Eight non-fluorinated solutes were used, and although the overall analysis time remains approximately the same in the two chromatograms (as is expected for iso-eluotropic systems), the specific effects are striking. The upper chromatogram corresponds to a methanol–water (50:50) mobile phase on the RP-18 column. The solutes are numbered in order of appearance and are listed in Table II, together with the logarithms of their capacity factors. The lower chromatogram in Fig. 3 shows the elution of the same mixture on the
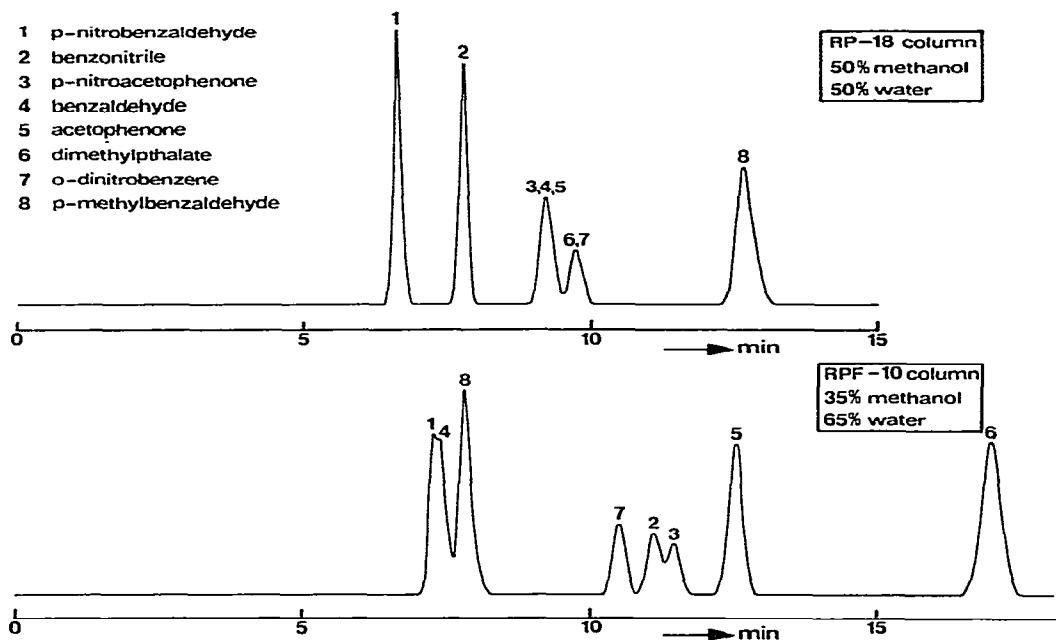
Fig. 3. Chromatograms illustrating the specific effects observed on an RPF-10 column for non-fluorinated solutes. Retention data taken from Fig. 2. Column: 30 cm × 4.6 mm I.D. Flow-rate: 1.5 ml/min.

iso-eluotropic RPF-10 system with a methanol–water (35:65) mobile phase. The appropriate retention data are also shown in Table II. The last column in this table gives the specificities for the present mixture of eight solutes according to eqn. 4. The values for S_i demonstrate once more the large specific effects that can be observed for non-fluorinated molecules. Dimethyl phthalate shows an almost two-fold increase in retention on the RPF-10 column, while the opposite is true for p-methylbenzaldehyde. Of course, the fluorinated chains at the silica surface should not be held responsible for all the observed specific effects. Since the content of water and that of methanol in the mobile phase are changed when RPF-10 is substituted for RP-18, the specific effects

TABLE II

RETENTION AND SPECIFICITY FOR THE SOLUTES IN FIG. 3

Peak no.	Solute	ln k_{18} 50% MeOH	ln k_F 35% MeOH	S_i
1	p-Nitrobenzaldehyde	0.77	0.92	0.14
2	Benzonitrile	1.00	1.47	0.47
3	p-Nitroacetophenone	1.23	1.51	0.28
4	Benzaldehyde	1.23	0.95	−0.28
5	Acetophenone	1.24	1.62	0.37
6	Dimethyl phthalate	1.30	1.97	0.67
7	o-Dinitrobenzene	1.31	1.40	0.09
8	p-Methylbenzaldehyde	1.62	1.02	−0.61

may also be caused by interactions with water or methanol. For example, the specific retardation of acetophenone and dimethyl phthalate on the RPF-10 system could easily be explained by assuming a specific interaction between methanol and the carbonyl groups of these solute molecules.

