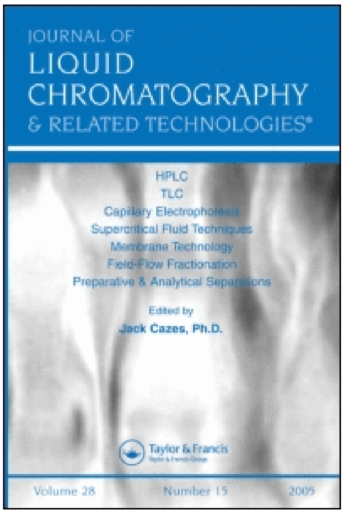

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COMPETITIVE INTERACTIONS OF PHENOL DERIVATIVES AND ALIPHATIC ALCOHOLS FOR ALKENYL AND DIOL SILICA SURFACES

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ABSTRACT

A thermodynamic equation is used to analyze the retention behavior of phenolic solutes at low modifier concentrations on alkenyl and diol chemically modified silica packings. These materials were prepared by attaching alkenyl and diol ligands with four, six, eight and ten carbon atoms to the surface of LiChrosorb Si-60 silica. The thermodynamic analysis of the capacity ratios of various phenolic solutes measured at different concentrations of simple aliphatic alkohols (used as modifiers) in n-hexane have provided information about solute and solvent interactions with the alkenyl and diol modified silicas. This analysis shows that the solute-alcohol competitive interaction for the alkenyl bonded phases changes significantly with chain length, whereas this effect is not observed for the diol phases. Also, the influence of polarity and geometric structure of functional groups on solute retention have been examined.

INTRODUCTION

For many years chromatography has been used successfully to study molecular interactions at both gas-solid and liquid-solid interfaces. Knowledge of these interactions is necessary not only for developing retention theory but first of all it is needed for understanding the mechanisms of chromatographic separations and for designing and optimizing these separations. Fundamental studies of the role of molecular interactions in tsolute retention accelerated considerably development of optimization methods for chromatographic separations (e.g., see works[1-3] and references therein).

While retention mechanisms at the gas-solid interfaces are relatively simple because they are controlled almost solely by solute-solid interactions, they are much more complex at liquid-solid interfaces.[4,5] Even in the simplest case of liquid chromatography, where a single component mobile phase is used, a solute's retention is controlled by at least four different types of interactions, i.e., solute-solvent, solvent-solvent, solute-solid and solvent-solid interactions. The molecular picture is even more complex for binary solvent mixtures, which are frequently used in carrying out liquid chromatography separations.[6,7] In this latter case, the number of types of interactions controlling a solute retention increases at least up to eight. This number is higher for LC with chemically bonded phases, where the solute and solvent molecules can interact with bonded ligands and with unreacted surface groups of the solid support. In addition, one should consider that solute-solvent and solvent-solvent interactions in the stationary phase differ from those in the mobile phase because they are under the influence of the forces acting between solid and surface molecules.[8] Although the unified statistico-thermodynamical description of LC with mixed-mobile phases[9,10] automatically incorporates all types of molecular interactions, the final expressions resulting from this description are complicated and their practical utility is limited. Therefore, simple models are frequently used to represent solute retention in LSC systems (see papers[11-16] and references therein). Usually, solute retention in normal-phase systems is represented by the displacement (competitive sorption) models,[11,12] whereas for reversed phase systems, it is represented by the partition models.[8,13,14,17,18]

In the current paper, a simple thermodynamic equation, which is based on a displacement model, is employed to analyze the dependencies of the capacity ratios of phenolic derivatives on the modifier concentration. These dependencies were measured at low concentrations of simple aliphatic alcohols (used as modifier's) on alkenyl and diol modified silica surfaces and, at present, they are unique in the chromatographic literature. Up to now, these types of measurements have been reported only for selected alcohol-hydrocarbon mobile phases on unmodified silicas.[19,20] Analysis of the measured capacity ratios by means of the above mentioned thermodynamic equation provides information about solute-alcohol competitive interactions for alkenyl and diol bonded phases and permits comparison of chromatographic properties of these phases.

