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SOLVENT COMPOSITION EFFECTS ON POLAR SOLUTES WITH A SILICA–DIMETHYL SULFOXIDE–CARBON TETRACHLORIDE CHROMATOGRAPHIC SYSTEM

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SUMMARY

The chromatographic adsorption model of Snyder was considered for the separation of polar solutes on a high-performance μPorasil silica stationary phase. Dimethyl sulfoxide (DMSO)–carbon tetrachloride mobile phases were used to evaluate the ability of the Snyder model to approximately describe the retention of nitrogen heterocycles and hydroxyl aromatics on the silica column. It was found that log k' *vs.* log mole fraction DMSO plots showed good linearity for all the solutes. Nitrogen heterocycles showed slight curvature in the plots, while the more strongly retained hydroxyl aromatics exhibited more linear behavior. Small slope values for the solutes were explained by a vertical adsorption configuration of the solute on the stationary phase.

INTRODUCTION

High-performance liquid chromatography (HPLC) has gained acceptance as a widely used chromatographic tool for the separation of complex organic mixtures. While a majority of chromatographers practice their separations using bonded-phase columns with water–organic mobile phases (*i.e.* reversed-phase systems), normal-phase separations are still of considerable importance. In general, normal-phase systems offer superior separation of compounds into functional classes as well as better resolution of isomeric mixtures[1].

The mechanistic roles of the solute, solvent and stationary phase are often complex and several authors have presented models for normal-phase chromatographic interactions[2–13]. If a chromatographic system can be described by a particular model, then one can predict the retention for solutes at various mobile phase compositions. This can be useful information for selecting mobile phases which will yield an optimum degree of selectivity.

Snyder and co-workers[5,14,15] have developed an adsorption model based upon the displacement of solvent molecules by solute molecules from stationary phase sites. This model has been used to predict retention of solutes in a number of normal-phase systems. Soczewiński and co-workers[2–4] developed a similar model for

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adsorption chromatography. Hurtubise *et al.*[16] concluded that the Snyder and Soczewiński models approximately described the behavior of alkylphenols on μBondapak NH_2. Hussain *et al.*[17] concluded that the Snyder–Soczewiński models also approximated the retention of alkylphenols on high-performance cyano and silica gel stationary phases over certain mobile phase compositions. Snyder and Schunk[18] were able to describe the behavior of solutes on an amino bonded-phase column using the displacement model with mobile phases containing no alcohols. Snyder's displacement model was also successfully applied to an amino bonded-phase by Hammers *et al.*[19], who concluded that the stationary phase was similar to silica gel which was partially deactivated. The solutes investigated displayed the same general elution order but exhibited diminished k' values compared to silica. Weiser *et al.*[20] successfully applied the Snyder model to a high-performance cyanopropyl bonded-phase and also concluded that the column functioned similar to deactivated silica. Hara *et al.*[21] applied the Snyder model to the chromatography of steroid derivatives on silica. The results indicated that the retention of the solutes could be approximated by using Snyder's model.

Scott and co-workers[8–13] have developed a model emphasizing solute–mobile phase interactions. Snyder[22] and Snyder and Poppe[6] have investigated various aspects of the Snyder, Soczewiński, and Scott models. Slaats *et al.*[23] investigated the influence of solute–solvent competition on retention in adsorption chromatography by measurement of activity coefficients in various mobile phases. Jaroniec and co-workers[24–28] have discussed various aspects of adsorption chromatography and derived equations for capacity factors based upon specific solute, solvent and stationary phase interactions.

There have been many investigations in which theoretical adsorption models have been applied to normal-phase chromatographic systems, particularly those utilizing alumina and silica stationary phases. Most of these reports involve the use of low-molecular-weight standard solutes and relatively weak organic modifying solvents. In this work, we have investigated a μPorasil–carbon tetrachloride system modified with a very strong aprotic, dipolar solvent, dimethylsulfoxide (DMSO). In addition, the standards used are polar and have somewhat larger molecular weights compared to compounds used in other studies.