To elucidate further the nature of the specific effects observed for both fluorinated and non-fluorinated molecules, we used a fluorinated mobile phase, 2,2,2-trifluoroethanol (TFE), as the organic modifier in binary mixtures with water. If the specific effects are indeed due to specific interactions with fluorine, through the very low dispersive interaction observed for perfluorinated molecules (*cf.*, ref. 11), then we may expect a fluorinated mobile phase to lead to a specific acceleration of fluorinated molecules relative to their hydrocarbon analogues.

TABLE III

RETENTION AND SPECIFICITY OBSERVED WITH 2,2,2-TRIFLUOROETHANOL (TFE) IN THE MOBILE PHASE

Solute	23% TFE		40% TFE		50% TFE	
	ln k_i	S_i	ln k_i	S_i	ln k_i	S_i
Benzene	3.01	−0.16	1.77	−0.42	1.30	−0.37
Fluorobenzene	3.20	−0.16	1.75	−0.35	1.23	−0.30
o-Difluorobenzene	3.25	−0.07	1.74	−0.21	1.19	−0.16
1,2,4-Trifluorobenzene	3.23	−0.08	1.64	0.16	1.06	−0.09
Pentafluorobenzene	3.56	0.62	1.71	0.27	1.08	0.30
Hexafluorobenzene	3.77	0.32	1.80	0.52	1.15	0.57
Dimethyl phthalate	3.72	−1.13	1.70	−1.10	1.04	−0.92
Acetophenone	3.27	−0.99	1.56	−0.93	0.97	−0.77
p-Fluoronitrobenzene	2.73	−0.30	1.06	−0.12	0.42	0.11
m-Fluoronitrobenzene	2.86	−0.05	1.17	0.04	0.65	0.12
o-Fluoronitrobenzene	2.62	−0.05	0.98	0.26	0.44	0.39
Toluene	4.01	0.06	2.37	−0.36	1.85	−0.39
Chlorobenzene	4.14	0.11	2.49	−0.45	1.99	−0.53
2,4-Dinitrofluorobenzene	1.66	0.37	0.14	0.55	−0.36	0.64
Nitrobenzene	2.92	0.39	1.30	0.26	0.77	−0.14
α,α,α-Trifluorotoluene	4.36	0.40	2.32	−0.12	1.70	−0.17
Phenol	0.42	0.74	−0.35	0.29	−0.64	0.25
p-Fluorophenol	0.42	1.13	−0.47	0.60	−0.77	0.53
p-Nitrophenol	0.27	1.53	−0.82	1.17	−1.14	1.11
Reference composition (% MeOH): 35			58		65	

The nineteen solutes of Table I were eluted with three different binary mixtures of TFE and water, containing 23, 40 and 50 % TFE, respectively. For each of these mobile phases we can calculate the composition of the binary methanol–water mixture that can be used as the iso-eluotropic reference system. These compositions are shown at the bottom of Table III. In this case, specificity should be defined as

$$S_i = \ln k_i^* - \ln k_i \tag{6}$$

because this results in a positive specificity when the specific interaction between solute and mobile phase causes a specific acceleration.

The observed retention data, together with the calculated specificities from eqn. 6, are presented in Table III. The S_i values show that large specific effects are observed, again for fluorinated as well as for non-fluorinated solutes. Remarkably, the highest specificities are observed, not for the highly fluorinated benzenes, but for phenol and two substituted phenols. The occurrence of such strong specific effects leads to an (average) reference methanol–water composition, such that benzene derivatives with a low degree of fluorination do not show positive specificities. However, the effect of fluorination can be seen in the series benzene, monofluorobenzene, trifluorobenzene, pentafluorobenzene and hexafluorobenzene. Since the specificities increase in this order a positive specific effect is observed for fluorine, which could be interpreted as a specific fluorine–fluorine interaction.