EXPERIMENTAL

Reagents

The HPLC grade solvents were obtained from the Fisher Scientific Company (Fairlawn, N.J.) and the reagent grade compounds used as test substances were from the Aldrich Chemical Company (Milwaukee,WI). Water used for preparation of chromatographic packings was purified using a Milli-Q reagent water system from Millipore Model Continental Water Systems (El Paso, TX). The 1,3-butadiene, 1,5-hexadiene, 1,7-octadiene, 1,9-decadiene and triethoxysilane, also purchased from Aldrich, were used without further purification. The synthesis of alkenyltriethoxysilane was carried out as follows: about 20 mL of a given diene was placed in a 52cm x 11mm i.d. stainless steel reactor tube which was flushed with a stream of dry nitrogen gas and placed in a dewar containing dry ice and acetone. Next, 10 mL of triethoxysilane were added to the reactor, followed by 10 drops of a 1% solution of H_2PtCl_6 in 2-propanol. The reactor was sealed, removed from the dry ice-acetone,and allowed to warm. The reactor was placed in an oven and heated for 12 hours at 383K. After the reaction was completed, the tube was again placed in dry ice-acetone and allowed to cool for 1 hr. The reactor was opened and its contents were transferred to a 50mL round bottom flask and vacuum distilled. The identity of the silane product was verified by FTIR.

Chromatographic Packings

The chromatographic packings were prepared in-house by the following procedures. Four grams of LiChrosorb Si-60 silica (E. Merck, Cherry Hill, N.J.; specific surface area 550 m^2/g) were preconditioned with dionized water and dried overnight in an oven at 383K. The dry silica was placed in a reaction vessel with 100 mL of 1-propanol and allowed to stand for 6 hours. Half of the 1-propanol was removed and 10 mL of a given alkenyltriethoxysilane and 10 drops of n-butylamine were added to the reaction vessel. The mixture was refluxed for 24 hr using a stream of dry nitrogen for stirring. Excess solvent was removed using a sintered glass filter under vacuum.

The modified silica was washed several times with methanol and diethylether, and dried overnight in an oven at 383K. This procedure was used to attach 3-butenyl, 5-hexenyl, 7-octenyl and 9-decenyl ligands to silica.

Two grams of a given alkenyl modified silica were stirred with 75 mL of persuccinic acid for 24 hr at 323K; this acid was prepared by reacting succinic anhydride with hydrogen peroxide according to literature procedures.[21,22] The modified silica was washed several times with methanol and then diethylether and dried overnight in an oven at 383K. By stirring alkenyl modified silica with persuccinic acid, the terminal double bond in the alkenyl ligand was converted to a diol group; this conversion was confirmed using diffusive reflectance FTIR and CP/MAS^{13}C solid state NMR.[21] By this procedure, the alkenyl bonded phases were converted to suitable phases with dihydroxyalkyl (diol) ligands, i.e., the 3-butenyl, 5-hexenyl, 7-octenyl and 9-decenyl ligands on the silica surface gave, respectively, 3,4-dihydroxybutyl, 5,6-dihydroxyhexyl, 7,8-dihydroxyoctyl and 9,10-dihydroxydecyl bonded ligands.

The alkenyl and diol modified silicas were packed into 25cm x 1.8mm i.d. stainless steel columns by using a dynamic packing procedure. One gram of each packing material was stirred with 30mL of isopropanol in the solvent reservoir and was pressurized into the empty column using methanol as the delivery solvent. The packing procedure was continued for an hour using a Haskel (Burbank, CA) Model DSTV-52C air-driven fluid pump.

Characterization of Modified Silicas

Summmarized in Table 1 are the surface coverages (i.e., % carbon) for the alkenyl and diol bonded phases determined by combustion analysis using a Leco Corporation (St. Joseph, MI) Model CS-244 Carbon Analyzer. The levels of coverage for the alkenyl bonded phases are greater than those for the corresponding diol phases. In addition, the alkenyl and diol phases were characterized by diffuse reflectance infrared spectroscopy and solid state CP/MAS^{13}C NMR spectrometry.[21] The diffusive reflectance infrared spectra for the modified silicas with alkenyl bonded ligands had the 3080 cm^{-1} band (also present in the IR spectra for synthesized alkenyltriethoxysilanes), which results from the =C-H stretch. When the double bond in alkenyl bonded ligands was converted to the diol group, this band disappeared. However, the -OH stretch band was not observed because of the background interferences. The unreacted surface silanol groups gave a broad -OH stretch band, which obscured the band for the ligand hydroxyls.

