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## SOLVENT COMPOSITION EFFECTS WITH A CYANO AND A SILICA GEL STATIONARY PHASE IN NORMAL-PHASE LIQUID CHROMATOGRAPHY OF ALKYLPHENOLS AND NAPHTHOLS

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### SUMMARY

Several liquid chromatographic models were investigated with  $\mu$ Bondapak CN and  $\mu$ Porasil stationary phases. *n*-Heptane-2-propanol and *n*-heptane-ethyl acetate mobile phases of different composition were used, and alkylphenols and naphthols were employed as model compounds. The linear relationships obtained from graphs of  $\log k'$  vs.  $\log$  mole fraction of the strong solvent were found useful in understanding the retention behavior of the solutes.

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### INTRODUCTION

Solvent composition effects in normal-phase high-performance liquid chromatography (HPLC) are important in both practical and theoretical work. The role of the mobile phase in effecting separations for liquid-solid adsorption chromatography was discussed by Snyder<sup>1,2</sup> and Snyder and Poppe<sup>3</sup>. Snyder and Glajch<sup>4,5</sup> have considered solvent strength of multicomponent mobile phases in liquid-solid chromatography (LSC). Scott and Kucera<sup>6-10</sup> have studied solute interactions with mobile and stationary phases in LSC with emphasis on silica gel. A molecular model was developed by Soczewinski<sup>11</sup> and Soczewinski and Głokiewicz<sup>12,13</sup> for adsorption chromatography on silica gel in which adsorption from solution was considered the result of competition between the solute and solvent for active sites on the stationary phase. Soczewinski<sup>14</sup> commented on the relationships between his model, the Scott and Kucera<sup>6</sup> model, and the Snyder<sup>1</sup> model. He concluded that all the three models for silica gel yield equivalent results in routine chromatographic work with silica gel. Narkiewicz *et al.*<sup>15</sup> reported the dependence of the capacity ratio on the composition of binary mobile phases with silica gel in liquid-solid adsorption chromatography. Jaroniec and co-workers<sup>16-18</sup> discussed several aspects of liquid-solid adsorption chromatography and developed a new equation for the capacity ratio involving solute-solvent interactions<sup>17</sup>. Callmer *et al.*<sup>19</sup> investigated the retention behavior of alkyl-

phenols in normal-phase HPLC systems on cyano stationary phases. Husain *et al.*<sup>20</sup> discussed the separation of isomeric alkylphenols on silica gel columns of 30 and 5  $\mu\text{m}$  particle size. Hurtubise *et al.*<sup>21</sup> considered the chromatographic models of Snyder<sup>1</sup>; Scott and Kucera<sup>6</sup>, and Soczewinski<sup>11</sup> using an amino-bonded phase. Hennion *et al.*<sup>22</sup> studied the behavior of various solutes on an amino-bonded phase in equilibrium with binary mobile phases.

Our previous work showed that graphs of  $\log k'$  vs. log mole fraction of the strong solvent in a binary mobile phase gave linear relationships for an amino-bonded phase with alkylphenols and naphthols<sup>21</sup>. In this work, experimental data were obtained for several alkylphenols and naphthols in the normal-phase mode on high-performance cyano and silica gel columns. The experimental results were related to the chromatographic models of Snyder, Scott and Kucera, and Soczewinski.

## EXPERIMENTAL

### *High-performance liquid chromatograph*

The liquid chromatograph used was a Waters Model ALC/GPC 244 equipped with a Model 6000A pump, a U6K injector, a dual-channel free-standing UV detector set at 254 nm and 280 nm, and a dual-channel 10-mV strip chart recorder.

### *Columns*

The columns used were 30 cm  $\times$  3.9 mm I.D. prepacked and obtained from Waters Assoc. (Millford, MA, U.S.A.).  $\mu$ Porasil, packed with 10- $\mu\text{m}$  porous silica, and  $\mu$ Bondapak CN (normal-phase) with propyl nitrile groups chemically bonded to Waters  $\mu$ Porasil (10- $\mu\text{m}$  porous silica) were used.

### *Programmable calculators*

All calculator-generated data were obtained with Texas Instruments TI-59 and SR-52 programmable calculators and TI-PC-100C data printer.