However, the esters (e.g., dimethyl phthalate) and ketones (e.g., acetophenone) that showed large positive specificities on the RF-10 column now show large negative S_i values. Hence, the underlying specific interactions do not originate from the introduction of fluorine atoms in the system. Rather, these observations should be
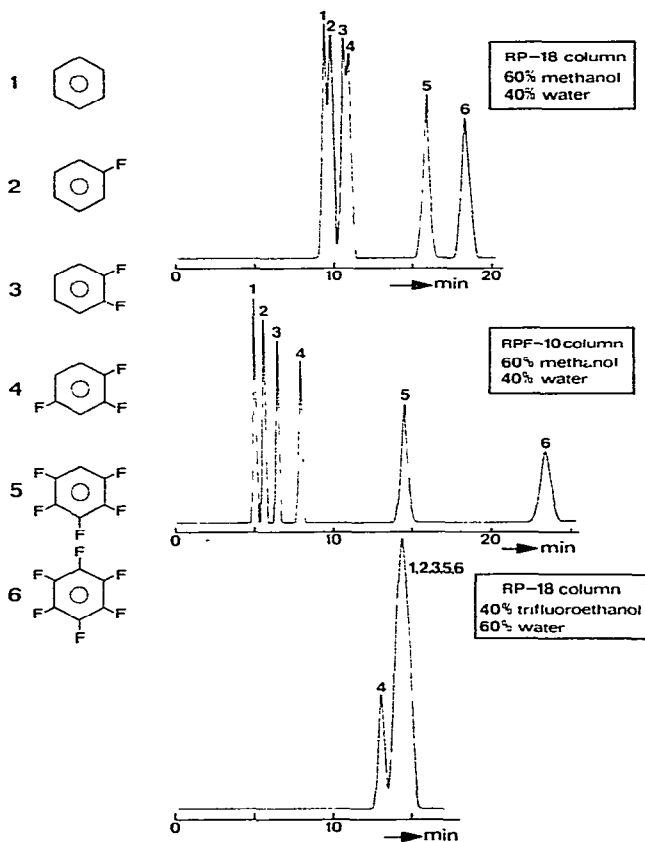

Fig. 4. Chromatograms illustrating the effects of specific fluorine–fluorine interactions in both the stationary and the mobile phase. Chromatograms constructed using experimental retention data. Other details as in Fig. 3.

ascribed to the change in mobile phase composition, when RP-18 is substituted by RPF-10, or methanol by TFE.

The exploitation of the large specific effects observed with TFE in practical RPLC will, of course, be restricted by the high cost of TFE.

The specific effects observed for fluorinated solutes, both on the RPF-10 stationary phase and with the TFE mobile phase, enable us to manipulate the separation of fluorinated molecules. This is demonstrated by the three chromatograms in Fig. 4. In the upper chromatogram, we show the separation that can be obtained for benzene and five fluorinated benzenes, all with different numbers of fluorine atoms, in a conventional RPLC system, applying an RP-18 column and a methanol–water (60:40) mobile phase. The separation is poor for two solute pairs: benzene and fluorobenzene (peaks 1 and 2), and o-difluorobenzene and 1,2,4-trifluorobenzene (peaks 3 and 4). The second chromatogram shows how the separation can be enhanced by substituting RPF-10 for RP-18. The mobile phase used is the same as for the upper chromatogram. Hence, the two systems are not iso-eluotropic. The overall retention time, however, remains largely unaltered, due to the specific retardation of the fluorinated solutes. The separation is excellent. The final chromatogram underlines our control of specific fluorine–fluorine interactions. With a mobile phase of 2,2,2-trifluoroethanol–water (40:60) on an RP-18 column, the separation deteriorates quite remarkably. Somewhat surprisingly, trifluorobenzene is eluted first, but all other solutes overlap to give a single peak.

Hence, the RPF-10 column has considerable advantages for the separation of solutes with different degrees of fluorination, while a fluorinated mobile phase shows the opposite behaviour. This is borne out by practical RPLC separation problems; an application of RPF-10 for the separation of some herbicides was studied previously[10], and we are at present investigating the application of RPF-10 to the separation of some fluorine-containing drugs.

CONCLUSIONS

The RPF-10 stationary phase behaves as a material of extremely low polarity, relative to the non-polar RP-18. The observed differences in behaviour between these phases are strictly due to the change in polarity, and not to the shorter chain length of the RPF-10 phase. The low polarity of the RPF-10 material results in a decrease in retention time, provided that the mobile phase is kept constant. Alternatively, the same retention is obtained if the water content of the mobile phase is increased, thus creating iso-eluotropic phase systems.

When these iso-eluotropic systems are compared, the general selectivity of the RPF-10 system is expected to be larger than that of the RP-18 system. Although this might be true in practice, the gain in selectivity is overshadowed by large specific effects.

Such effects occur not only for fluorinated solutes, but also for several non-fluorinated classes of compounds, e.g., esters and ketones. The specificities shown by the RPF-10 column lead to astonishing effects on the separation of simple organic mixtures, even if no fluorine atoms are present in the solutes.

The specific effect towards fluorine can be reversed, if fluorine atoms are introduced in the mobile phase, rather than in the stationary phase. It is shown that

fluorine–fluorine interactions can be controlled, either to enhance the separation of fluorinated molecules on an RPF-10 system, or to suppress separation by using TFE in the mobile phase.

     The RPF-10 material provides an intriguing stationary phase for RPLC, with many possible applications to the separation of fluorinated as well as non-fluorinated solutes.

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