The μPorasil–DMSO–carbon tetrachloride system is a relatively novel chromatographic combination first described by Chmielowiec[29] for the separation of compounds containing different functional classes. Chmielowiec[29] used DMSO–carbon tetrachloride mobile phases on silica to obtain good functional class separation of standard compounds and was able to apply this system to coal liquids. Ruckmick and Hurtubise[30] reported excellent separation of nitrogen heterocycles and hydroxyl aromatics utilizing DMSO–carbon tetrachloride mobile phases on μPorasil in a later publication. While silica has historically been a very common adsorbent, the use of DMSO–carbon tetrachloride mobile phases is apparently a new approach to gaining functional class selectivity on this adsorbent. Because of the exceptional selectivity, it was of interest to investigate the applicability of the Snyder adsorption model to the silica–DMSO–carbon tetrachloride chromatographic system.

EXPERIMENTAL

Experimental equipment, conditions, procedures, and k' values for DMSO–carbon tetrachloride mobile phases 0.25:99.75, 0.50:99.50, 1.00:99.00 and 1.25:98.75 have been previously reported[30].

Computer

Linear regression calculations were carried out using a Hewlett-Packard HP-87 computer with an HP Model 82901M flexible disk drive and HP Model 82905B printer.

RESULTS AND DISCUSSION

Theoretical considerations

The following equation forms the basis of the Snyder model

$$X_m + nS_a \leftrightarrows X_a + nS_m \tag{1}$$

The subscripts m and a refer to molecules in the mobile and adsorbed phases, respectively. The adsorption of a solute X results in the displacement of n molecules of adsorbed solvent. The following equation was derived by Snyder[22] for binary mobile phases and was applied to the μPorasil column in this work

$$\log k' = \log k'_0 - \left(\frac{A_s}{n_b}\right) \log X_s \tag{2}$$

where A_s is the solute molecular area, n_b is the molecular area of the strong solvent, k' is the capacity factor of a solute eluted with a binary mobile phase, k'_0 is the capacity factor of a solute eluted with only the strong solvent, and X_s is the mole fraction of the strong solvent in the binary mobile phase.

The A_s values for the solutes in Table I were calculated according to Snyder[31] using the following formula for substituted aromatic hydrocarbons

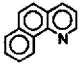
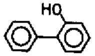
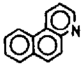
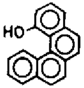
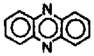
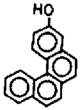
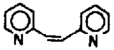
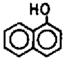
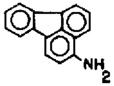
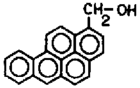
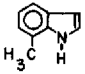
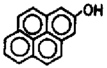
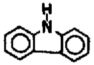
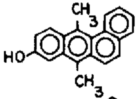
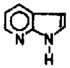
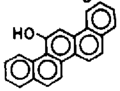
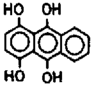
$$A_s = 6 + 0.80\,(h - 6) + 0.25\,(c - h) \tag{3}$$

where h is the number of aromatic hydrogens in the solute molecule and c is the number of aromatic carbons. For nitrogen heterocycles, when =N– replaces =CH–, A_s increases by *ca.* 8 units for SiO_2 (ref. 31). For hydroxyl aromatics, each –OH increases A_s by 7.6 units. For other functionality, –NH increases A_s by 8.4 units, aromatic NH_2 increases A_s by 8.7 units, and aliphatic –OH increases A_s by 8.5 units[31].

Snyder[22] has indicated that the slope (A_s/n_b) for monofunctional solutes is equal to the ratio of the number of solute to polar solvent molecules which are exchanged on the adsorbent surface. Snyder[22] has also stated that the experimental A_s value for a solute molecule is a function of it's configuration in the adsorbed state.