### *Reagents*

*Solvents.* HPLC grade *n*-heptane, 2-propanol, ethyl acetate, and chloroform were obtained from J. T. Baker (Phillipsburg, NJ, U.S.A.). These solvents were pre-filtered through a Millipore type F-H 0.5- $\mu\text{m}$  filter. *n*-Heptane and 2-propanol were degassed separately by bubbling helium gas for *ca.* 1 h before mixing these solvents.

*Phenol and naphthol standards.* Phenol and naphthol standards were obtained from commercially available sources and were purified by recrystallization in absolute ethanol when necessary. Solutions of 10 mg/ml of the standards were prepared in chloroform except 2-naphthol, 4-phenylphenol, and 1,7-dihydroxynaphthalene. These compounds were only partially soluble in chloroform and were prepared in 2-propanol.

### *Chromatographic systems studied*

(1) Normal-phase,  $\mu$ Bondapak CN with *n*-heptane–2-propanol mobile phase at 2 ml/min.

(2) Normal-phase,  $\mu$ Bondapak CN with *n*-heptane–ethyl acetate mobile phase at 2 ml/min.

(3) Normal-phase,  $\mu$ Porasil with *n*-heptane–2-propanol mobile phase at 2 ml/min.

(4) Normal-phase,  $\mu$ Porasil with *n*-heptane–acetate mobile phase at 2 ml/min.

#### Calculation of $k'$ values

The retention volumes of the standards were determined by injecting 2  $\mu$ l of the standard solutions onto the chromatographic systems listed above. The capacity factor ( $k'$ ) was calculated from the relationship

$$k' = \frac{V_R - V_m}{V_m} \quad (1)$$

where  $V_R$  (ml) is the measured retention volume and  $V_m$  (ml) is the column void volume. The value of  $V_m$  was determined to be 3.3 ml for the systems studied and was obtained by eluting toluene in the normal-phase systems.

## RESULTS AND DISCUSSION

#### Theoretical considerations

In this work, the chromatographic models for silica gel and alumina developed by Snyder<sup>1</sup>, Soczewinski<sup>11,14</sup>, Soczewinski and Golkiewicz<sup>12,13</sup> and Scott and Kucera<sup>6</sup> were investigated for alkylphenols and naphthols with binary mobile phases and cyano and silica gel high-performance columns. Considering only solute–adsorbent and solvent–adsorbent interactions, the simple model of Soczewinski<sup>11</sup> is described by the following equilibrium reactions:



Here X refers to a solute molecule, S the strong solvent in the binary mobile phase, and A on active site on the stationary phase.  $K_{AX}$  and  $K_{AS}$  are the adsorption constants of the solute and solvent, respectively. Using Soczewinski's approach<sup>11</sup>, the following equation can be derived:

$$\log k' = \log \left[ \frac{K_{AX} X_{AS}}{K_{AS}} \right] - \log X_s \quad (4)$$

$X_{AS}$  is the mole fraction of the strong solvent adsorbed on the stationary phase, and  $X_s$  is the mole fraction of the strong solvent in the binary mobile phase.

When the solvent interacts strongly with the solute to form a solute–solvent complex the following equilibrium reaction is considered<sup>11</sup>:



$K_{SX}$  is the equilibrium constant of the solute–solvent reaction. Assuming a solute–solvent complex the following equation can be derived:

$$\log k' = \log \left[ \frac{X_{AS} K_{AX}}{K_{AS} K_{SX}} \right] - 2 \log X_s \quad (6)$$

Snyder's chromatographic model for silica gel and alumina is similar to Soczewinski's model. The following equation derived by Snyder<sup>2</sup> for binary mobile phases was applied to an amino high-performance column<sup>21</sup>:

$$\log k'_2 = \log k'_1 - \left( \frac{A_s}{n_b} \right) \log X_s \quad (7)$$

where  $A_s$  is the molecular area of the solute,  $n_b$  is the molecular area of the strong solvent,  $k'_2$  is the capacity factor for a solute eluted with the binary mobile phase, and  $k'_1$  is the capacity factor of the solute eluted with just the strong solvent.

