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INVESTIGATION OF STATIONARY PHASE FORMATION FOR RP-18 USING VARIOUS ORGANIC MODIFIERS

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SUMMARY

Additional support for a model of the stationary phase consisting of solvent molecules absorbed to both the bonded organic moiety and residual silanols on the silica surface is presented. The enrichment of the stationary phase by the bonded organic moiety in solvents having a large solvent strength for C_{18} was observed. Stationary phase formation for RP-18 is seen to be dependent on two mechanisms, whereas for RP-8 stationary phase formation is under the control of the residual silanols present on the surface. A relationship between ln θ (phase ratio) and stationary phase formation was derived and evaluated for the solvents methanol, acetonitrile and tetrahydrofuran (THF). Acetonitrile is shown to have anomalous behavior when compared with methanol and THF. A qualitative relationship between α and solvent strength is also developed and discussed.

INTRODUCTION

In a previous paper[1], the formation of the stationary phase was found to be dependent on both the solvation of the bonded moiety and the residual silanols on the substrate surface for RP-18 and RP-8. The efficiency with which the bonded carbon chain can undergo solvation is dependent on the Van der Waals interactions between the bonded moiety and the solvent. For RP-18 and RP-8 dispersion interactions between the mobile phase and the chain are one driving force in the mechanism behind stationary phase formation. Therefore, one could predict a greater solvation of a bonded carbon chain by solvents whose dispersion interactions are large. This hypothesis has been given support by workers who have studied the absorption isothersm for solvents commonly used in reversed-phase chromatography (RPC), *i.e.*, methanol, acetonitrile and tetrahydrofuran (THF)[2,3]. The solvation of the bonded moiety should result in a change in the volume of the stationary phase (V_s) together with enrichment of the stationary phase in solvent molecules capable of undergoing more effective dispersion interactions. Berendsen *et al.*[4], have addressed the question of change in stationary phase volume on changing the percentage of organic modifier

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in methanol–water systems for various bonded phase columns. Additional supporting evidence can be found in the works of Tilly-Melin *et al.*[5] for LiChrosorb RP-8 and Westerlund and Theodorsen[6] for LiChrosorb RP-8 and Spherisorb ODS. One can deduce from the above work that the phase ratio (θ), which is defined as V_s/V_m, where V_m is the volume of mobile phase in the column, changes with varying mobile phase compositions.

The phase ratio is another important parameter that must be taken into account in any separation process. As stated above and from the data presented later in this paper (see Tables I–III), θ can change with varying mobile phase composition. For chromatographic separation processes a general equation can be derived to describe the phenomena that occur[7]:

$$V_R = V_m + K_D V_s \tag{1}$$

where K_D is the distribution coefficient, defined as

$$K_D = k'/\theta \tag{2}$$

where k' is the retention factor. One can see from eqn. 2 that the distribution coefficient is reciprocally related to the phase ratio and the retention factor is proportional to the phase ratio. The retention factor is most often reported for chromatographic separations with the assumption being made that the phase ratio is constant throughout the mobile phase compositional range used. The data presented in this paper prove this is not the case, θ cannot necessarily be considered constant and this effect on the separation processes must be taken into account.

In RPC k' has been found to fit an equation of the form

$$k' = Ae^{-B(\%\text{Org})} \tag{3}$$

where A and B are constants and %Org is the percentage of organic modifier in the mobile phase[8]. On rearranging eqn. 3, one obtains

$$\ln k' = \ln A - B(\%\text{Org}) \tag{4}$$

ln k' is a linear function of the percentage of organic modifier in the mobile phase. Substituting eqn. 2 into eqn. 4, we obtain

$$\ln K_D\theta = \ln A - B(\%\text{Org}) \tag{5}$$

and rearranging,

$$\ln \theta = \ln A/K_D - B(\%\text{Org}) \tag{6}$$

Eqn. 6, relating ln θ to the percentage of organic modifier in the mobile phase, predicts there to be a linear relationship between the two variables.

In this work we have studied the enrichment of LiChrosorb RP-18 by methanol, acetonitrile and THF at organic modifier concentrations from 0 to 100%. The

effect that this enrichment has on stationary phase volume, the phase ratio and the selectivity of RP-18 is discussed.