Table 1

Surface Coverages of Chemically Modified Lichrosorb Si-60 Silicas

Bonded Ligand	Code	Total % C
3-butenyl	A4C	4.99
3,4-dihydroxybutyl	D4C	1.89
5-hexenyl	A6C	6.07
5,6-dihydroxyhexyl	D6C	4.39
7-octenyl	A8C	8.39
7,8-dihydroxyoctyl	D8C	6.60
9-decenyl	A10C	9.59
9,10-dihydroxydecyl	D10C	8.06

The solid state CP/MAS ^{13}C NMR spectra for alkenyl modified silicas had resonances at 112 PPM and 138 PPM, which are characteristic for =C-H and $=CH_2$ groups. Two additional resonances at 125 and 132 PPM were observed because of migration of the double bond from the terminal to the 2nd and 3rd positions. A similar effect has been observed during isomerization of 1-pentene adsorbed on silica.[23] After conversion of the alkenyl ligands to dihydroxyalkyl (diol) bonded ligands the above mentioned resonances either disappeared completely or their intensities were reduced significantly. Appearance of two new resonances between 68 and 78 PPM confirmed the presence of -C-OH groups[24] and showed that hydrolysis of the epoxy groups to diols took place during the chemical conversion of the alkenyl ligands. Other experimental details including the IR and NMR spectra with band assignments for alkenyl and diol modified silicas are reported elsewhere.[21]

Chromatographic Measurements

All retention data were recorded and processed on an IBM Instruments Model 9000 data system. Column temperature was maintained at 298K in a water bath using a Fisher Model 730 controller (Pittsburgh, PA). All columns were preconditioned using the procedure reported by Gilpin and Sisco.[25] Before each change in the mobile phase composition, each chromatographic column was conditioned with 500mL of n-hexane and 200mL of the weakest mobile phase and, before the first solute injection, it was additionally equilibrated with at least 100mL of the mobile phase of a selected composition. The retention measurements were performed for the mobile phase compositions changing from low to higher concentrations of the polar modifier. Simple aliphatic alcohols, i.e., methanol, ethanol, 1-propanol, 2-propanol, 2-butanol and t-butanol, were used as modifiers. The capacity factors of phenol and its o-, m- and p-derivatives with fluoro, chloro, bromo, iodo, hydroxy, nitro and cyano groups were measured at different concentrations of a given aliphatic alcohol in n-hexane, i.e., 0.8, 1.2, 1.6, 2.0, 2.5 and 3.0 v/v% of the modifier in n-hexane. In the case of the methanol-hexane mobile phase the highest concentration was equal to 2.0% modifier because of the low solubility of methanol in n-hexane. The flow rate of the mobile phase was equal 1mL/min. The void volume for each column was evaluated using n-pentane. Each solute was injected separately. The reported values of the capacity ratio, k'_s, are averages from at least duplicate injections.

RESULTS AND DISCUSSION

The chromatographic systems studied in this paper can be considered to be normal-phase because the modified silica surfaces contained polar groups (unreacted silanols and alkenyl or diol ligands) and the hexane-based mobile phases contained only small amounts of aliphatic alcohols used as modifiers. In these systems, the competitive interactions between solute and modifier molecules for active surface groups should dominate over the non-specific interactions characteristic for solute retention on alkyl bonded phases.[8] The competitive interactions of solute (s) and alcohol (a) molecules with the specific surface groups can be represented by a displacement mechanism,[11,12] which is described quantitatively by the following equilibrium constant, K_{sa} :[26]

$$K_{sa} = (a_s^{\sigma}/a_s^{l})\,(a_a^{l}/a_a^{\sigma})^{r} \qquad (1)$$

where a_s^{α} and $a_a^{\alpha}(\alpha = \sigma, l)$ are respectively activities of solute and alcohol (modifier) in the α-phase, the superscripts σ and l refer, respectively, to the stationary (surface) and mobile (bulk) phases, and r is the ratio of molecular areas occupied by the solute and alcohol molecules in the surface phase. Since the solute concentrations in both phases are infinitely dilute and the modifier concentrations are low, the activity coefficients can be approximated by concentration-independent constants and included in the K_{sa}-constant; then equation (1) can be rewritten as follows:

$$K_{sa}^{*} = (x_s^{\sigma}/x_s^{l})\,(x_a^{l}/x_a^{\sigma})^{r} \qquad (2)$$

Here K^*_{sa} is the modified constant K_{sa}, which includes the solute and modifier activity coefficients, x^{α}_{s} and x^{α}_{a} ($\alpha = \sigma$, l) are, respectively, the solute and modifier mole fractions in the α-phase. The solute capacity factor can be defined as follows:[6]