Scott and Kucera<sup>6</sup> and Scott<sup>7</sup> derived an equation that accounts for the solute interactions in LSC. One form of the equation is

$$\frac{1}{V'} = A + BC_p \quad (8)$$

where  $A$  and  $B$  are constants,  $V'$  is the corrected retention volume and  $C_p$  is the concentration of the stronger solvent in a binary mobile phase. The constants  $A$  and  $B$  are difficult to interpret because they include several parameters.

#### *μBondapak CN and n-heptane-2-propanol*

Alkylphenols, naphthols, and dihydroxyl compounds were studied using a  $\mu$ Bondapak CN column and several *n*-heptane-2-propanol mobile phase concentrations. Linear relationships were observed for  $\log k'$  vs.  $\log X_s$  plots for the compounds investigated. Table I gives the chromatographic data for the compounds. Table II gives the least-squares slope and intercept values from  $\log k'$  vs.  $\log X_s$  plots and the corresponding linear correlation coefficients for all the compounds in Table I. 2-Propanol is the predominant competitor for sites on the cyano phase at relatively large concentrations of 2-propanol, as indicated by the decrease in  $k'$  values in Table I. Because residual silanol groups are not readily accessible<sup>23</sup>, a simple hydrogen-bonding interaction of solute or solvent with cyano groups in the stationary phase is expected.

If Soczewinski's model were followed, the slopes from  $\log k'$  vs.  $\log X_s$  graphs should be  $-1.0$ . In Table II, only the compounds 3,4-dimethylphenol, 3,5-diisopropylphenol, and 3,5-di-*tert.*-butylphenol have slope values very close to  $-1.0$ , suggesting a single-point attachment for these compounds. Several other compounds in Table II have slope values in the range from  $-0.75$  to  $-0.88$ . A single-point attachment is possibly occurring for these compounds, but the slope values suggest other interactions are involved. *o*-Cresol, 2-phenylphenol, 2,6-dimethylphenol, 2,3,6-trimethylphenol, and 2,4,6-trimethylphenol have slope values of  $-0.67$ ,  $-0.49$ ,  $-0.48$ ,  $-0.36$ , and  $-0.57$ , respectively. The hydroxyl group in these compounds is sterically hindered and the data in Table I indicate that these compounds are weakly retained. The slope values seem to reflect this condition. Interestingly, sterically hindered 2-isopropylphenol has a slope value of  $-0.82$ . This suggests that specific structural

TABLE I

LOG  $k'$  VALUES FOR PHENOLS, NAPHTHOLS AND DIHYDROXYL COMPOUNDS ON  $\mu$ BONDAPAK CN WITH *n*-HEPTANE-2-PROPANOL MOBILE PHASES

Compound	Mole fraction ( $X_2$ )				
	<i>n</i> -Heptane-2-propanol (v/v)				
	0.019	0.056	0.092	0.126	0.175
	99:1 (v/v)	97:3 (v/v)	95:5 (v/v)	93:7 (v/v)	90:10 (v/v)
<b>Non-ortho-substituted</b>					
Phenol	0.57	0.19	0.03	-0.09	-0.19
<i>m</i> -Cresol	0.54	0.16	0.00	-0.09	-0.34
<i>p</i> -Cresol	0.53	0.16	-0.04	-0.14	-0.26
3,4-Dimethylphenol	0.53	0.16	-0.09	-0.19	-0.34
4-Ethylphenol	0.51	0.10	0.04	-0.19	-0.26
3,5-Diisopropylphenol	0.39		-0.19	-0.34	-0.56
3,5-Di- <i>tert.</i> -butylphenol	0.34	-0.04	-0.34	-0.56	-0.56
5,6,7,8-Tetrahydro-2-naphthol	0.51	0.16	-0.09	-0.14	-0.26
2-Naphthol	0.75	0.37	0.19	0.07	-0.09
4-Phenylphenol	0.74	0.35	0.16	0.07	-0.14
<b>Mono-ortho-substituted</b>					
<i>o</i> -Cresol	0.43	0.10	-0.09	-0.14	-0.19
2,4-Dimethylphenol	0.39	0.04	-0.14	-0.26	-0.44
2-Isopropylphenol	0.39	0.07	-0.14	-0.19	-0.44
5,6,7,8-Tetrahydro-1-naphthol	0.40	0.07	-0.09	-0.19	-0.34
1-Naphthol	0.68	0.32	0.13	0.04	-0.14
2-Phenylphenol	0.32	0.10	0.00	-0.09	-0.14
<b>Di-ortho-substituted</b>					
2,6-Dimethylphenol	0.13	-0.09	-0.19	-0.26	-0.34
2,3,6-Trimethylphenol	0.10	-0.09	-0.14	-0.19	-0.26
2,4,6-Trimethylphenol	0.04	-0.14	-0.26	-0.34	-0.56
<b>Dihydroxyl</b>					
1,7-Dihydroxynaphthalene	1.80	1.16	0.89	0.71	0.53
1,2-Dihydroxybenzene (catechol)	1.00	0.60	0.43	0.32	0.16

