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PHENYL-BONDED PHASE LIQUID CHROMATOGRAPHY OF STYRENE OLIGOMERS

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SUMMARY

Styrene oligomers can be separated isocratically on phenyl-bonded phases using tetrahydrofuran-water, tetrahydrofuran-hexane and acetonitrile-water eluents. The retention of the styrene oligomers follows Snyder's capacity factor formulation. An equation which incorporates the Martin and the Snyder relations between $\log k'$ and degree of polymerization and solvent composition can be used to estimate the isocratic retention of styrene oligomers.

INTRODUCTION

Recently, several papers have been published on the separation of styrene oligomers and polystyrenes¹⁻⁸. As emphasized by Curtis *et al.*¹, the separation of styrene oligomers on any given chemically-bonded stationary phase can be used as a model for the separation of other types of oligomers. Larman *et al.*² demonstrated that gradient elution (tetrahydrofuran-water) on octadecyl-bonded phases can be used to determine isocratic retention parameters for high-molecular-weight solutes in reasonable agreement with experimental data. Mourey and Smith³ showed that Snyder's model for solvent-displacement⁹⁻¹¹ on a silica substrate for small organic molecules adequately explains solvent selectivity for oligostyrene stereoisomer separations; the effects on adsorption of oligomer length and structural complexity need not to be considered. Mourey⁶ showed that styrene oligomers of equivalent length but with different end-groups caused significant differences in retention on silica using isocratic dichloromethane-hexane eluents, and that the methylene backbone groups of styrene oligomers made only a minor contribution to the adsorption process. Armstrong and Bui⁷ used a precipitation mechanism to account for the retention behavior of high-molecular-weight polystyrenes on reversed-phase thin-layer chromatography (TLC) plates and liquid chromatography (LC) columns with methanol-tetrahydrofuran eluents. Holt-Sackett *et al.*⁴ used a silica column to separate styrene oligomers. We

demonstrated previously⁵ that a nitrile-bonded phase column can be used to separate styrene oligomers.

In this paper, we show that styrene oligomers can be separated on a phenyl-bonded phase using tetrahydrofuran–water, acetonitrile–water, hexane and tetrahydrofuran–hexane eluents. Significant differences in retention are observed among the various mobile phase systems for oligomers of the same length and the same end-group. The selectivity comes mainly from the interaction of the phenyl-groups of the styrene oligomers and the phenyl-groups on the stationary phase. The importance of this specific interaction diminishes as tetrahydrofuran and acetonitrile fraction increase. In pure tetrahydrofuran eluent, the phenyl-bonded phase column becomes a size exclusion medium⁸. The ability of the phenyl-bonded phase to separate styrene oligomers of increasing degree of polymerization in both polar acetonitrile–water and nonpolar (hexane, or hexane–tetrahydrofuran) eluents blurs the distinction between reversed-phase and normal-phase modes of retention. In both modes, retention decreases as the volume fraction ϕ of the stronger solvent increases in the mobile phase. This further confirms our view^{8,12,13} that chemically-bonded phases behave as multi-mode substrate.

Snyder's¹⁴ formulation of the linear relationship between capacity factor ($\log k'$) and volume fraction ϕ of organic solvent in the aqueous mobile phase is also applicable to the binary solvent systems used for separating styrene oligomers on phenyl-bonded phase. Here ϕ refers to the volume fraction of the stronger solvent for the oligomers. Martin's¹⁵ equation, which predicts oligomer $\log k'$ values are directly proportional to the degree of polymerization (n), also holds for the phenyl-bonded phase. An equation incorporating both relationships can be written

$$\log k' = (A - B\phi) + (C - D\phi)n \quad (1)$$

where A , B , C and D are constants for a given binary solvent system. For constant volume fraction ϕ , *i.e.* isocratic elution, eqn. 1 is identical to Martin's equation. For constant n , *i.e.* comparing the same oligomer peak at different solvent compositions, eqn. 1 can be written as

$$\log k' = (A + Cn) - (B + Dn)\phi \quad (2)$$

which is the same form as Snyder's equation

$$\log k' = \log k_s - S\phi \quad (3)$$

Here, k_s is the solute k' value in the pure poorer solvent, and S is the slope of the $\log k'$ vs. ϕ plot. A recent study¹⁹ indicates that the retention of polyethylene glycol oligomers also follows eqn. 1. The fitness of eqn. 1 with some other oligomeric and homologous series is currently under investigation.

EXPERIMENTAL

HPLC

The chromatographic system included a Perkin-Elmer 2/2 pump, a Beckman

165 variable-wavelength detector and a Perkin-Elmer Sigma 10B chromatography data system. The UV detector was set at a wavelength of 260 nm. A 25 cm \times 4.6 mm Excaliber Spherisorb S5P (5 μ m) phenyl-bonded phase column (Applied Science) was used for the entire experiment. The retention volume of carbon tetrachloride in hexane (3.32 ml) was taken to be the void volume for the capacity factor (k') calculation. A negative solvent peak (3.30 ml) was observed in tetrahydrofuran–water elutions, so the void volume based on carbon tetrachloride was assumed to be correct. Retention data used for calculations were the values averaged from four duplicate runs of the same isocratic elution. The separations were run at ambient temperature. The flow-rates are described in the figure captions.

Standard

Styrene oligomer standard PS 600 (average mol.wt. 600) was purchased from Perkin-Elmer.

Solvents

Solvents used in this experiment are HPLC grade (Burdick & Jackson Labs., Muskegon, MI, U.S.A.).