EXPERIMENTAL

The experimental details have already been described[1], but exceptions were made for the determination of acetonitrile in the stationary phase. In the gas chromatographic (GC) measurement of the amount of acetonitrile in the stationary phase, methanol was used as the internal standard because of the co-elution of acetonitrile and isopropanol. Therefore, a calibration graph was constructed of volume of acetonitrile *versus* peak-area ratio of acetonitrile to methanol, for 1 ml of methanol as internal standard and from 0.0 to 1.4 ml of acetonitrile diluted to 50 ml with dioxane. The determination of both the elution time of a non-retained component, t_0, and the amount of THF in the stationary phase was carried out as described in the previous paper[1].

RESULTS AND DISCUSSION

From Fig. 1 and Tables I–III, it can be seen that t_0 changes on increasing the percentage of organic modifier in the mobile phase. Fig. 1 also shows that t_0 is also dependent on which organic solvent is used in the mobile phase. This change in t_0 or V_m on using different organic solvents in the mobile phase must require a compensating change in the volume of the stationary phase. Using the model of the stationary phase as proposed in the previous paper[1], the stationary phase was considered to be a

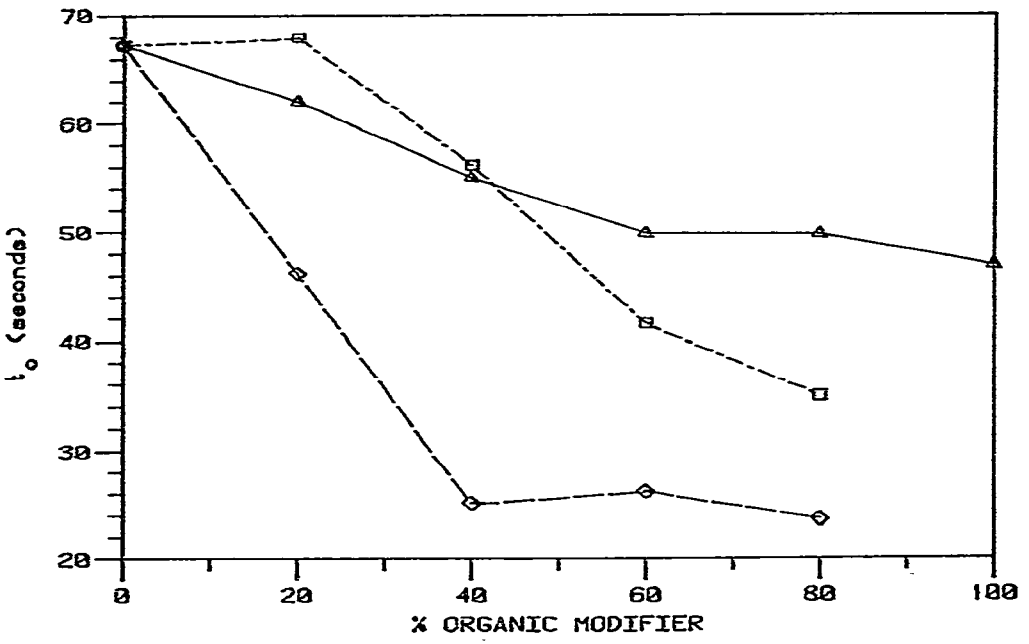

Fig. 1. Retention time of a non-retained solute (t_0) *versus* percentage of organic modifier in the mobile phase for methanol (△), acetonitrile (□) and THF (◇).

TABLE I

EFFECT OF METHANOL–WATER MOBILE PHASE COMPOSITION ON FORMATION OF RP-18 STATIONARY PHASE

RP-18: surface area 150 m^2/g; pore size 150 Å; length of chain C_{18}; carbon content 19.8%; functional group bonded dimethyloctyldecylchlorosilane; calculated degree of derivatization 42%: surface coverage 5.5 μmol C/m^2; weight in column 0.8948 g.