$$k'_s = \phi\ (x^{\sigma}_{s}/x^{l}_{s})\ \ for\ x^{l}_{s} \longrightarrow O \tag{3}$$

where ϕ is the phase ratio. Combination of equations (2) and (3) allows to express k'_s by means of the mole fractions of modifier in both phases:

$$k'_s = \phi\ K^*_{sa}\ (x^{\sigma}_{a}/x^{l}_{a})^r \tag{4}$$

Since, in the systems studied here, the specific interactions of solute and modifier molecules with the active surface groups are similar, the solute-modifier ratio r of molecular areas can be approximated by unity. Then equation (4) simplifies as follows:

$$k'_s = \phi\ K^*_{sa}\ (x^{\sigma}_{a}/x^{l}_{a}) \tag{5}$$

While the mole fraction of modifier (in the current case, alcohol) in the mobile phase, x^{l}_{a}, is known, its mole fraction in the surface phase is unknown. If chromatographic measurements are carried out at sufficiently high concentrations of the polar solvent (e.g., $x^{l}_{a} > 0.1$-0.2), its mole fraction in the surface phase can be approximated by unity and then equation (4) reduces to the well-known Snyder-Soczewinski relationship:[11,12,27]

$$\log k'_s = \log\left(\phi K^*_{sa}\right) - r \log x^{l}_{a} \tag{6}$$

Since the retention measurements presented in the experimental section were carried out at low concentrations of modifier, equation (6) cannot be used for analyzing these data. In this region the surface composition x^{σ}_{a} changes with the mobile phase composition. Low concentrations of modifier in the mobile phase permit the modifier-solvent composition in the surface phase to be represented by an ideal displacement model;[12,28] then

$$x^{\sigma}_{a} = K^*_{ah}\ x^{l}_{a}/(x^{l}_{h} + K^*_{ah}\ x^{l}_{a}) \tag{7}$$

where K^*_{ah} is the modifier-solvent equilibrium constant (K^*_{ah} denotes the constant for the alcohol-hexane liquid mixture). Replacing x^σ_a in equation (5) by equation (7), one can obtain:

$$1/k'_s = (\phi K^*_{sa} K^*_{ah})^{-1} (x^l_h + K^*_{ah} x^l_a) \qquad (8)$$

Since x^l_a is small (below 0.03), the mole fraction x^l_h can be replaced by unity because $x^l_a + x^l_h = 1$ for $x^l_s \rightarrow 0$. Then, equation (8) simplifies as follows:

$$1/k'_s = (\phi K^*_{sh})^{-1} + (\phi K^*_{sa})^{-1} x^l_a \qquad (9)$$

where $K^*_{sh} = K^*_{sa} K^*_{ah}$. Equation (9) shows that, in the region of low concentrations of modifier, the reciprocal of the capacity ratio is linearly dependent on the modifier's concentration.

It is noteworthy that the same type of dependence of the capacity ratio on the modifier concentration has been predicted by Scott and Kucera,[19] who defined k'_s as the ratio of total forces acting on the solute in the stationary phase to the total forces acting on the solute in the mobile phase. In contrast to their probabilistic description, equation (9) is based on a displacement model, which assumes competitive interactions between solute, modifier and solvent molecules for active sites on the solid surface. This model is commonly accepted for describing the physical adsorption of multicomponent non-electrolytic liquid mixtures on solid surfaces.[5] In the current paper equation (9) will be used to analyze the measured dependences of the capacity ratio on the modifier concentration.

Capacity ratios were measured for 22 phenolic solutes (i.e., phenol, o-, m- and p-fluorophenols, o-, m- and p-chlorophenols, o-, m- and p-bromophenols, o-, m- and p-iodophenols, o-, m- and p-cresols, o-, m- and p-nitrophenols, and o- m- and p-cyanophenols), in six alcohol/n-hexane mobile phases (i.e., methanol, ethanol, 1-propanol, 2-propanol, 2-butanol and t-butanol) and nine silicas (i.e., unmodified Lichrosorb Si-60, four modified silicas with C4, C6, and C8 and C10 alkenyl ligands and four modified silicas with C4, C6, C8, C10 dihydroxyalkyl ligands). For each chromatographic system, the capacity ratio was measured as a function of the modifier's concentration up to 3 v/v% in the mobile phase. These data were plotted according to equation (9) (i.e., the reciprocal of the capacity factor against the mole fraction of modifier in the mobile phase) giving 1188 linear plots. Analysis of these plots showed that equation (9) is a good representation for the capacity ratios measured at the