RESULTS AND DISCUSSION

Fig. 1 shows a typical separation of the components of polystyrene PS 600 on a 5- μ m phenyl-bonded phase column with pure hexane eluent. Partial resolution is observed of stereoisomers of the individual oligomers, corresponding to syndiotactic, isotactic and atactic microstructures^{3,6}, respectively. Addition of tetrahydrofuran to the hexane mobile phase diminishes the resolution of the stereoisomers, and only the separation of oligomers can be observed. Fig. 2 shows the separation of PS 600 on the same phenyl-bonded phase using acetonitrile–water mobile phase. These two examples demonstrate that the separation of styrene oligomers on the phenyl-bonded phase satisfies both reversed-phase (acetonitrile–water) and normal-phase (hexane) liquid chromatographic definitions. For acetonitrile–water eluents, the mobile phase is more polar than phenyl-bonded stationary phase, and retention decreases as the

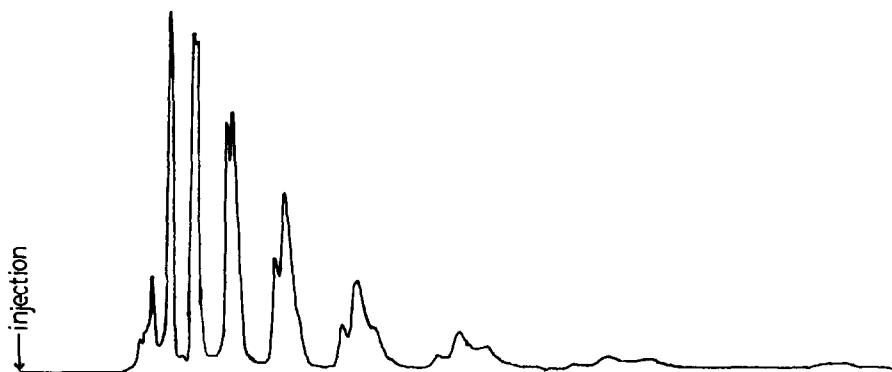


Fig. 1. Separation of styrene oligomers PS600 on phenyl-bonded phase in pure hexane mobile phase, at a flow-rate of 0.2 ml/min, UV detection at 260 nm.

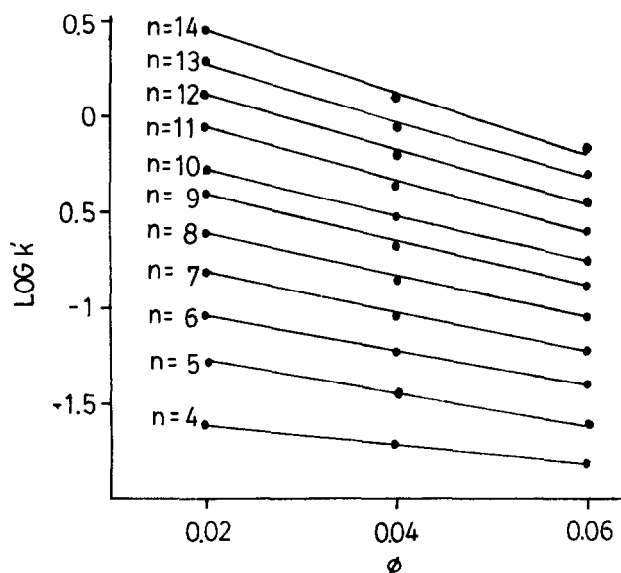


Fig. 4. Dependence of $\log k'$ on mobile phase composition, ϕ , for oligomer peaks of different degree of polymerization (n), flow-rate of 2 ml/min, in tetrahydrofuran-hexane (2:98, 4:96, and 6:94) mobile phase system.

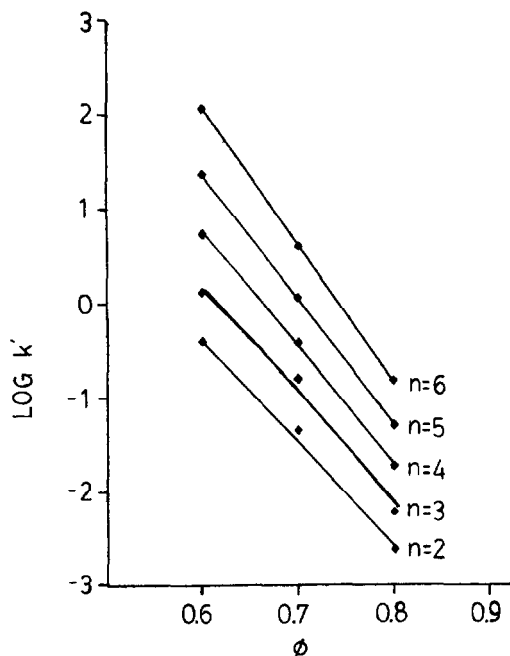


Fig. 5. Dependence of $\log k'$ on mobile phase composition, ϕ , for styrene oligomers peaks of different degree of polymerization (n), flow-rate of 1 ml/min, in acetonitrile-water (60:40, 70:30, and 80:20) mobile phase system.