Parameter	*Methanol–water composition*					
	0:100	*20:80*	*40:60*	*60:40*	*80:20*	*100:0*
t_0 (sec)	67.18	61.95	54.85	49.72	49.68	46.91
V_m (ml)	1.12	1.03	0.91	0.83	0.83	0.78
Volume of methanol present in stationary phase (ml/g) (±0.03)	0.00	0.04	0.16	0.25	0.30	0.37
Volume of water present in stationary phase (ml/g) (±0.03)	0.27	0.04	0.08	0.09	0.03	0.00
Total volume of stationary phase (ml/g) (±0.04)	0.27	0.09	0.24	0.34	0.33	0.37
α	4.06	3.48	2.59	1.90	1.54	1.46
Methanol in stationary phase (%, v/v)	0	50	65	72	91	100
Phase ratio (θ)	0.22	0.08	0.24	0.37	0.35	0.43

TABLE II

EFFECT OF ACETONITRILE–WATER MOBILE PHASE COMPOSITION ON FORMATION OF RP-18 STATIONARY PHASE

Parameter	*Acetonitrile–water composition*					
	0:100	*20:80*	*40:60*	*60:40*	*80:20*	*100:0*
t_0 (sec)	67.18	67.88	56.12	41.47	34.89	–
V_m (ml)	1.12	1.13	0.94	0.69	0.58	–
Volume of acetonitrile present in stationary phase (ml/g) (±0.03)	0.00	0.10	0.19	0.39	0.50	–
Volume of water present in stationary phase (ml/g) (±0.03)	0.27	0.00	0.04	0.14	0.13	0.04
Total volume of stationary phase (ml/g) (±0.04)	0.27	0.10	0.23	0.53	0.63	–
α	4.06	2.99	1.97	1.55	1.43	–
Acetonitrile in stationary phase (%, v/v)	0	–	84	73	80	–
Phase ratio (θ)	0.22	–	0.21	0.69	0.96	–

TABLE III

EFFECT OF THF–WATER MOBILE PHASE COMPOSITION ON FORMATION OF RP-18 STATIONARY PHASE

Parameter	*THF–water composition*					
	0:100	*20:80*	*40:60*	*60:40*	*80:20*	*100:0*
t_0 (sec)	67.18	46.17	25.14	26.16	23.68	–
V_m (ml)	1.12	0.76	0.41	0.43	0.38	–
Volume of THF present in stationary phase (ml/g) (±0.03)	0.00	0.21	0.49	0.61	0.71	–
Volume of water present in stationary phase (ml/g) (±0.03)	0.27	0.16	0.29	0.19	0.06	0.00
Total volume of stationary phase (ml/g) (±0.04)	0.27	0.37	0.78	0.80	0.77	–
α	4.06	2.80	1.49	1.14	1.09	–
THF in stationary phase (%, v/v)	0	57	63	76	92	–
Phase ratio (θ)	0.27	0.44	1.70	1.70	1.80	–

ternary system containing the bonded organic moiety and solvent molecules adsorbed by both the bonded moiety and residual silanols on the silica substrate. The solvation of the bonded moiety (in this case, for RP-18, the bonded phase is octyldecyldimethylchlorosilane) depends on the intermolecular interactions between the solvent molecules and the bonded chain.

Intermolecular interactions between the solvent and the chain can be either specific or non-specific. For RP-18 non-specific interactions are the main driving force behind solvation of the C_{18} chain. Therefore, the stronger the non-specific dispersion interactions a solvent molecule can undergo the more effectively that solvent molecule can interact with the C_{18} chain. V_s is seen to increase throughout the entire mobile phase compositional range owing to the ability of the C_{18} to be solvated by the non-aqueous modifier. As V_s increases, V_m must decrease to keep the total volume for the column constant. These data for RP-18 are supported by work of Karger and McCormick[2] for RP-8.

If the enrichment of RP-18 by solvent molecules from the mobile phase is truly dependent on dispersion interactions, then for the three solvents commonly used in RPC, *i.e.*, methanol, acetonitrile and THF, the amount of modifier absorbed should follow the order of increasing dispersion interactions, which is methanol < acetonitrile < THF[9]. From Fig. 2, the volume of organic modifier absorbed by the C_{18} increases in the order methanol < acetonitrile < THF. This view is a simplification of the overall solvation process for RP-18. Non-specific interactions play a major role in stationary phase formation, but one also needs to consider the specific interactions between the solvent molecules of the mobile phase and the residual silanols on the silica surface. Comparing the specific intermolecular interactions of solvent molecules with residual silanols, the most prominent will be the solvent's acid–base properties, *i.e.*, its ability to be either a hydrogen-bond donor or acceptor