TABLE I

COMPOUNDS INVESTIGATED ON μPORASIL

No.	*Compound*	*Structure*	*No.*	*Compound*	*Structure*
Basic nitrogen heterocycles			*Monohydroxyl aromatic compounds*		
1	7,8-Benzoquinoline		11	2-Phenylphenol	
2	5,6-Benzoquinoline		12	4-Phenylphenol	
3	Quinoline		13	1-Hydroxybenzo[*c*]phenanthrene	
4	4-Azafluorene				
5	Phenazine		14	3-Hydroxybenzo[*c*]phenanthrene	
6	1,2-Bis(2-pyridyl)ethylene		15	1-Naphthol	
Amino substituted compound					
7	3-Aminofluoranthene		16	1-(Hydroxymethyl)benzo[*a*]pyrene	
Pyrrolic substituted compounds					
8	7-Methylindole		17	2-Hydroxypyrene	
9	Carbazole		18	7,12-Dimethyl-9-hydroxybenzo[*a*]anthracene	
10	7-Azaindole		19	13-Hydroxypicene	
			Tetrahydroxyl aromatic compound		
			20	1,4,9,10-Tetrahydroxyanthracene	

Plots of log k' vs. log mole fraction DMSO

The nitrogen heterocycles and hydroxyl aromatics which were investigated appear in Table I. It is apparent from eqn. 2 that if the Snyder model can approximate the behavior of the μPorasil–DMSO–carbon tetrachloride system, log k' *vs.* log mole fraction DMSO plots should be linear. Table II shows that the linear correlation coefficients for the solutes ranged from 0.947 to 0.999. The lower correlation coefficients found for the nitrogen heterocycles were probably due to the very weak retention of these compounds ($k' < 1.00$ in all the DMSO–carbon tetrachloride mobile phases) compared to the hydroxyl aromatics. In one extreme case, phenazine eluted at the void volume of the column with both 1.00:99.00 and 1.25:98.75 DMSO–carbon tetrachloride mobile phases.

The hydroxyl aromatics retained more strongly and exhibited higher correlation coefficients ranging from 0.969 to 0.999. With the exception of phenazine and 2,2-bis(2-pyridyl)ethylene, all the solutes showed slight curvature in the plots. This is illustrated in Fig. 1 for 7-methylindole. Table II shows that the more strongly retained hydroxyl aromatic solutes generally gave higher correlation coefficients. This more linear behavior of hydroxyl aromatics is illustrated in Fig. 2 for 13-hydroxypicene.

TABLE II

A_s/n_b, INTERCEPT AND CORRELATION COEFFICIENT VALUES FOR LOG k' *vs.* LOG MOLE FRACTION DMSO PLOTS

Mobile phase compositions: 99.75:0.25, 99.50:0.50, 99:1.00, and 98.75:1.25 (carbon tetrachloride–DMSO).

Compound	*Experimental,* A_s/n_b	*Intercept*	*Correlation coefficient*
Nitrogen heterocycles			
7,8-Benzoquinoline	0.25	−1.50	0.947
7-Methylindole	0.53	−0.69	0.990
Carbazole	0.61	−0.82	0.994
5,6-Benzoquinoline	0.75	−2.19	0.967
4-Azafluorene	0.79	−2.42	0.962
2,2-Bis(2-pyridyl)ethylene	0.87	−2.29	0.995
Quinoline	0.93	−2.77	0.960
7-Azaindole	1.32	−2.28	0.990
Phenazine	1.36	−4.47	0.992
Amino substituted compound			
3-Aminofluoranthene	0.40	0.07	0.979
Hydroxyl aromatics			
1,4,9,10-Tetrahydroxyanthracene	0.39	−0.79	0.989
1-Hydroxybenzo[*c*]phenanthrene	0.40	−0.27	0.981
2-Phenylphenol	0.42	−0.35	0.969
1-Naphthol	0.72	−0.84	0.995
4-Phenylphenol	0.73	−0.82	0.997
1-(Hydroxymethyl)benzo[*a*]pyrene	0.75	−0.85	0.996
7,12-Dimethyl-9-hydroxybenz[*a*]pyrene	0.77	−0.89	0.994
3-Hydroxybenzo[*c*]phenanthrene	0.79	−0.84	0.999
13-Hydroxypicene	0.79	−0.91	0.999
2-Hydroxypyrene	0.80	−0.85	0.998