TABLE I
LOG k' RETENTION DATA FOR STYRENE OLIGOMERS

Calculated values in parentheses are from eqn. 1 with parameters of Table II.

n	Acetonitrile-water			Tetrahydrofuran-water			Tetrahydrofuran-hexane		
	φ			φ			φ		
	0.6	0.7	0.8	0.64	0.67	0.70	0.02	0.04	0.06
2	-0.40 (-0.45)	-1.33 (-1.51)	-2.63 (-2.57)	-0.30 (-0.20)	-0.63 (-0.56)	-1.00 (-0.92)	-2.22 (-2.02)		
3	0.14 (0.19)	-0.89 (-0.96)	-2.22 (-2.12)	-0.05 (-0.02)	-0.41 (-0.40)	-0.81 (-0.79)	-1.85 (-1.80)	-2.02 (-1.85)	
4	0.74 (0.83)	-0.40 (-0.42)	-1.74 (-1.67)	0.19 (0.16)	-0.21 (-0.25)	-0.64 (-0.66)	-1.62 (-1.58)	-1.71 (-1.67)	-1.82 (-1.75)
5	1.37 (1.46)	0.08 (0.12)	-1.30 (-1.22)	0.39 (0.34)	-0.04 (-0.09)	-0.49 (-0.53)	-1.28 (-1.37)	-1.47 (-1.48)	-1.62 (-1.59)
6	2.06 (2.10)	0.61 (0.66)	-0.82 (-0.78)	0.59 (0.52)	0.11 (0.06)	-0.35 (-0.40)	-1.03 (-1.15)	-1.24 (-1.29)	-1.40 (-1.59)
7		1.20 (1.20)	-0.25 (-0.33)	0.75 (0.70)	0.27 (0.22)	-0.23 (-0.26)	-0.81 (-0.93)	-1.05 (-1.10)	-1.22 (-1.26)
8			0.20 (0.12)	0.91 (0.88)	0.40 (0.38)	-0.11 (-0.13)	-0.61 (-0.72)	-0.86 (-0.91)	-1.03 (-1.10)
9			0.78 (0.56)	1.07 (1.06)	0.53 (0.53)	0.02 (0.002)	-0.41 (-0.50)	-0.70 (-0.72)	-0.88 (-0.94)
10				1.21 (1.24)	0.66 (0.69)	0.11 (0.13)	-0.23 (-0.28)	-0.53 (-0.53)	-0.73 (-0.78)
11				1.36 (1.42)	0.78 (0.84)	0.22 (0.27)	-0.05 (-0.07)	-0.37 (-0.34)	-0.58 (-0.62)
12							0.13 (0.15)	-0.21 (-0.15)	-0.44 (-0.46)
13							0.30 (0.37)	-0.07 (0.04)	-0.30 (-0.30)
14							0.47 (0.58)	0.08 (0.22)	-0.17 (-0.13)

values of capacity factor ($\log k_s$) and slope (S) are calculated from eqn. 3 and are listed in Table II. These isocratic data can be fitted to eqn. 1 as

$$\log k' = U + Vn \tag{4}$$

$$U = A - B\varphi \tag{5}$$

and

$$V = C - D\varphi \tag{6}$$

The U and V data in Table II confirm the linear relationships of U and V as a function of φ (as depicted in Figs. 10-12). In Table II the constants A , B , C and D are also given.

Comparing eqns. 2 and 3, S corresponds to $(B + Dn)$; and $\log k_s$ to $(A + Cn)$, i.e. S and $\log k_s$ are a form of the Martin equation as shown at Figs. 13 and 14. The

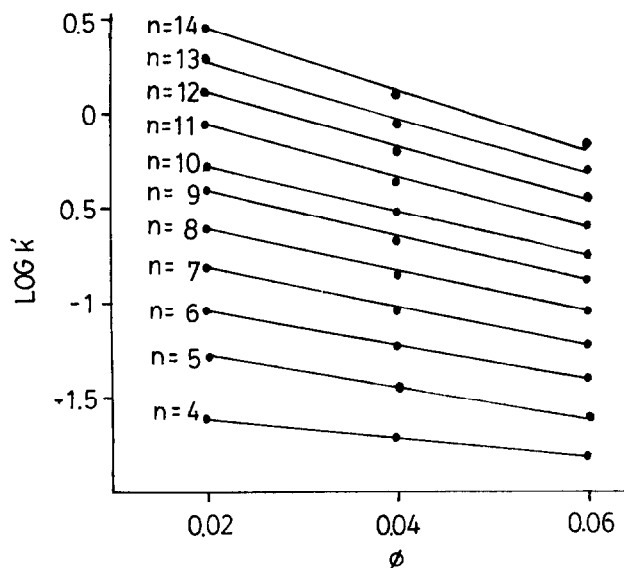


Fig. 4. Dependence of $\log k'$ on mobile phase composition, ϕ , for oligomer peaks of different degree of polymerization (n), flow-rate of 2 ml/min, in tetrahydrofuran-hexane (2:98, 4:96, and 6:94) mobile phase system.

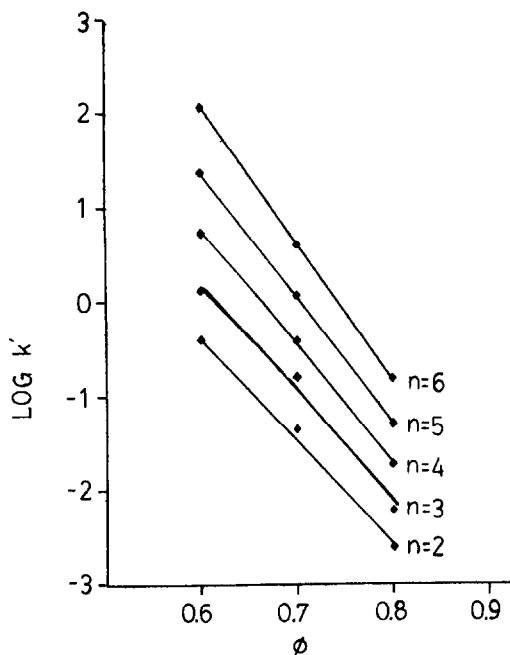


Fig. 5. Dependence of $\log k'$ on mobile phase composition, ϕ , for styrene oligomers peaks of different degree of polymerization (n), flow-rate of 1 ml/min, in acetonitrile-water (60:40, 70:30, and 80:20) mobile phase system.