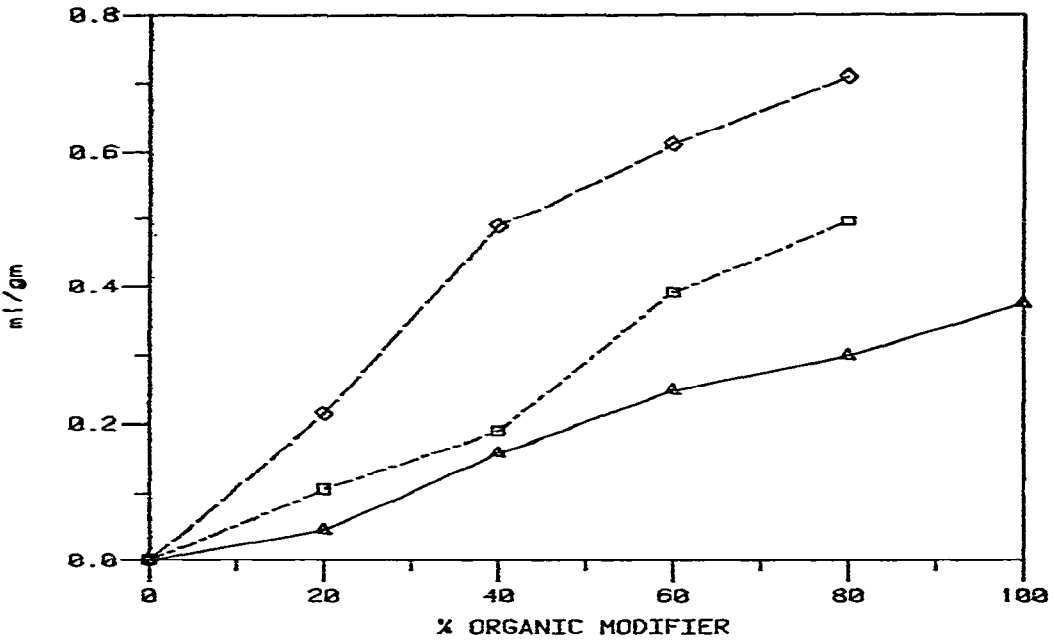

Fig. 2. Concentration of organic modifier in the stationary phase (ml/g) *versus* percentage of organic modifier in the mobile phase for methanol (△), acetonitrile (□) and THF (◇).

when interacting with the silanol. The hydrogen-bond donor strengths of the three solvents based on regular solution theory (Hildebrand solubility parameters) are ranked methanol ≫ THF = acetonitrile, while the hydrogen-bond acceptor strengths of the solvents follow the order methanol > THF > acetonitrile[9]. If one was to base the solvation of a non-bonded silica surface on the acid–base properties of these three solvents the solvation order would be methanol ≫ THF ≈ acetonitrile. Non-bonded silanols are present on the surface and they can enter into the retention process, as demonstrated by Horvath and Nahum[8]. Therefore, the solvation of the silanols must be considered with the solvation of the C_{18} chain in stationary phase formation. These specific interactions play a minor role in stationary phase formation for RP-18; as seen from Fig. 2, the absorption of organic modifier is under the control of the bonded carbon chain. However, under very low surface coverage conditions the specific intermolecular interactions between the solvent molecules and the silanols could dominate stationary phase formation.

Fig. 3 depicts the amount of water found in the stationary phase for the three solvents used. The amount of water in the stationary phase is seen to be dependent on the solvent used and the percentage of that particular solvent in the mobile phase; this has also been demonstrated for batch extraction methods[10]. For ease of discussion, Fig. 3 can be divided into three regions: (I) from 20 to 50%, (II) from 50 to 70% and (III) from 70 to 100% organic modifier concentrations. In region I the amount of water in the stationary phase is dependent on the hydrogen-bonding characteristics of the solvent and on the solubility parameter of the solvent for C_{18}. Therefore, THF, having the greatest ability to solvate the C_{18} chain and reasonable hydrogen-bond