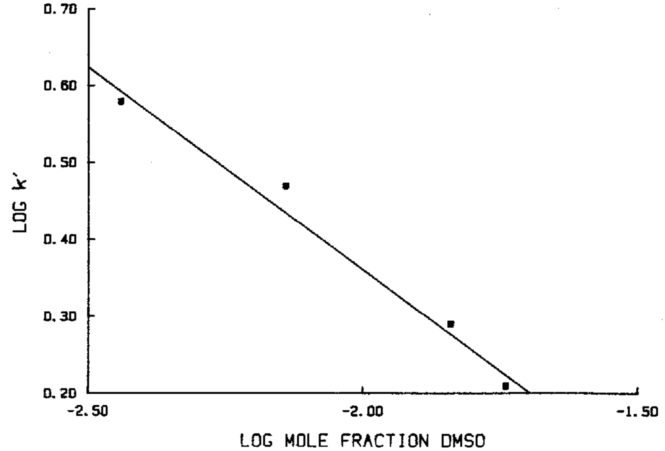


Fig. 1. Plot of log k' vs. log mole fraction DMSO for 7-methylindole using mobile phases of DMSO–carbon tetrachloride (0.25:99.75, 0.50:99.50, 1.00:99.00 and 1.25:98.75).

Theoretical interpretations

It can be seen from Table II that the A_s/n_b values for all the compounds are less than one except for the difunctional solutes, 7-azaindole and phenazine. Soczewiński and Golkiewiecz[32] have indicated that a slope value of very close to one is expected for monofunctional solutes for plots of R_M vs. X_s. Snyder[22,33] has stated that for silica systems which employ polar solvents and solutes the A_s/n_b (see eqn. 2) term is approximately equal to the number of polar solute groups adsorbed on the stationary phase surface. With predicted A_s/n_b values, flatwise adsorption of the solute onto the adsorbent is normally assumed. Assuming flatwise adsorption, one can calculate A_s/n_b values as described in the experimental section. Snyder[34] has stated that for all non-aromatic solvents with solvent strength values larger than 0.38, a n_b

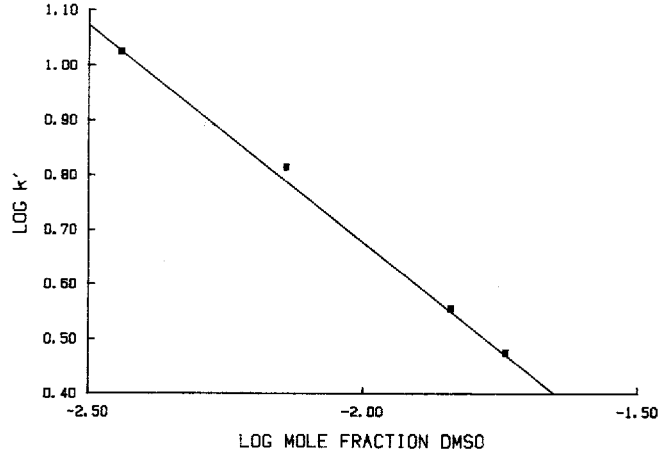


Fig. 2. Plot of log k' vs. log mole fraction DMSO for 13-hydroxypicene using mobile phases of DMSO–carbon tetrachloride (0.25:99.75, 0.50:99.50, 1.00:99.00 and 1.25:98.75).

value of *ca.* 10 is required to compensate for strong solvent stationary phase localization effects observed on alumina and particularly silica. Snyder[34] gives a solvent strength value of 0.62 for DMSO on alumina which indicates that on silica, a n_b value of 10 would be appropriate. Using eqn. 3 and assuming $n_b = 10$, the calculated A_s/n_b values for flat adsorption of the solutes, described in Table I, are compared with the experimental A_s/n_b values in Table III.