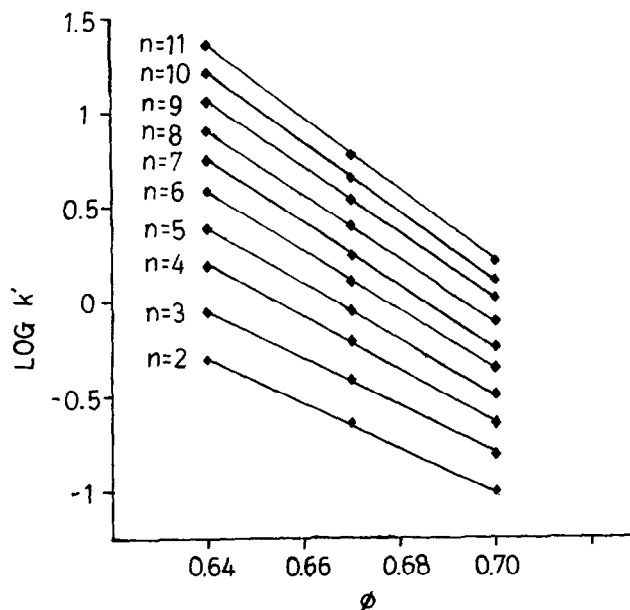


Fig. 6. Dependence of $\log k'$ on mobile phase composition, ϕ , for styrene oligomer peaks of different degree of polymerization (n), flow-rate of 0.5 ml/min, in tetrahydrofuran-water (64:36, 67:33, and 70:30) mobile phase system.

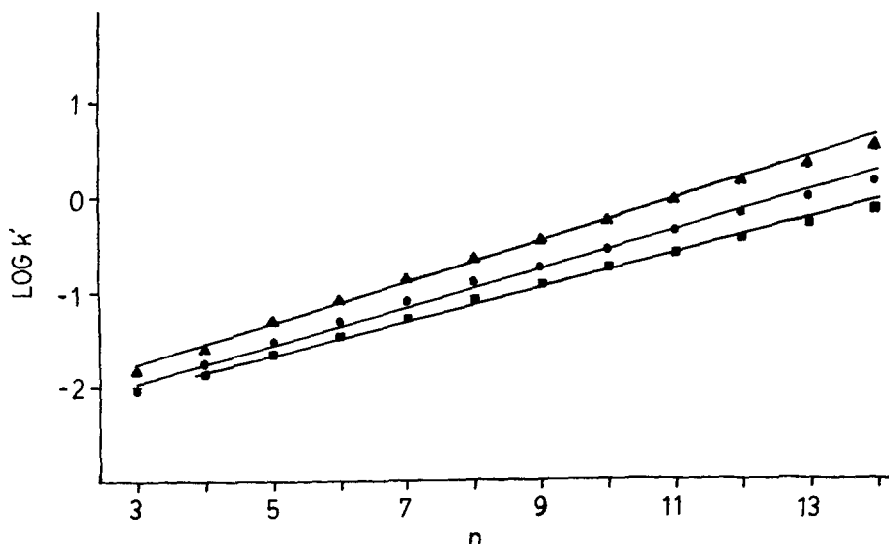


Fig. 7. Verification of Martin equation for styrene oligomers of different degree of polymerization (n) in tetrahydrofuran-hexane mobile phase. \blacktriangle , $\phi = 0.02$ (2:98); \bullet , $\phi = 0.04$ (4:96); \blacksquare , $\phi = 0.06$ (6:94).

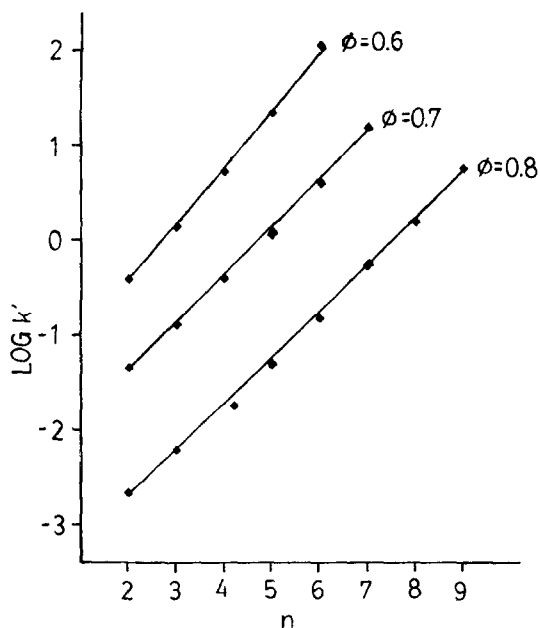


Fig. 8. Verification of Martin equation for styrene oligomers of different degree of polymerization (n) in acetonitrile-water (60:40, 70:30, and 80:20) mobile phase.

linear dependence of S values on the degree of polymerization (n) is in agreement with the results of Tanaka and Thorton¹⁶. As is clear from eqn. 3, and as seen in Fig. 13, the weaker the solvent the larger the slope of the plot of S vs. n . Tetrahydrofuran is a better solvent for styrenes than acetonitrile. As expected, the slopes of S vs. n plot for tetrahydrofuran-water and tetrahydrofuran-hexane mobile phase systems are the same.