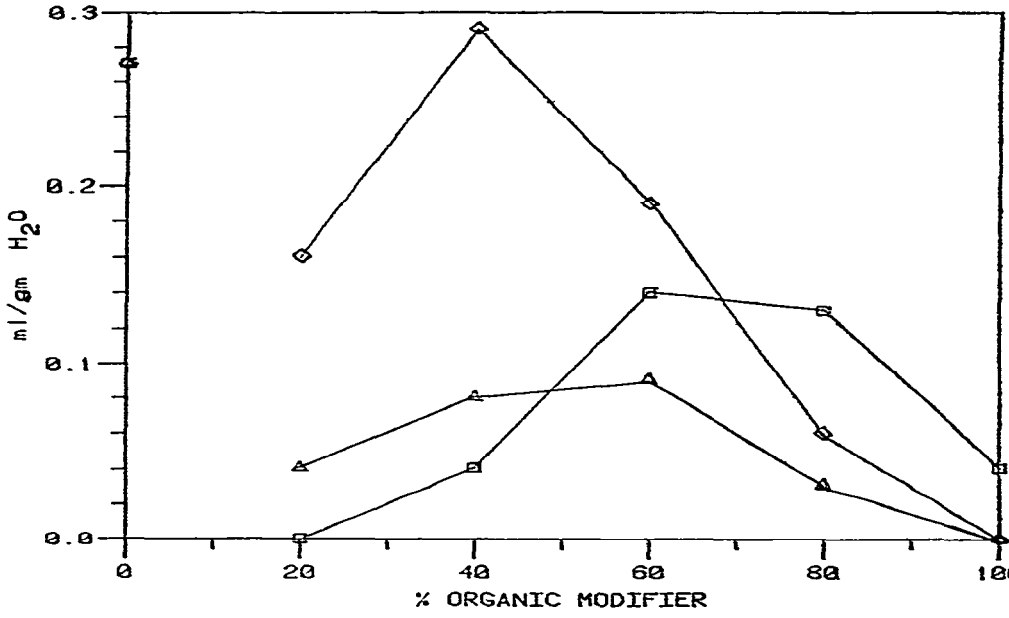

Fig. 3. Concentration of water in the stationary phase (ml/g) *versus* percentage of organic modifier concentration in the mobile phase for methanol (△), acetonitrile (□) and THF (◇).

acceptor properties, brings the most water with it upon formation of the stationary phase. Methanol, on the other hand, has the weakest dispersive interaction for C_{18}, but it is easily the strongest hydrogen bonder of the three solvents. Thus, even though a smaller amount of methanol will solvate the C_{18} compared with THF and acetonitrile, methanol will bring over with it a larger percentage of water than THF or acetonitrile (see Table I). Whereas acetonitrile has a dispersive interaction for C_{18} slightly larger than that of methanol, but it is the weakest of the three solvents in hydrogen-bond strength. Thus acetonitrile will bring the smallest amount of water into the stationary phase compared with methanol and THF. For 20% acetonitrile, we report essentially 0.00 ml/g of water in the stationary phase. We feel that there was water present in the stationary phase, but only a very small amount. In region II in Fig. 3, for methanol and THF the amount of water in the stationary phase is seen to decrease, whereas for acetonitrile there is an increase in the amount of water present. A possible explanation is as the amount of methanol and THF increases in the stationary phase a mass-action effect takes over. These solvents can effectively compete with and displace water from the residual silanols present. THF can displace water because of the overwhelming amount of it in the stationary phase and its hydrogen-bonding ability, whereas for methanol, the smaller amount present in the stationary phase can more easily displace water because of its stronger acid–base properties. Acetonitrile, owing to its weaker hydrogen-bonding strength and dispersive interactions, cannot overwhelm the water by its presence in the stationary phase or displace it from the residual silanols. Therefore, water will increase in concentration in the stationary phase with acetonitrile as organic modifier. Finally, in region III, the mechanism for the removal of water from the stationary phase is the organic

solvents mass-action effect, which overwhelms any water left associated with the residual silanols and the solvent's hydrogen-bonding ability. Therefore, acetonitrile, having the weakest hydrogen-bonding ability and a similar solvating ability for C_{18} as methanol, cannot displace all of the water from the residual silanols.

Overall, the amount of water found in the stationary phase was observed to be dependent on the organic modifiers solvent strength for C_{18}, and on the solvent's hydrogen-bonding capabilities. Methanol and THF display very similar curves in Fig. 3, with acetonitrile showing anomalous behavior in comparison with these two solvents. The anomalous behavior of acetonitrile will manifest itself through selectivity and the overall separation processes.