features of the alkyl substituents are important in retention. 1,7-Dihydroxynaphthalene has a slope value of  $-1.32$  and 1,2-dihydroxybenzene has a value of  $-0.86$ . The data suggest a single-point attachment for these compounds, but other interactions are probably occurring. Soczewinski<sup>11</sup> stated that for silica gel, a slope less than  $-1.0$  can be obtained for solute molecules that are large enough to displace vicinal solvent molecules. Soczewinski and Golkiewicz<sup>13</sup> have reported slopes of *ca.*  $-2.0$  for dihydroxynaphthalenes on silica gel. Their results for dihydroxynaphthalenes suggest different modes of interaction for the compounds on silica gel compared to the cyano column. In Tables I and II, the compounds are categorized as non-*ortho*-substituted, mono-*ortho*-substituted, and di-*ortho*-substituted because of separation schemes developed by Schabron *et al.*<sup>24</sup> and Callmer *et al.*<sup>19</sup>.

Graphs of  $(1/V')$  vs.  $\%$ (w/v) of 2-propanol gave linear relationships only for 2-naphthol, 1-naphthol and 4-phenylphenol and dihydroxyl compounds. All other compounds gave linear relationships over limited mobile phase composition ranges

TABLE II

SLOPE, INTERCEPT, AND CORRELATION COEFFICIENT VALUES FROM LOG  $k'$  vs. LOG  $X_2$  PLOTS FOR  $\mu$ BONDAPAK CN WITH *n*-HEPTANE-2-PROPANOL FOR THE DATA IN TABLE I

Compound	Slope	Intercept	Correlation coefficient
Non- <i>ortho</i> -substituted			
Phenol	-0.79	-0.80	1.00
<i>m</i> -Cresol	-0.86	-0.92	0.989
<i>p</i> -Cresol	-0.83	-0.89	0.999
3,4-Dimethylphenol	-0.91	-1.02	0.997
4-Ethylphenol	-0.81	-0.90	0.998
3,5-Diisopropylphenol	-0.95	-1.22	0.992
3,5-Di- <i>tert.</i> -butylphenol	-1.01	-1.38	0.985
5,6,7,8-Tetrahydro-2-naphthol	-0.81	-0.89	0.995
2-Naphthol	-0.86	-0.72	0.998
4-Phenylphenol	-0.88	-0.77	0.995
Mono- <i>ortho</i> -substituted			
<i>o</i> -Cresol	-0.67	-0.74	0.992
2,4-Dimethylphenol	-0.84	-1.04	0.995
2-Isopropylphenol	-0.82	-0.99	0.985
5,6,7,8-Tetrahydro-1-naphthol	-0.75	-0.88	0.998
1-Naphthol	-0.83	-0.74	0.997
2-Phenylphenol	-0.49	-0.51	0.999
Di- <i>ortho</i> -substituted			
2,6-Dimethylphenol	-0.48	-0.70	0.999
2,3,6-Trimethylphenyl	-0.36	-0.53	0.996
2,4,6-Trimethylphenol	-0.57	-0.90	0.957
Dihydroxyl			
1,7-Dihydroxynaphthalene	-1.32	-0.48	1.00
1,2-Dihydroxybenzene (catechol)	-0.86	-0.47	0.999

(Fig. 1). The graph in Fig. 1 is atypical compared with those for the other compounds. Data from the other compounds are better represented by the shape of the graph in Fig. 2. These results show that Scott's model is not followed over the entire mobile phase composition range investigated, and possibly more than one mechanism is operative.