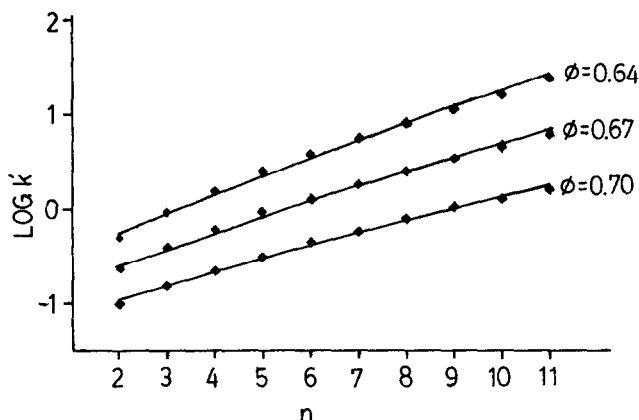


Fig. 9. Verification of Martin equation for styrene oligomers of different degree of polymerization (n) in tetrahydrofuran-water (64:36, 67:33, and 70:30) mobile phase.

TABLE II

VALUES OF LOG k_s , S , U , V , A , B , C and D FOR STYRENE OLIGOMERS ON PHENYL-BONDED PHASE

Acetonitrile-water			Tetrahydrofuran-water			Tetrahydrofuran-hexane		
n	$\log k_s$	S	n	$\log k_s$	S	n	$\log k_s$	S
2	6.261	10.995	2	7.183	11.688	5	-1.126	8.303
3	7.151	11.598	3	8.157	12.808	6	-0.861	9.099
4	8.169	12.315	4	9.094	13.902	7	-0.614	10.306
5	9.345	13.257	5	9.817	14.72	8	-0.172	19.656
6	10.653	14.319	6	10.503	15.507	9	-0.199	11.659
7	11.407	14.5	7	11.179	16.292	10	0.005	11.659
8	13.536	16.675	8	11.787	16.992	11	0.198	13.25
9	14.759	17.477	9	12.274	17.517	12	0.394	14.223
			10	12.939	18.325	13	0.577	14.986
			11	13.539	19.035	14	0.764	15.952
ϕ	U	V	ϕ	U	V	ϕ	U	V
0	3.925	1.098	0	6.189	0.686	0.02	-2.45	0.218
0.6	-1.678	0.615	0.64	-0.566	0.181	0.04	-2.417	0.185
0.7	-2.388	0.504	0.67	-0.855	0.154	0.06	-2.395	0.163
0.8	-3.677	0.487	0.70	-1.198	0.134			
A	3.943			6.189			-2.476	
B	9.316			10.540			-1.375	
C	1.093			0.686			0.244	
D	0.791			0.791			1.375	

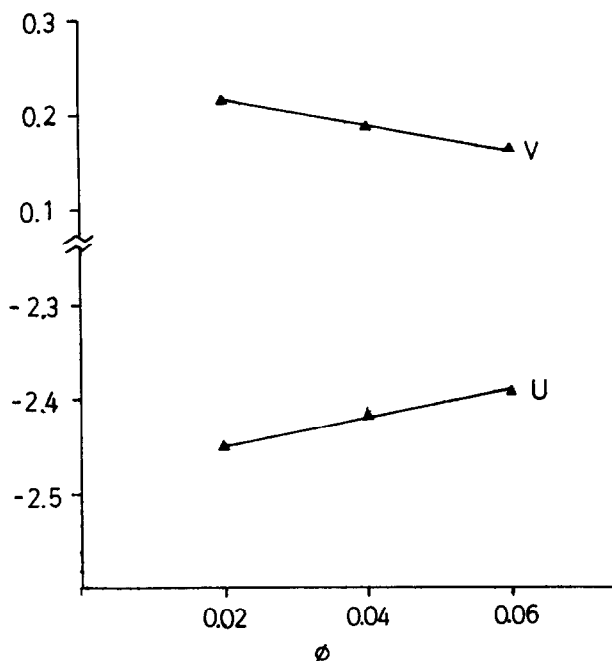


Fig. 10. Dependence of U and V on the mobile phase composition, ϕ , in tetrahydrofuran-hexane (2:98, 4.96 and 6:94) mobile phase.

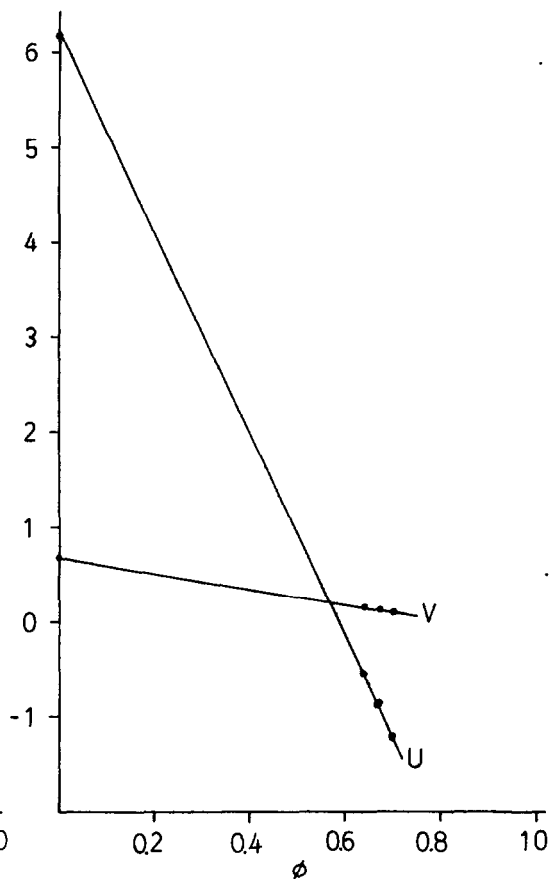
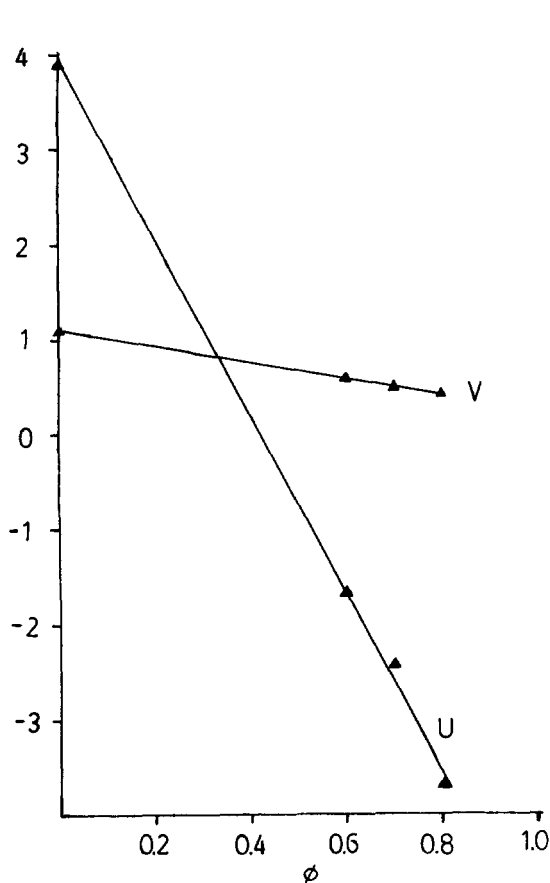