One final point to be discussed, which is relevant for RP-18, is stationary phase formation with 100% water as the mobile phase. From Tables I–III and Fig. 4, a large stationary phase volume is found at this mobile phase composition. A possible explanation for this observation is two-fold: (1) the residual silanols present on the silica surface are involved in hydrogen-bonding with the water present in the mobile phase and (2) water can be trapped on the substrate surface by a "tent" of C_{18} chains. This trapping of water is caused by the "freezing" of the bonded chains. The "freezing" of the bonded chains results from the intra- and/or intermolecular interactions amongst the chains themselves. Such interactions would be expected to be energetically favorable when compared only with interactions between the water matrix and the hydrocarbon. With 100% water as the mobile phase an adsorption mechanism is probably responsible for chromatographic retention in contrast to a partition mechanism in a solvation layer.

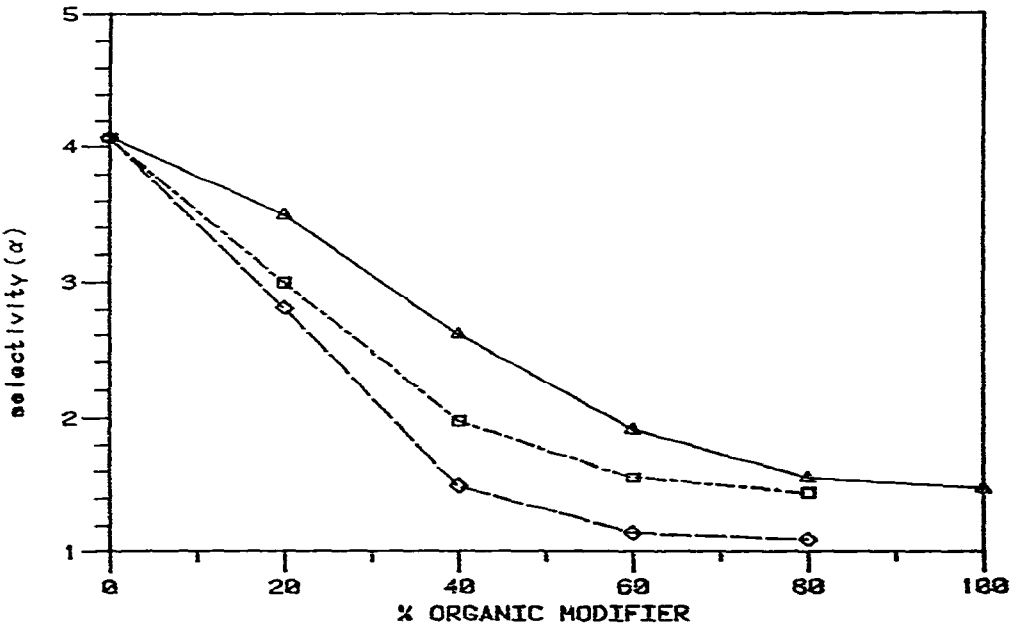

Fig. 4. Selectivity (α) *versus* percentage of organic modifier in the mobile phase for methanol (△), acetonitrile (□) and THF (◇).

The selectivity (α) of the stationary phase for the homologous series of alcohols used as probes is indicative of the effect that solvation and therefore the composition of the stationary phase has on the separation process. Selectivity in these experiments is based on the change of one methylene group (ΔCH_2) in the *n*-alcohol chain. The effect on α of enrichment of the stationary phase by the organic modifier is depicted in Fig. 4. Two features of these curves are clearly evident: (1) α gradually reaches a plateau value and (2) this plateau value and the rate at which the plateau is reached are solvent dependent. A possible explanation for the above mentioned features is that the stationary phase becomes enriched by the solvent (see the values in Tables I–III, for the volume of organic modifier in the stationary phase) and appears less "polar" to the solute, *i.e.*, the absorbed solvent molecules in the stationary phase are a stronger solvent for the solute than the mobile phase. Therefore, the value for ΔCH_2 will be greatest for the largest difference in solvent strength between the stationary phase and the mobile phase.