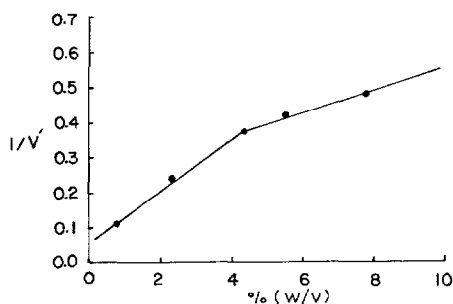


Fig. 1. Graph of  $(1/V')$  vs.  $\%$ (w/v) for *o*-cresol with  $\mu$ Bondapak CN and *n*-heptane-2-propanol.

*μBondapak CN and n-heptane-ethyl acetate*

The effects of various mobile-phase compositions of *n*-heptane-ethyl acetate were studied for the same phenolic and naphtholic compounds discussed earlier. Ethyl acetate was used as a second solvent because it is a weaker solvent than 2-propanol and it does not donate hydrogen in hydrogen-bond formation. Table III shows  $\log k'$  data and Table IV shows least-squares slope, intercept and correlation coefficient values from  $\log k'$  vs.  $\log X_s$  plots for the compounds investigated. Reasonably good linear relationships for the plot of  $\log k'$  vs.  $\log X_s$  were observed for most of the phenolic compounds. The two dihydroxyl compounds studied showed good linearity, although the  $k'$  value for 1,7-dihydroxynaphthalene with 99:1 (v/v) was not used because of its long retention time (Table III). The slope values for phenolic compounds in Table IV range from  $-0.95$  to  $-0.53$ , suggesting similar interactions to those discussed for *n*-heptane-2-propanol solvent. The slope value for

TABLE III

LOG  $k'$  VALUES FOR PHENOLS, NAPHTHOLS, AND DIHYDROXYL COMPOUNDS ON  $\mu$ BONDAPAK CN WITH *n*-HEPTANE-ETHYL ACETATE MOBILE PHASES

Compound	Mole fraction ( $X_s$ ) <sub>s</sub>				
	<i>n</i> -Heptane-ethyl acetate (v/v)				
	0.015 99:1 (v/v)	0.045 97:3 (v/v)	0.072 95:5 (v/v)	0.101 93:7 (v/v)	0.142 90:10 (v/v)
Non- <i>ortho</i> -substituted					
Phenol	0.71	0.35	0.16	0.04	-0.14
<i>m</i> -Cresol	0.68	0.35	0.13	0.00	-0.19
<i>p</i> -Cresol	0.68	0.39	0.13	0.00	-0.19
3,4-Dimethylphenol	0.69	0.35	0.13	0.00	-0.19
4-Ethylphenol	0.68	0.39	0.13	0.00	-0.19
3,5-Diisopropylphenol	0.55	0.21	0.04	-0.14	-0.34
3,5-Di- <i>tert.</i> -butylphenol	0.53	0.19	-0.04	-0.19	-0.44
5,6,7,8-Tetrahydro-2-naphthol	0.69	0.39	0.13	0.00	-0.19
2-Naphthol	0.90	0.51	0.30	0.16	-0.04
4-Phenylphenol	0.91	0.54	0.32	0.16	0.00
Mono- <i>ortho</i> -substituted					
<i>o</i> -Cresol	0.51	0.19	0.00	-0.09	-0.34
2,4-Dimethylphenol	0.48	0.16	0.00	-0.14	-0.34
2-Isopropylphenol	0.45	0.10	-0.09	-0.19	-0.44
5,6,7,8-Tetrahydro-1-naphthol	0.50	0.19	0.00	-0.09	-0.34
1-Naphthol	0.80	0.42	0.24	0.07	-0.09
2-Phenylphenol	0.35	0.19	0.04	-0.04	-0.19
Di- <i>ortho</i> -substituted					
2,6-Dimethylphenol	0.13	-0.09	-0.19	-0.26	-0.44
2,3,6-Trimethylphenol	0.07	-0.09	-0.26	-0.44	-0.56
2,4,6-Trimethylphenol	0.07	-0.14	-0.26	-0.44	-0.56
Dihydroxyl					
1,7-Dihydroxynaphthalene	-*	1.65	1.29	1.06	0.78
1,2-Dihydroxybenzene (catechol)	1.20	0.80	0.59	0.45	0.28

\* Elution volume was greater than 282 ml.