It is evident in Table III that the experimental A_s/n_b values are significantly smaller than the A_s/n_b values which were calculated assuming flatwise adsorption. Snyder[22] states that experimental A_s values can be smaller than the calculated values if vertical adsorption of the solute onto the stationary phase occurs. The experimental A_s/n_b values in Table III suggest that vertical adsorption is taking place due to the relatively small numerical values obtained. In fact, for very strong solvents and silica as adsorbent, vertical adsorption for many solutes is favored[22].

It is interesting to note that difunctional solutes such as phenazine and 7-azaindole have much larger slopes than the other monofunctional solutes. These compounds may be able to adsorb somewhat more flatly on the silica surface. The experimental A_s/n_b values of phenazine and 7-azaindole are 1.36 and 1.32, respectively, which are larger than the A_s/n_b experimental values for monosubstituted solutes in Table III. If one assumes vertical adsorption of the solute onto the adsorbent surface, then the polar functional group of the solute should be the primary site of interaction with the surface silanol groups. If one only considers the A_s value for the polar functional group and disregards the molecular area of the rest of the molecule, a better calculated A_s/n_b value should be obtained. In Table III it can be seen that calculated A_s/n_b values in the third column of numbers are much closer to experimental A_s/n_b values when only A_s for the functional group is considered. An approximate vertical adsorption configuration may actually be more descriptive for the nitrogen heterocycles as indicated in Table III. Since the nitrogen atom is incorporated into the ring system, the molecule is unable to interact in the same fashion with the silica surface as a functional group projecting from the aromatic ring system such as a hydroxyl group in 1-naphthol. For the solute phenazine, only one of the two nitrogen atoms can be considered in the A_s calculation if the molecule is to assume an approximate vertical configuration because the nitrogen atoms are substituted opposite one another in the ring (see Table I). For this compound, the two aromatic carbons on either side of the nitrogen may contribute to the adsorption interaction. If one includes one nitrogen and two aromatic carbons into the A_s value for adsorption, an A_s/n_b value of 0.98 is obtained which is somewhat closer to the experimental A_s/n_b value. However, because of the limited data in this work, it is not possible to determine specifically the exact configuration of the solute molecules.

The solute 1,2-bis(2-pyridyl)ethylene has two nitrogens which could adsorb onto the silica surface simultaneously in a "edgewise" fashion. If one assumes this kind of "edgewise" adsorption and includes both nitrogens in the A_s/n_b calculation a value of 1.60 is obtained. The experimental value is 0.87 which suggests that only one nitrogen atom is adsorbing onto the silica surface. 3-Aminofluoranthene has a $-NH_2$ group substituted onto the aromatic ring system and should therefore be capable of vertical adsorption. The calculated A_s/n_b value for vertical adsorption is roughly twice as large as the experimental value indicating that other interactions are occurring.

TABLE III

CALCULATED AND EXPERIMENTAL A_s/n_b VALUES

Compound	A_s/n_b* *Calculated (flat adsorption)*	A_s/n_b *Experimental*	A_s/n_b** *Calculated (approximate vertical adsorption)*
Basic nitrogen heterocycles			
Quinoline	1.61	0.93	0.80
4-Azafluorene	1.80	0.79	0.80
7,8-Benzoquinoline	1.82	0.25	0.80
5,6-Benzoquinoline	1.82	0.75	0.80
1,2-Bis(2-pyridyl)ethylene	3.00	0.87	1.60
Phenazine	2.62	1.36	0.80
Pyrrolic substituted			
7-Methylindole	1.81	0.53	0.84
Carbazole	1.84	0.61	0.84
7-Azaindole	2.53	1.32	1.60 *(vertical adsorption)*
Amino substituted			
3-Aminofluoranthene	1.94	0.40	0.87
Monohydroxyl aromatics			
1-Naphthol	1.57	0.72	0.76
2-Hydroxypyrene	1.83	0.80	0.76
2-Phenylphenol	1.57	0.42	0.76
4-Phenylphenol	1.57	0.73	0.76
1-Hydroxybenzo[*c*]phenanthrene	2.04	0.40	0.76
3-Hydroxybenzo[*c*]phenanthrene	2.04	0.79	0.76
7,12-Dimethyl-9-hydroxybenz[*a*]-anthracene	2.15	0.77	0.76
13-Hydroxypicene	2.20	0.79	0.76
1-(Hydroxymethyl)benzo[*a*]pyrene	2.32	0.75	0.85
Tetrahydroxyl aromatic			
1,4,9,10-Tetrahydroxyanthracene	4.06	0.39	1.52