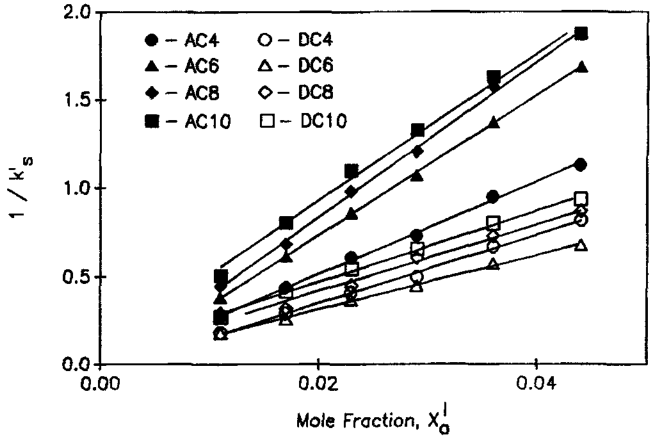

Figure 1. Reciprocal of the capacity ratio plotted as a function of the mole fraction of modifier in the mobile phase for phenol chromatographed in 2-butanol/n-hexane on various alkenyl and diol bonded phases.

low modifier concentrations. For the majority of the systems studied the values of the correlation coefficient were at least 0.99 or better. For the purpose of illustration Figure 1 contains the linear plots of $1/k_{s'}$ vs. x_a^l for phenol chromatographed in the 2-butanol/n-hexane mobile phase on the columns packed with modified silicas.

According to Snyder[6] the phase ratioϕ, to a first approximation, is a fundamental property of the solid phase and is independent of the nature of the solvent. Thus, the intercept and the slope of the linear relationship given by equation (9) are respectively proportional to the equilibrium constants $K_{hs}^* = 1/K_{sh}^*$ and $K_{as}^* = 1/K_{sa}^*$. These constants are proportional to the differences in the sorption energies of solute, solvent and modifier as follows:

$$K_{hs}^* \sim \exp\left(\frac{\epsilon_h - \epsilon_s}{RT}\right) \quad (10)$$

and

$$K_{as}^* \sim \exp\left(\frac{\epsilon_a - \epsilon_s}{RT}\right) \quad (11)$$

Here ε_h, ε_s and ε_a denote, respectively, the sorption energies of n-hexane, solute and modifier molecules, R and T have their usual meaning. Since ε_s is considerably greater than ε_h, the difference $\varepsilon_h - \varepsilon_s$ is a relatively large negative number and the constant K^*_{hs} is very small. Thus, the quantity $1/\phi K^*_{sh}$ [cf., equation (9)] is succeptable to a large error; in some cases even a negative value of $1/\phi K^*_{sh}$ is obtained, which has no physical meaning according to equation (9). It is noteworthy that negative values of the intercept also have been reported by Scott and Kucera,[19] who tried to interpret them in terms of their retention model. The constant K^*_{hs} characterizes competitive interactions between molecules of solute and nonpolar solvent (in the current case, n-hexane) for active surface groups but the solvent plays a less significant role in the retention mechanism in comparison to the modifier, which influences strongly the solute-surface interactions. Therefore, the values of $1/\phi K^*_{sh}$ are not discussed in this paper, whereas the analysis of the values of $1/\phi K^*_{sa}$, which characterize the competitive interactions between solute and modifier molecules for active surface groups, is emphasized. These interactions control the solute retention in the chromatographic systems studied. As mentioned above, the slope, $1/\phi K^*_{sa}$, is proportional to the equilibrium constant K^*_{as} which, through equation (11), is associated with the solute and modifier sorption energies. While the difference between the sorption energies of n-hexane and solute is a large negative number, the difference between the sorption energies of alcohol and solute is considerably smaller but still negative. If $\varepsilon_a - \varepsilon_s$ tends to zero, the exponential energy term (<1) tends to unity. The observed values of K^*_{as}/ϕ are greater than unity because ϕ is a small number and the pre-exponential entropy factor in the K^*_{as}/ϕ - constant can be greater than unity.