TABLE IV

SLOPE, INTERCEPT, AND CORRELATION COEFFICIENT VALUES FROM LOG  $k'$  vs. LOG  $X_2$  PLOTS  $\mu$ BONDAPAK CN WITH *n*-HEPTANE-ETHYL ACETATE FOR THE DATA IN TABLE III

Compound	Slope	Intercept	Correlation coefficient
Non- <i>ortho</i> -substituted			
Phenol	-0.85	-0.82	0.993
<i>m</i> -Cresol	-0.87	-0.88	0.992
<i>p</i> -Cresol	-0.88	-0.88	0.987
3,4-Dimethylphenol	-0.88	-0.89	0.993
4-Ethylphenol	-0.88	-0.88	0.987
3,5-Diisopropylphenol	-0.88	-1.02	0.988
3,5-Di- <i>tert.</i> -butylphenol	-0.95	-1.16	0.985
5,6,7,8-Tetrahydro-2-naphthol	-0.89	-0.89	0.988
2-Naphthol	-0.93	-0.79	0.996
4-Phenylphenol	-0.92	-0.75	0.996
Mono- <i>ortho</i> -substituted			
<i>o</i> -Cresol	-0.82	-0.95	0.985
2,4-Dimethylphenol	-0.80	-0.96	0.989
2-Isopropylphenol	-0.86	-1.09	0.988
5,6,7,8-Tetrahydro-1-naphthol	-0.81	-0.94	0.984
1-Naphthol	-0.89	-0.81	0.996
2-Phenylphenol	-0.53	-0.58	0.975
Di- <i>ortho</i> -substituted			
2,6-Dimethylphenol	-0.54	-0.83	0.980
2,3,6-Trimethylphenol	-0.64	-1.05	0.962
2,4,6-Trimethylphenol	-0.63	-1.04	0.976
Dihydroxyl			
1,7-Dihydroxynaphthalene	-1.71	-0.66	0.999
1,2-Dihydroxybenzene (catechol)	-0.93	-0.48	0.998

1,7-dihydroxynaphthalene was  $-1.71$ , suggesting that a two-point attachment interaction was probably occurring or strong solvation of the solute<sup>2,11,13</sup>.

Plots of  $(1/V')$  vs.  $\%$ (w/v) of ethyl acetate did not show linear relationships for the compounds over the entire solvent composition range investigated. The lines were curved upward (Fig. 2), suggesting different interactions in the two regions.

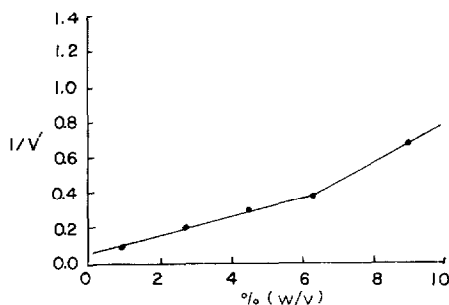


Fig. 2. Graph of  $(1/V')$  vs.  $\%$ (w/v) for *o*-cresol with  $\mu$ Bondapak CN and *n*-heptane-ethyl acetate.



*μPorasil and n-heptane-2-propanol*

Several phenolic compounds were studied with *n*-heptane-2-propanol mobile phase. The compounds studied with mobile phase composition *n*-heptane-2-propanol 99:1 (v/v) in all cases gave a capacity factor less than 4. Due to low retention behavior of the phenolic compounds with this chromatographic system it was expected that retention volumes of other phenolic compounds at higher 2-propanol concentration would be close to the void volume of the column. At concentrations above *n*-heptane-2-propanol 99:1 (v/v), the retention volumes of the compounds were found to be less than the void volume of the column. Only three phenolic compounds, phenol, *p*-cresol, and *o*-cresol, were studied with several mobile-phase compositions to find a useful correlation between solvent compositions and retention behavior of the compounds on the adsorbent.