* A_s for entire molecule considered.

** Only A_s for functional group considered.

Since hydroxyl groups are substituted onto the aromatic ring system and project out from the rest of the molecule, vertical adsorption of hydroxyl aromatic compounds should be possible as mentioned earlier. Table III illustrates that very good agreement between experimental and calculated A_s/n_b values are obtained, with the exception of the sterically hindered 1-hydroxybenzo[*c*]phenanthrene and 2-phenylphenol, if vertical adsorption is assumed. 1,4,9,10-Tetrahydroxyanthracene behaves anomalously as discussed previously[30] and exhibits a small experimental A_s/n_b value of 0.39 for a tetrahydroxyl solute. In considering the geometry of this compound (see Table I) only two hydroxyl groups were considered in the vertical A_s/n_b calculation.

Steric hindrance to the nitrogen atom or the hydroxyl group appears to significantly decrease the experimental A_s/n_b value (see Tables II and III). The isomers, 5,6-benzoquinoline and 7,8-benzoquinoline, yield slope values of 0.75 and 0.25 respectively. Similarly, 3-hydroxybenzo[*c*]phenanthrene and 1-hydroxybenzo[*c*]phenanthrene gave slope values of 0.79 and 0.40 respectively.

Soczewiński[3] has stated that similar and possibly identical slopes for solutes with different molecular sizes, but analogous steric conditions for hydrogen bonding with the silanol groups of silica, would indicate vertical orientation of the molecules on the surface. Several of the compounds in Table III have similar experimental slopes but differ widely in size. These data seem to support the conclusions reached by Soczewiński[3]. Because of the complexity of the interactions of polar solutes and polar solvents with silica, additional work is necessary to determine if the simple comparison of experimental A_s/n_b values with calculated A_s/n_b values is highly accurate. Nevertheless, the correlation of the data in Table III is very good.

CONCLUSIONS

Approximate linear log k' *vs.* log mole fraction DMSO plots were obtained for all the solutes investigated. Nitrogen heterocycles exhibited slightly more curvature in the plots, due to the small k' values for these less polar solutes compared to the hydroxyl aromatics. Relatively high correlation coefficient values for the solutes implies that the simple Snyder model can approximately describe the retention behavior of nitrogen heterocycles and hydroxyl aromatics on μPorasil utilizing the DMSO–carbon tetrachloride mobile phases which were investigated. Evidence was presented for the vertical adsorption of hydroxyl aromatics and approximate vertical adsorption of nitrogen heterocycles; however, additional work is needed to fully substantiate the vertical adsorption of the molecules.

Vertical adsorption may be favored due to the strong hydrogen bonding interaction of DMSO with surface silanol groups. At low concentrations of DMSO the polar functional group of the solute may vertically interact with silanol groups because adjacent DMSO molecules on nearby silanols may hinder the flatwise adsorption of the solute. Additional experiments are needed to access the importance of localization effects and solute mobile phase interactions[5].

In practical applications the log k' *vs.* log mole fraction DMSO plots should be useful in predicting retention of nitrogen heterocycles and hydroxyl aromatics on μPorasil with the DMSO–carbon tetrachloride mobile phases which were investigated.

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