The quantity K^*_{as}/ϕ characterizes the competitive interactions of solute and modifier molecules with the active surface groups and ligands. Analysis of the values of K^*_{as}/ϕ obtained for all systems studied has provided information about the influence of the solute, modifier and ligand on the retention process. Based on these values it was possible to distinguish two groups of solutes: the first group contains halophenols and cresols, the other one contains nitro- and cyanophenols. The values of K^*_{as}/ϕ for halophenols and cresols chromatographed in the same system usually varied up to 10%; higher

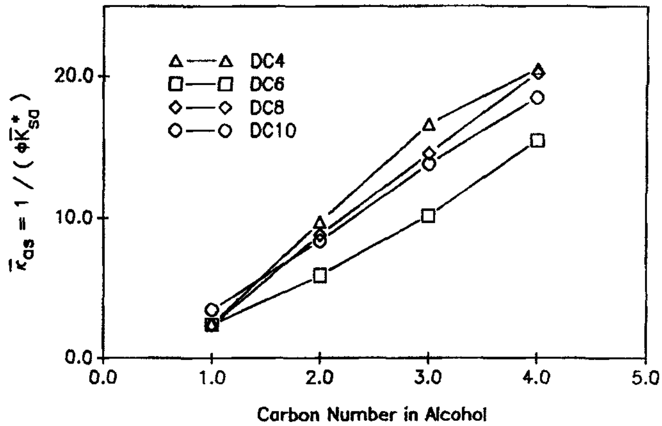

Figure 2. Dependencies of $\overline{\kappa}_{as}$ on the number of carbon atoms in the modifier for halophenols chromatographed in various alcohol/n-hexane mobile phases on the diol bonded phases. Modifiers: methanol, ethanol, 1-propanol and 2-butanol.

variations were observed for the ortho-derivatives of phenol phases chromatographed in the methanol/n-hexane and ethanol/n-hexane mobile phases. These variations show a regular tendency and can be associated with the size and position of the halogen atom in phenol (this problem will be discussed later).

In order to study the effect of the mobile phase on solute retention, the average value $\overline{\kappa}_{as} = \overline{K}_{as} / \phi$ was calculated by taking into account the values of K^*_{as} / ϕ for halophenols and cresols. Figures 2 and 3 show, respectively, the dependencies of $\overline{\kappa}_{as}$ on the number of carbon atoms in the modifier (alcohol) for the dihydroxyalkyl and alkenyl bonded phases. In both cases an increase in the $\overline{\kappa}_{as}$ -value denotes an increase in the adsorption energy of the alcohol since the solute is fixed. Thus, for all bonded phases, the interaction energy between modifier and surface groups and ligands increased in direction from methanol to butanol. In the case of the alkenyl bonded phases this energy increase was about 2.5 times stronger than that observed for the dihydroxyalkyl phases. For the alkenyl phases, the increase in the $\overline{\kappa}_{as}$ -values associated with addition of the methylene group to the alcohol molecule are not additive and decrease with increasing number of carbon atoms. However, these increases are more regular for the dihydroxyalkyl phases. The increasing dependencies of $\overline{\kappa}_{as}$ vs. n_C shown in Figures 2 and 3 are expected because the adsorption energies of

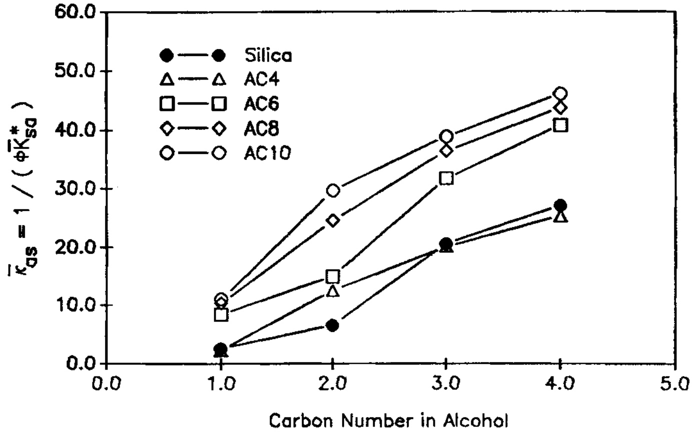

Figure 3. Dependencies as in Figure 2 for the alkenyl bonded phases

organics usually increase with their molecular weights. It is more difficult to explain the differences in these dependencies for alkenyl and dihydroxyalkyl bonded phases. For example, the difference in $\bar{K}_{as}$ for methanol and 2-butanol on the decenyl phase is about 35, whereas this difference for the dihydroxydecyl phase is about 15. The higher values of $\bar{K}_{as}$ for alcohols on the alkenyl phases in comparison to those on the dihydroxyalkyl phases may be due to additional interactions from polar and nonpolar parts of the alcohol molecule with the bonded phase, i.e., specific interaction of the hydroxyl group of an alcohol with the unreacted silanol group and additional nonspecific interactions of the alcohol nonpolar chain with the alkenyl ligand.