Linear relationships were obtained for the plots of  $\log k'$  vs.  $\log X_s$  for the three compounds investigated, indicating correspondence with Snyder's and Soczewinski's models. The slope values for these compounds for the plots of  $\log k'$  vs.  $\log X_s$  ranged from  $-1.34$  to  $-1.22$ . The hydrogen-bonding interactions occurring between the phenolic hydroxyl group and the silica silanol group were discussed by Snyder<sup>1</sup> and

TABLE V

LOG  $k'$  VALUES FOR PHENOLS AND NAPHTHOLS ON  $\mu$ PORASIL WITH *n*-HEPTANE-ETHYL ACETATE MOBILE PHASES

Compound	Mole fraction ( $X_s$ )				
	<i>n</i> -Heptane-ethyl acetate (v/v)				
	0.015 99:1 (v/v)	0.045 97:3 (v/v)	0.072 95:5 (v/v)	0.101 93:7 (v/v)	0.142 90:10 (v/v)
<b>Non-ortho-substituted</b>					
Phenol	1.23	0.77	0.55	0.37	0.16
<i>m</i> -Cresol	1.22	0.74	0.50	0.32	0.13
<i>p</i> -Cresol	1.25	0.76	0.55	0.35	0.13
3,4-Dimethylphenol	1.26	0.75	0.50	0.32	0.07
4-Ethylphenol	1.21	0.75	0.48	0.30	0.10
3,5-Diisopropylphenol	1.18	0.65	0.39	0.19	-0.04
3,5-Di- <i>tert</i> -butylphenol	1.17	0.61	0.35	0.13	-0.09
5,6,7,8-Tetrahydro-2-naphthol	1.27	0.77	0.51	0.34	0.10
2-Naphthol	1.34	0.85	0.60	0.43	0.26
4-Phenylphenol	1.40	0.91	0.66	0.50	0.30
<b>Mono-ortho-substituted</b>					
<i>o</i> -Cresol	1.02	0.59	0.39	0.24	0.00
2,4-Dimethylphenol	1.03	0.56	0.32	0.16	-0.04
2-Isopropylphenol	0.87	0.43	0.19	0.04	-0.14
5,6,7,8-Tetrahydro-1-naphthol	0.10	0.54	0.30	0.07	-0.09
1-Naphthol	1.10	0.69	0.49	0.32	0.13
2-Phenylphenol	0.74	0.42	0.28	0.16	-0.04
<b>Di-ortho-substituted</b>					
2,6-Dimethylphenol	0.65	0.32	0.13	0.00	-0.19
2,3,6-Trimethylphenol	0.61	0.24	0.04	-0.09	-0.26
2,4,6-Trimethylphenol	0.67	0.28	0.07	-0.04	-0.19

Callmer *et al.*<sup>19</sup>. The major interaction takes place between the silanol hydrogen and the phenolic oxygen. The dissociation constants of most phenolic hydroxyl hydrogens are about  $10^{-10}$  and the dissociation constants of silanol hydrogens are *ca.*  $10^{-6}$  to  $10^{-8}$  (ref. 25). Due to the acidic behavior of phenols and silanol groups, the bonding interaction between them would be weaker than the interaction of phenols with a cyano-bonded phase.

Two dihydroxyl compounds (1,7-dihydroxynaphthalene and 1,2-dihydroxybenzene) were studied with only three solvent compositions and more data are needed to comment on the relationship of these compounds to the chromatographic models.

#### *μPorasil and n-heptane-ethyl acetate*

Twelve alkylphenols and seven phenolic type compounds were investigated. Table V lists the chromatographic data and Table VI gives the least-squares slope, intercept, and correlation coefficient values from graphs of  $\log k'$  vs.  $\log X_s$  for the compounds investigated. Linear relationships were obtained for the graphs of  $\log k'$  vs.  $\log X_s$  for all the phenolic compounds. Table VI shows a range of slope values from  $-1.30$  to  $-0.76$  suggesting interactions other than simple single point attachment are probably occurring except possibly for *o*-cresol, 2-isopropylphenol, and 1-naphthol. 3,5-Di-*tert.*-butylphenol and 3,5-diisopropylphenol have slope values con-