Fig. 11. Dependence of U and V on the mobile phase composition, ϕ , in acetonitrile-water (60:40, 70:30, and 80:20) mobile phase.

Fig. 12. Dependence of U and V on the mobile phase composition, ϕ , in tetrahydrofuran-water (64:36, 67.33, and 70:30) mobile phase.

As listed in Table II and as seen in Fig. 14, the extrapolated values of capacity factor ($\log k_s$) in aqueous mobile phase derived from tetrahydrofuran-water system are different from those of acetonitrile-water system. This reflects that the configuration of polymeric series is influenced by the surrounding mobile phase solution. Especially, at lower concentration of organic solvents, the styrene oligomers might fold into different degree of compactness in different solution environment and have different surface area to contact with phenyl-bonded stationary phase, which will influence the retention of styrenes. As expected, larger differences in $\log k_s$ values are observed for the larger molecules. The same kind of folding and unfolding structures of polymers can also be expected from using the same composition of mobile phase but running at different temperature, and this has been demonstrated by Larman *et al.*².

We further extend the application of eqn. 1 to the retention data of styrene oligomers at other liquid chromatographic system. Table III lists the experimental

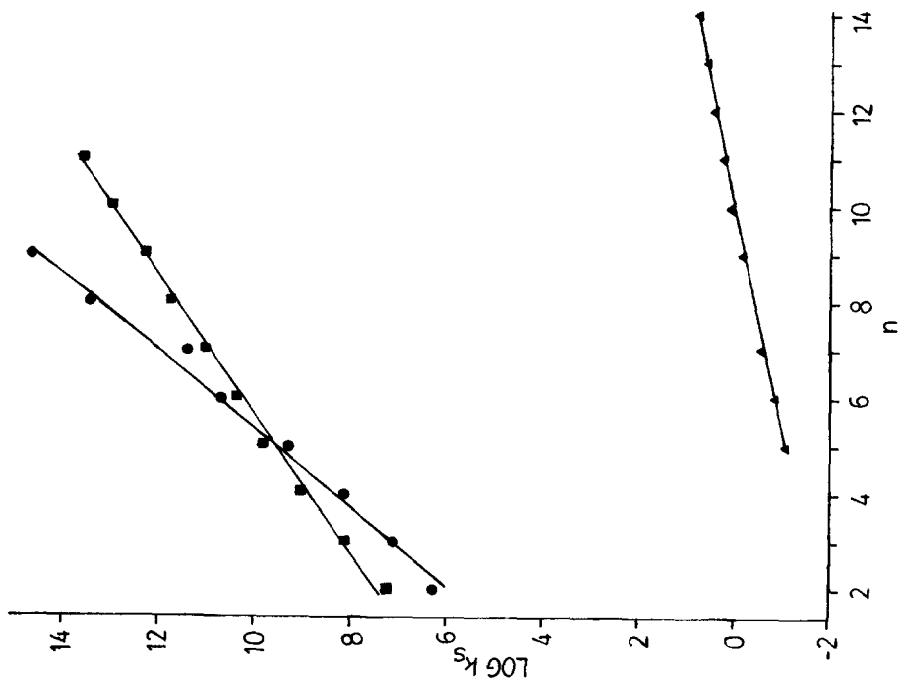
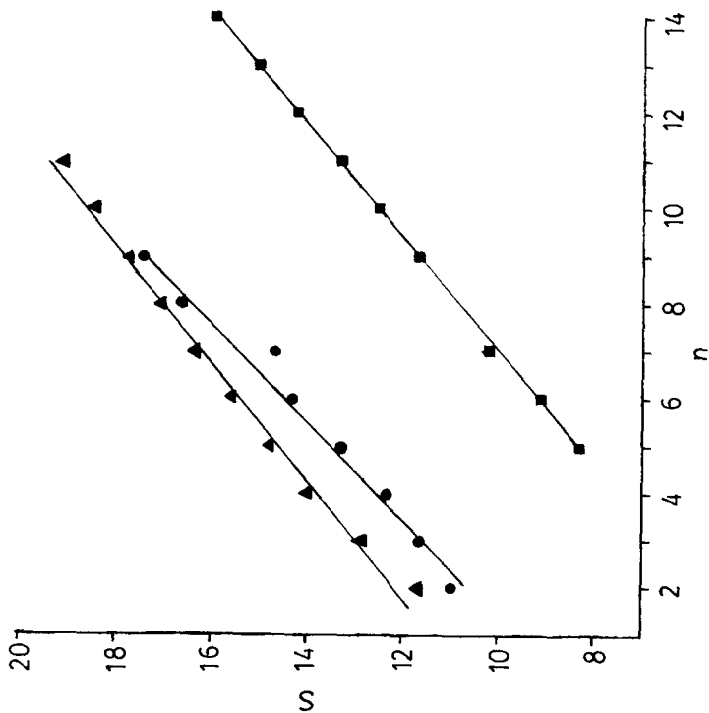