When eluent molecules with different solubility parameters solvate the bonded phase, they create stationary phases with different solvent strengths. The stationary phases formed by methanol, acetonitrile and THF will have different selectivities based on their abilities to discriminate between a ΔCH_2 group. Methanol, with a dispersive interaction solubility parameter of 6.2 (ref. 9), will undergo the least effective interaction with a methylene group, whereas THF, whose solubility parameter is 7.6 (ref. 9), will undergo the most effective interaction with a methylene group. The ability of acetonitrile to interact with a methylene group is between those of methanol and THF. Therefore, methanol will see the greatest difference between two solutes differing by a ΔCH_2. This difference can be expressed by the change in free energy of selecting between the two solutes, and is expressed by the equation

$$\Delta\Delta G_{N+1-N} = -RT \ln \alpha \tag{7}$$

where the assumption is made that the change in the free energy of transfer of the solutes from the mobile phase to the stationary phase is due only to the addition of one methylene group from the *N*-carbon homologue to the $N + 1$-carbon homologue. Table IV lists these changes in free energy and it can be seen that the largest free energy change for a ΔCH_2 group is for methanol and the smallest is for THF. Therefore, the order of selectivity shown in a column of data points is determined by the solvent's solubility parameter for the particular interaction being investigated. Selectivity and solvent strength are reciprocally related, but the rate at which the α

TABLE IV

$\Delta\Delta G_{N+1-N}$ VALUES FOR ALCOHOL HOMOLOGUES AT 25°C EXPRESSED IN cal/mole FROM EQN. 7

Solvent	*Concentration of solvent (%)*					
	0	*20*	*40*	*60*	*80*	*100*
Methanol	−830	−738	−564	−380	−256	−224
Acetonitrile	−830	−649	−402	−260	−212	–
THF	−830	−610	236	− 78	− 51	–

plateau is approached is proportional to solvent strength, owing to the ability of the stronger solvent to solvate the C_{18} chain more efficiently.

For methanol–water and THF–water the largest difference in solvent strength occurs at 0% modifier concentration, the difference becoming smaller as one continues to 100% modifier concentration. Therefore, α is largest in the beginning and decreases with increasing percentage of organic modifier. The α values reach a plateau when the enrichment of the stationary phase by a solvent no longer contributes to a change in the differences of the solvent strengths between the stationary and mobile phases.

The selectivity of acetonitrile is not as easily analysed as those of methanol and THF because of its anomalous behavior during stationary phase formation, as discussed earlier concerning the amount of water found in the stationary phase. However, a qualitative statement can be made for the selectivity in acetonitrile–water systems. The selectivity of acetonitrile–water seems to follow the solvent strength for C_{18} because these selectivity values fall between those for methanol and THF (see Fig. 4).

In summary, selectivity for a ΔCH_2 group through a compositional range of one solvent is controlled by the solvent strength of the stationary phase as compared with the solvent strength of the mobile phase. In comparison, at any one specific mobile phase composition the selectivity is reciprocally related to the dispersion interaction solubility parameter for that specific solvent with respect to the bonded moiety.