TABLE VI

SLOPE, INTERCEPT, AND CORRELATION COEFFICIENT VALUES FROM  $\log k'$  vs.  $\log X_s$  PLOTS FOR  $\mu$ PORASIL WITH *n*-HEPTANE-ETHYL ACETATE FOR THE DATA IN TABLE V

<i>Compound</i>	<i>Slope</i>	<i>Intercept</i>	<i>Correlation coefficient</i>
Non- <i>ortho</i> -substituted			
Phenol	-1.07	-0.70	0.997
<i>m</i> -Cresol	-1.10	-0.77	0.998
<i>p</i> -Cresol	-1.11	-0.76	0.996
3,4-Dimethylphenol	-1.18	-0.87	0.996
4-Ethylphenol	-1.11	-0.81	0.997
3,5-Diisopropylphenol	-1.30	-1.17	0.976
3,5-Di- <i>tert.</i> -butylphenol	-1.27	-1.26	0.998
5,6,7,8-Tetrahydro-2-naphthol	-1.16	-0.84	0.997
2-Naphthol	-1.10	-0.66	0.999
4-Phenylphenol	-1.11	-0.61	0.999
Mono- <i>ortho</i> -substituted			
<i>o</i> -Cresol	-1.00	-0.78	0.994
2,4-Dimethylphenol	-1.07	-0.92	0.998
2-Isopropylphenol	-1.02	-0.98	0.998
5,6,7,8-Tetrahydro-1-naphthol	-1.11	-1.00	0.996
1-Naphthol	-0.97	-0.65	0.996
2-Phenylphenol	-0.76	-0.62	0.990
Di- <i>ortho</i> -substituted			
2,6-Dimethylphenol	-0.83	-0.84	0.993
2,3,6-Trimethylphenol	-0.87	-0.96	0.997
2,4,6-Trimethylphenol	-0.87	-0.91	0.999

siderably less than  $-1.0$ . The bulky groups in these compounds are involved in weakening the interactions of the alkylphenols with the stationary phase as discussed earlier for the  $\mu$ Bondapak CN column.

Graphs of  $(1/V')$  vs.  $\%$ (w/v) of ethyl acetate did not give linear relationships over the entire range of mobile-phase compositions studied. Up to *ca.* 6.0% (w/v) of ethyl acetate (93:7, v/v), linearity was well observed. At higher concentrations, there was a sharp break to a larger slope value suggesting different interactions in the two regions.

Dihydroxyl compounds were studied with only two solvent compositions of *n*-heptane-ethyl acetate 93:7 (v/v) and 90:10 (v/v) on a  $\mu$ Porasil column. The retention volumes of 1,7-dihydroxynaphthalene in the two different solvent compositions were 114 ml and 51.3 ml, respectively. 1,2-Dihydroxybenzene had retention volumes of 33.9 ml and 20.1 ml, respectively. Neither compound was eluted from the column after 360 ml of *n*-heptane-ethyl acetate 99:1 (v/v) passed through the column. The previous data indicate strong interactions of the two dihydroxyl compounds with the silanol groups of the  $\mu$ Porasil column.

## CONCLUSIONS

The experimental data presented in this work indicate that the simple Snyder model and the simple Soczewinski model approximately describe the retention behavior of alkylphenols on  $\mu$ Bondapak CN and  $\mu$ Porasil stationary phases in the normal-phases studied. Various secondary effects discussed by Snyder<sup>1</sup> were not considered. In addition, "solvent localization" effects reported by Snyder and Glajch<sup>4</sup> were not investigated. In practical applications the linear relationships between  $\log k'$  vs.  $\log X_s$  will be useful in predicting solvent compositions for the separation of complex mixtures of alkylphenols.

The results from the  $\mu$ Bondapak CN and  $\mu$ Porasil columns compared to our earlier data with  $\mu$ Bondapak NH<sub>2</sub><sup>21</sup> showed that the  $\mu$ Bondapak CN and  $\mu$ Porasil columns did not show good selectivity for an efficient separation of alkylphenols with the particular mobile phases used in this work.  $\mu$ Bondapak CN and  $\mu$ Porasil columns, however, appear to be suitable stationary phases for the separation of dihydroxyl compounds with the mobile phases studied.

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