Fig. 13 Dependence of S on the degree of polymerization, n . \blacktriangle , Tetrahydrofuran-water; \bullet , acetonitrile-water; \blacksquare , tetrahydrofuran-hexane.

Fig. 14. Dependence of $\log k_s$ on the degree of polymerization, n . \bullet , Acetonitrile-water; \blacksquare , tetrahydrofuran-water; \blacktriangle , tetrahydrofuran-hexane; \blacktriangle , tetrahydrofuran-hexane. $\log k_s$ is the logarithm of the rate constant for the propagation step in the anionic polymerization of styrene in the corresponding solvent and tetrahydrofuran under mobile phase.

TABLE III

LOG *k'* RETENTION DATA OF STYRENE OLIGOMERS ON OCTADECYL-BONDED PHASE IN TETRAHYDROFURAN-WATER MOBILE PHASE
 Experimental data taken from ref. 2, p. 174. Calculated values in parentheses are from eqn. 1. ODS reversed-phase columns of different average pore diameter were used. For 6 nm: *A* = 2.853, *B* = 3.893; *C* = 0.358; *D* = 0.393; for 15 nm: *A* = 2.55, *B* = 3.72, *C* = 0.38, *D* = 0.436; for 30 nm: *A* = 2.262, *B* = 3.853, *C* = 0.325, *D* = 0.374.

<i>n</i>	Average pore diameter (nm)												
	6				15				30				
<i>φ</i>	0.7	0.72	0.75	0.78	0.65	0.68	0.70	0.72	0.75	0.63	0.65	0.68	0.70
2	0.27 (0.29)	0.18 (0.20)	0.04 (0.06)	-0.10 (-0.08)	0.30 (0.32)	0.17 (0.17)	0.08 (0.09)	-0.02 (0.004)	-0.16 (-0.13)	-0.04 (0.01)	-0.13 (-0.08)	-0.27 (-0.22)	-0.34 (-0.30)
3	0.37 (0.37)	0.27 (0.27)	0.12 (0.12)	-0.03 (-0.03)	0.41 (0.42)	0.27 (0.27)	0.17 (0.17)	0.07 (0.07)	-0.08 (-0.08)	0.09 (0.10)	0.02 (0.001)	-0.16 (-0.14)	-0.25 (-0.24)
4	0.47 (0.46)	0.36 (0.35)	0.19 (0.18)	0.03 (0.02)	0.53 (0.52)	0.36 (0.35)	0.26 (0.24)	0.15 (0.14)	-0.02 (-0.3)	0.20 (0.19)	0.09 (0.08)	-0.09 (-0.07)	-0.17 (-0.18)
5	0.56 (0.55)	0.44 (0.43)	0.26 (0.25)	0.09 (0.07)	0.63 (0.62)	0.46 (0.44)	0.35 (0.32)	0.23 (0.23)	0.05 (0.02)	0.31 (0.28)	0.18 (0.16)	0.01 (-0.004)	-0.10 (-0.12)
6	0.64 (0.63)	0.52 (0.50)	0.32 (0.31)	0.14 (0.12)	0.73 (0.71)	0.53 (0.52)	0.41 (0.39)	0.34 (0.33)	0.09 (0.08)	0.40 (0.37)	0.27 (0.25)	0.08 (0.07)	-0.03 (-0.05)
7	0.73 (0.72)	0.59 (0.58)	0.39 (0.37)	0.19 (0.17)	0.82 (0.81)	0.61 (0.60)	0.48 (0.47)	0.40 (0.40)	0.14 (0.13)	0.49 (0.46)	0.35 (0.35)	0.15 (0.14)	0.03 (0.01)
8	0.80 (0.80)	0.66 (0.66)	0.44 (0.44)	0.24 (0.22)	0.91 (0.90)	0.68 (0.69)	0.54 (0.54)	0.46 (0.47)	0.19 (0.18)	0.57 (0.55)	0.43 (0.41)	0.21 (0.21)	0.09 (0.07)
9		0.73 (0.73)	0.50 (0.50)	0.28 (0.27)		0.76 (0.77)	0.61 (0.60)	0.52 (0.53)	0.24 (0.24)	0.65 (0.65)	0.50 (0.49)	0.28 (0.28)	0.15 (0.14)
10		0.79 (0.81)	0.55 (0.56)	0.33 (0.32)		0.83 (0.86)	0.67 (0.69)	0.57 (0.60)	0.29 (0.29)	0.73 (0.73)	0.57 (0.58)	0.34 (0.35)	0.20 (0.20)
11			0.60 (0.63)	0.36 (0.37)		0.90 (0.94)	0.74 (0.77)	0.63 (0.66)	0.31 (0.34)	0.80 (0.82)	0.63 (0.66)	0.40 (0.42)	0.25 (0.26)
12			0.65 (0.69)	0.41 (0.42)					0.38 (0.40)	0.88 (0.90)	0.71 (0.74)	0.45 (0.49)	0.30 (0.32)

TABLE IV
LOG k' RETENTION DATA OF HOMOLOGOUS SERIES OF N-ALKYLPHALIMIDES ON OCTYL-BONDED PHASE IN METHANOL-WATER MOBILE PHASE

Data taken from ref. 17, p. 51. Calculated values in parentheses are from eqn. 1 with parameters of $A = 2.147$, $B = 4.244$, $C = 1.048$ and $D = 0.924$. A , B , C and D are obtained from eqns. 3-6 using retention data from this table.