In the case of the dihydroxyalkyl bonded phases, these additional interactions are small because of the polar terminal diol groups. Thus, the alcohol chain effect for diol phases is smaller in comparison to that for alkenyl phases and therefore the differences between the $\bar{K}_{as}$ vs. n_C -curves for the DC4, DC8 and DC10 phases are not significant. These curves can be approximated by one line because the $\bar{K}_{as}$ -values representing averages for various halophenols and cresols contain about 10% error. Because the $\bar{K}_{as}$ -values for alkenyl phases are considerably greater than those for diol phases, the $\bar{K}_{as}$ -curves shown in Figure 3 for these phases change systematically from the AC4 to AC10 columns.

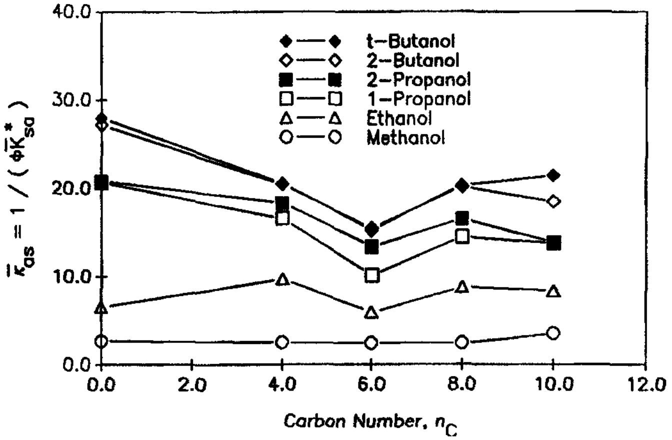

Figure 4. Dependencies of $\bar{\kappa}_{as}$ on the number of carbon atoms in the dihydroxyalkyl (diol) bonded ligands for halophenols chromatographed in various alcohol/n-hexane mobile phases. Points at $n_C = 0$ denote the $\bar{\kappa}_{as}$ -values for unmodified silica.

Figures 4 and 5 are interesting because they illustrate the effect of the surface ligand length on the $\bar{\kappa}_{as}$ -value. These figures show distinctly different behavior of the alkenyl and diol phases. For all modifiers the values of $\bar{\kappa}_{as}$ did not change significantly with increasing length of the diol ligands (see Figure 4). Generally, the values of $\bar{\kappa}_{as}$ on unmodified silica were greater than those on the diol phases. A comparison of the $\bar{\kappa}_{as}$ -values for the diol phases shows that they are similar for all phases studied except for the DC6 phase, where a small minimum was observed. The similar values of $\bar{\kappa}_{as}$ indicate that the differences between the modifier and solute adsorption energies were similar for the diol bonded phases, which is not surprising if one considers that, for these systems, the hydrogen bonding between the hydroxyls of the modifier and solute, and the diol groups is relatively strong. It is more difficult to explain why the DC6 phase was significantly different compared to the other diol phases. In contrast to the effect shown in Figure 4, the $\bar{\kappa}_{as}$ vs. n_C -curves presented in Figure 5 for the alkenyl phases increases with increasing length of the alkenyl ligands. The values of $\bar{\kappa}_{as}$ for unmodified silica and the AC4 phase are analogous and a rapid increase in $\bar{\kappa}_{as}$ was observed for the AC6 phase. For the AC8 and AC10 phases, an increase in $\bar{\kappa}_{as}$ was observed, but it was significantly smaller than that for the AC6 phase. An increase in the $\bar{\kappa}_{as}$ -