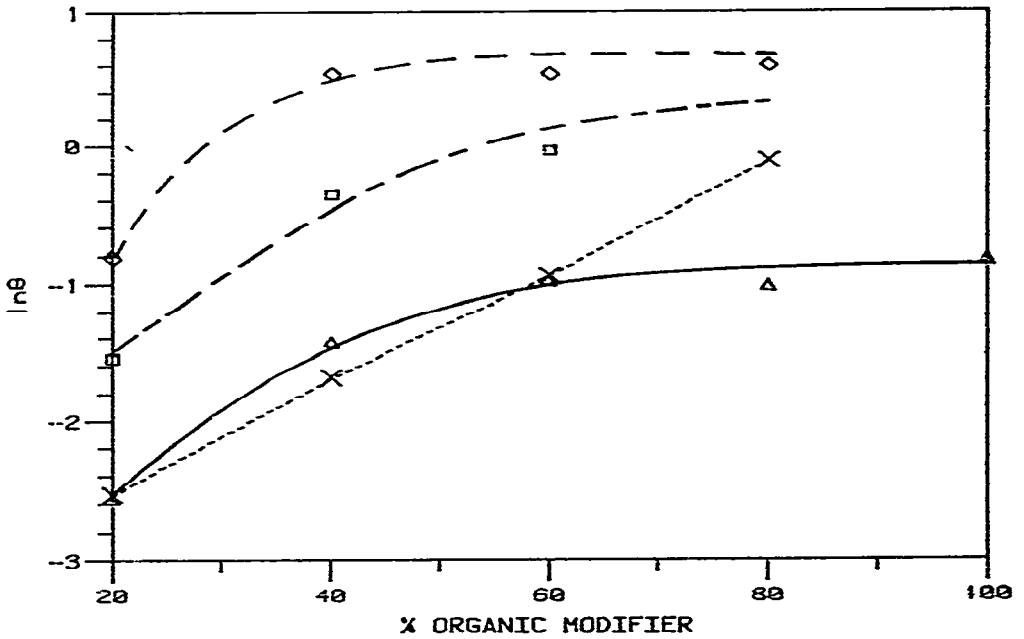

Fig. 5. Phase ratio (ln θ) *versus* percentage of organic modifier in the mobile phase for methanol (△), acetonitrile (□) and THF (◇). Data from ref. 1 for methanol and RP-8 (×) are also included for ease of comparison.

The above arguments on the dependence of the selectivity on the composition of the stationary phase again raise the question of the role of the volume of the stationary phase and therefore the phase ratio. A plot of the data in Tables I–III in the format of eqn. 6 can be seen in Fig. 5. Previous data for RP-8 (ref. 1) have also been included for comparison. The linear relationship predicted in eqn. 6 does not occur for RP-18 using the three solvents investigated, as there are two mechanisms controlling the formation of the stationary phase: (A) the solvation of the bonded organic moiety, which is dependent on non-specific interactions between the solvent and the bonded phase, and (B) the solvation of the substrate surface, which is dependent on specific interactions between the solvent and the surface. We have previously reported[1] that the solvation mechanism of RP-8 for methanol–water systems is dependent on process B. Therefore, one can conclude that the linear regions in the curves for RP-18 in Fig. 5 are dominated by stationary phase formation under control of the substrate surface. The transition between the linear region and the plateau region of the curves is where both mechanisms A and B are competing on equal terms in determining the composition of the stationary phase. The plateau region is controlled by the bonded moiety enriching itself in solvent molecules process A. Therefore, by plotting ln θ *versus* percentage of organic modifier one can tell more about the processes involved in stationary phase formation and the extent to which these two processes dominate.

In analysing Fig. 5, the stationary phase formation of THF–water systems is dominated by the enrichment of the bonded moiety in THF above *ca.* 40% THF in the mobile phase. Methanol, on the other hand, having a weaker dispersive interaction, does not reach its plateau until *ca.* 60%. In contrast, for acetonitrile over the entire compositional range there is no clear dominance of one stationary phase mechanism over the other.

Comparing eqn. 4 with eqn. 6, from the intercept of these two plots one can calculate K_D for a particular solute. This statement must be qualified because first of all a plot of ln θ *versus* percentage of organic modifier must be linear, and as both intercepts are determined from logarithmic plots the errors in these values will be magnified on solving for K_D. However, K_D values within an order of magnitude of their true values can be obtained by this method.

In conclusion, the stationary phase formation of RP-18 was found to be a combination of two mechanisms, non-specific interactions between the solvent-bonded moiety and specific interactions of the solvent with the substrate surface. The point at which the former mechanism begins to dominate stationary phase formation is related to the dispersive interaction solubility parameter: the stronger the solvent strength for C_{18} the earlier ln θ begins to plateau. Selectivity was also found to be dependent on solvent strength, which ultimately relates to the solubility parameter of a particular solvent for the bonded moiety. It is interesting that for both methanol and THF the α plateau and the ln θ plateau begin roughly at the same percentage of organic modifier. Acetonitrile was found to behave differently from methanol and THF both in the amount of water found in the stationary phase and in the mechanism of stationary phase formation. The conclusions in this paper further support our proposed model of a ternary stationary phase, and the hypotheses of stationary phase formation in RP-8 and RP-18 reported earlier. It should be noted that this approach to the question of selectivity in bonded phase chromatography emphasizes the active role of the stationary phase which results from the solvation of the bonded moiety

and the substrate by the components of the mobile phase.

Further investigations of stationary phase formation and its relationship to the solubility parameter of a solvent are being undertaken in order to gain a greater insight into the overall separation processes. Special emphasis is being placed on the role of ternary solvent mixtures and the role of temperature in stationary phase formation.

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