Alkyl group	n	ϕ	I															
			0.4	0.5	0.55	0.6	0.65	0.7	0.75	0.8	0.85	0.9	0.95	1				
H	0	0.59 (0.45)	-0.07 (0.02)	-0.46 (-0.19)	-0.56 (-0.40)	-0.78 (-0.61)	-1.02 (-0.82)	-1.31 (-1.04)	-1.35 (-1.25)	-1.47 (-1.46)	-1.61 (-1.67)	-1.66 (-1.88)	-1.83 (-2.10)					
Methyl	1	1.34 (1.13)	0.59 (0.61)	0.19 (0.35)	-0.02 (0.09)	-0.26 (-0.16)	-0.54 (-0.42)	-0.84 (-0.68)	-0.99 (-0.94)	-1.14 (-1.20)	-	-	-	-	-	-	-	
Ethyl	2	2.12 (1.81)	1.24 (1.20)	0.78 (0.89)	0.47 (0.59)	0.18 (0.28)	-0.15 (-0.02)	-0.47 (-0.33)	-0.67 (-0.63)	-0.89 (-0.94)	-	-	-	-	-	-	-	
Propyl	3	2.85 (2.48)	1.83 (1.78)	1.31 (1.43)	0.95 (1.08)	0.59 (0.73)	0.21 (0.38)	-0.18 (0.03)	-0.45 (-0.32)	-0.73 (-0.67)	-	-	-	-	-	-	-	
Butyl	4	-	2.50 (2.37)	1.94 (1.97)	1.50 (1.58)	1.07 (1.18)	0.61 (0.78)	0.18 (0.38)	-0.15 (-0.01)	-0.46 (-0.41)	-	-	-	-	-	-	-	
Pentyl	5	-	-	2.53 (2.51)	2.03 (2.07)	1.53 (1.62)	1.01 (1.18)	0.52 (0.74)	0.15 (0.30)	-0.25 (-0.15)	-0.58 (-0.59)	-0.92 (-1.03)	-	-	-	-	-	
Hexyl	6	-	-	-	2.56 (3.05)	2.01 (2.56)	1.42 (2.07)	0.88 (1.58)	0.43 (0.60)	-0.01 (0.12)	-0.43 (-0.37)	-0.82 (-1.03)	-1.14 (-1.35)	-	-	-	-	
Heptyl	7	-	-	-	-	2.50 (3.06)	1.84 (2.52)	1.25 (1.98)	0.73 (0.91)	0.23 (0.38)	-0.22 (-0.16)	-0.67 (-0.69)	-1.05 (-1.22)	-	-	-	-	
Octyl	8	-	-	-	-	-	2.97 (3.55)	2.26 (4.13)	1.61 (1.80)	1.03 (1.22)	-0.04 (0.06)	-0.54 (-0.52)	-0.97 (-1.10)	-	-	-	-	
Nonyl	9	-	-	-	-	-	-	2.67 (3.41)	1.97 (2.16)	1.32 (1.53)	0.16 (0.28)	-0.43 (-0.35)	-0.87 (-0.98)	-	-	-	-	
Decyl	10	-	-	-	-	-	-	3.09 (3.86)	2.33 (2.51)	1.61 (1.84)	0.94 (1.16)	-0.29 (-0.18)	-0.77 (-0.86)	-	-	-	-	
Undecyl	11	-	-	-	-	-	-	3.51 (4.31)	2.69 (2.87)	1.91 (2.14)	1.19 (1.43)	-0.15 (-0.01)	-0.71 (-0.62)	-	-	-	-	
Dodecyl	12	-	-	-	-	-	-	-	3.05 (3.22)	2.19 (2.46)	1.44 (1.69)	-0.01 (0.92)	-0.62 (-0.61)	-	-	-	-	
Tetradecyl	14	-	-	-	-	-	-	-	-	-	1.92 (3.07)	1.10 (2.21)	0.27 (0.50)	-0.43 (-0.36)	-	-	-	
Hexadecyl	16	-	-	-	-	-	-	-	-	-	2.42 (1.80)	1.49 (0.84)	0.54 (0.84)	-0.24 (-0.11)	-	-	-	

results of styrene oligomers on octadecyl-bonded reversed-phase taken from ref. 2. These retention data are used to find the constants of A , B , C and D for this reversed-phase system. Eqn. 1 can be written as

$$\log k' = (2.55 - 3.72 \phi) + (0.38 - 0.436 \phi) n \quad (7)$$

In Table III are also listed the calculated values of $\log k'$ using eqn. 7.

Dufek's¹⁷ retention data of a homologous series of N-alkylphthalimides on octyl-bonded phase in methanol-water isocratic elution is also applicable to eqn. 1. These values of $\log k'$ are listed in Table IV.

In summary, the retention behavior of styrene oligomers depends on the competition between the selective interaction of chemically-bonded phase and the solubility of oligomers in mobile phase. This further confirms the previous¹⁸ statement that in chemically-bonded phase LC small molecules of similar type are separated on the basis of their relative solubility in the mobile phase. The importance of mobile phase in chemically-bonded phase LC separations of oligomeric and homologous series is also emphasized.

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