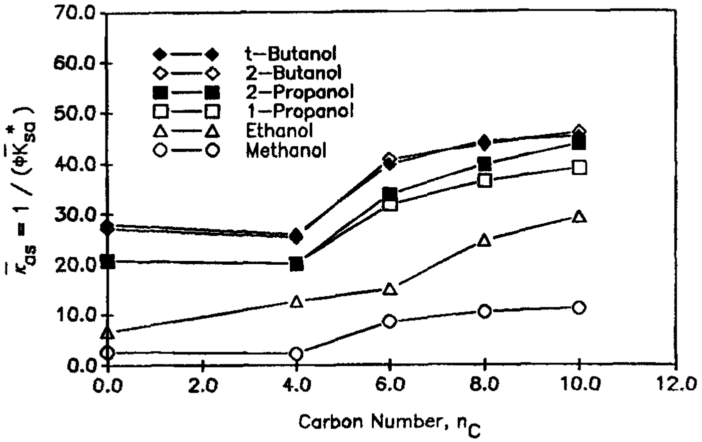

Figure 5. Dependencies as in Figure 4 for the alkenyl bonded ligands

value with increasing length of the alkenyl ligand shows that the absolute difference in the modifier and solute adsorption energies decrease. For longer ligands, the solute-ligand interaction can be weakened by the presence of other groups in the solute (e.g., halogen atom) which create an unfavorable steric situation. This weakening of solute-ligand interactions can explain a decrease of the absolute difference in the modifier and solute adsorption energies with increasing length of alkenyl ligands.

For both types of bonded phases, the C6-ligands showed a special behavior. The interactions of modifier molecules with the C6-diol ligands were weakest in comparison to the other diol phases, whereas these interactions with the hexenyl ligands were greater and comparable to those with octenyl and decenyl ligands. Perhaps the steric and orientational effects for solute and modifier molecules in the C6 phases are optimal.

In the case of the nitro- and cyanophenols, the retention was more complex because physicochemical properties of nitro and cyano groups differ considerably from those for halogens.[6] These groups are composed, respectively, from three and two atoms, and are capable of strong interactions with the surface groups and ligands. According to Snyder,[6] the solute localization on silica surfaces is considerably stronger for solutes with a cyano group than for solutes with a nitro group. Also, for these solutes, the isomeric effects associated with the o-, m- and p- positions of functional groups are strong. Thus, for nitro- and cyanophenols, the values of κ_{as} cannot be averaged because they show a strong dependence on chemical nature of the functional group and dependence on its position in the solute. Generally, the values of κ_{as} for cyano- and nitrophenols were up to twice time smaller than the corresponding values for halophenols. For a given chromatographic system, the adsorption energies of nitro- and cyanophenols are higher than those for halophenols. However, their κ_{as} -dependencies on the number of carbon atoms in the modifiers and the surface ligands are analogous to those observed for halophenols.

It is noteworthy that the values of κ_{as} for p-cyanophenol on various modified silicas were lower than the corresponding values of κ_{as} for m- and o-derivatives. This result means that, for these systems, the adsorption energies of p-cyanophenol are greater than those for o- and m- cyanophenols. This is not surprising because the para-position of hydroxy and cyano groups in a solute facilitates interactions of both these groups with the modified silica surface. The para-effect seems to be characteristic for bi-functional solutes with relatively polar groups. However, the isomeric effect for halophenols is smaller because the difference is the κ_{as} -values for o-, m- and p- derivatives do not exceed 10-15%. For these solutes this effect seems to be controlled by steric factors.

CONCLUSIONS

Analysis of the retention data for phenolic solutes which contain halo, hydroxy, nitro and cyano groups chromatographed at low concentrations of an aliphatic alcohol (methanol, ethanol, propanol or butanol) in n-hexane on the alkenyl and dihydroxyalkyl (diol) bonded phases have shown that the molecular interactions in these phases are different. This analysis, performed on the basis of a displacement model for solute retention, which takes additionally into account the alcohol composition in the stationary phase, has shown that the differences in the alcohol and solute adsorption energies are analogous betweem the unmodified silica and diol bonded phases. However, for alkenyl phases the difference decreases with increasing length of the bonded ligands. Although, for both types of bonded phases, the adsorption energies of alcohols increase with the number of carbon atoms in their chain, this effect is stronger for alkenyl ligands. The structure and polarity of functional groups in the solute mainly affect the magnitude of the interaction energies of solute and modifier with the bonded phase. For example, these energies are greater for phenol solutes with cyano and nitro groups than for halophenols. For cyano and nitrophenols, the positional isomeric effect is stronger than for halophenols.

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