

Changes in the enthalpy and entropy of hydroxyl aromatics in reversed-phase liquid chromatography with β -cyclodextrin in the mobile phase

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ABSTRACT

Standard enthalpy (ΔH°) and entropy (ΔS°) changes were obtained for several hydroxyl aromatics without β -cyclodextrin in the mobile phase, and enthalpy (ΔH°_f) and entropy (ΔS°_f) of complex formation were calculated for the hydroxyl aromatics with β -cyclodextrin in the mobile phase. Negative enthalpy and entropy values were obtained without β -cyclodextrin present in the mobile phase. With β -cyclodextrin in the mobile phase, negative values for the enthalpy of complex formation were obtained, but positive values were obtained for the entropy of complex formation. An equation was derived that relates the capacity factors with β -cyclodextrin in the mobile phase to ΔH° , ΔH°_f , ΔS° , ΔS°_f , phase ratio, formation constant, and equilibrium concentration of β -cyclodextrin. Several correlations were developed for the thermodynamic properties, and it was found that the model compounds could be classified into two groups based primarily on their thermodynamic properties.

INTRODUCTION

The effects of the column temperature on solute retention in reversed-phase liquid chromatography (RPLC) have been investigated by a number of researchers. For example, Melander *et al.* [1] reported the effects of temperature and solvent composition on the retention of oligo(ethylene glycol) derivatives in RPLC. Also, Melander *et al.* [2–4] considered the retention characteristics of solutes as a function of both column temperature and solvent composition. Other researchers have also considered the effects of temperature and mobile phase composition on the retention behavior of a variety of compounds [5,6].

The chromatographic results from temperature studies are also useful in exploring the thermodynamic aspects of solute retention in RPLC. Melander *et al.* [7] discussed enthalpy–entropy compensations in reversed-phase systems for several aromatic carboxylic acids and phenyl acetic acids. They showed that the reversible binding of solutes to hydrocarbonaceous bonded-phases conformed to the same

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mechanism under the experimental conditions used. Chmielowiec and Sawatzky [8] studied the effects of temperature on the thermodynamic behavior of polynuclear aromatic hydrocarbons on a silica C_{18} column in aqueous acetonitrile mobile phases. Sander and Field [9] reported the influence of mobile phase composition on the thermodynamic properties for *N,N*-diethylaniline and isopropylbenzene with a μ -Bondapak C_{18} column and a Zorbax CN column. Melander *et al.* [10] studied the characteristics of the stationary phase in RPLC as far as the length of the alkyl chain, column temperature, chemical nature of the hydrocarbonaceous ligands, and surface coverage. In other work, Melander and Horváth [11] analyzed a large amount of literature data from different hydrocarbonaceous bonded-phases to study the effect of stationary phase on the free energy increments for various structural elements of the solutes. Vigh and Varga-Puchony [12] reported the influence of temperature on the retention factors of C_6 – C_{16} *n*-alkanols, C_6 – C_{12} *n*-alkanal dinitrophenyl hydrazones, and C_6 – C_{11} 2-*n*-alkanone dinitrophenyl hydrazones at various temperatures on Micropak CH-10 and Nucleosil C_{18} octadecyl packings with aqueous methanol eluents.

In related work with cyclodextrins, Harrison and Eftink [13] studied the thermodynamics of the binding of adamantanecarboxylate to cyclodextrins as a function of temperature and methanol by using flow microcalorimetry. They believed that the binding of solutes to both α -cyclodextrin (α -CD) and β -cyclodextrin (β -CD) was driven by strong London dispersion forces between the delocalized charge on the solute and the polar groups, namely, ether-like oxygens lining the cavity of cyclodextrin. Catena and Bright [14] reported thermodynamic parameters and stoichiometries of the binding of anilinonaphthalenesulfonates to β -CD by steady-state fluorescence intensity and anisotropy measurements. They obtained formation constants and enthalpy and entropy values of the inclusion complexes for different analytes. Woodburn *et al.* [15] investigated the thermodynamic properties of anilinonaphthalenesulfonates from methanol–water solvent mixtures and used enthalpy–entropy compensation concepts to interpret their data.

In this paper, the fundamental thermodynamic parameters, ΔH° and ΔS° , were obtained with and without β -CD present in the mobile phase for several hydroxyl aromatics using a C_{18} column and methanol–water mobile phases. The main goals of the research were to compare the ΔH° and ΔS° values with and without β -CD in the mobile phase in order to gain insights into the chromatographic mechanism with β -CD in the mobile phase and to discern the effects of some of the structural features of the model compounds on their retention characteristics.

EXPERIMENTAL

Apparatus

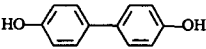
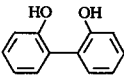

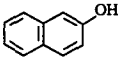
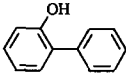
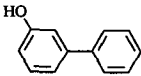
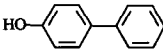
The liquid chromatograph used was a Waters unit with a Model 6000A pump (Milford, MA, U.S.A.), a U6K injector, a dual channel ultraviolet detector set at 254 nm, and an Omniscribe dual channel 10-mV strip chart recorder (Houston Instrument). A Model FIATron (Oconomowoc, WI, U.S.A.) constant temperature control system was used to keep the temperature of the column constant. The accuracy of the column heater was $\pm 0.1^\circ\text{C}$. The chromatographic column employed was a 5- μm C_{18} (250 mm \times 4.6 mm I.D.) obtained from Burdick and Jackson (Muskegon, MI,

U.S.A.). The carbon content and weight of the bonded packing material for the C₁₈ column were provided by Burdick and Jackson.

Reagents

The model compounds and β -CD were purchased from Aldrich (Milwaukee, WI, U.S.A.). The names and structures of the model compounds are given in Table I. Methanol was HPLC grade and obtained from Burdick and Jackson.

TABLE I
NAMES AND STRUCTURES OF THE MODEL COMPOUNDS

Compound	Structure
1 <i>p,p'</i> -Biphenol	
2 <i>o,o'</i> -Biphenol	
3 1-Naphthol	
4 2-Naphthol	
5 2-Phenylphenol	
6 3-Phenylphenol	
7 4-Phenylphenol	

Procedure

β -Cyclodextrin was vacuum dried under 0.78 atm pressure at 75°C for eight hours and then dissolved in prefiltered water. The appropriate amount of methanol was added to a water solution of β -CD. The largest analytical concentrations of β -CD in 50:50 and 60:40 methanol-water mixtures were 4.0 mM and 3.0 mM, respectively. The concentrations of the samples injected were 1 mg/ml in methanol. The column void volume was obtained by injection of a methanol solution of potassium nitrite.

RESULTS AND DISCUSSION

Theory

The equilibrium constant (K) of a solute binding to the stationary phase in reversed-phase systems can be related to the column temperature according to the following equations [7]:

$$\ln K = -\Delta G^\circ/RT \quad (1)$$

$$\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R \quad (2)$$

where ΔG° is the Gibbs free energy for the solute-stationary phase interaction; R is the gas constant; and T is the absolute temperature.

Since $k'_o = \phi K$, where k'_o is the solute capacity factor in the chromatographic system, and ϕ is the volume phase ratio of the stationary to the mobile phase, eqn. 2 can be written as

$$\ln k'_o = -\Delta H^\circ/RT + \Delta S^\circ/R + \ln \phi \quad (3)$$

where ΔH° and ΔS° are considered to be the standard enthalpy change and entropy change, respectively, as a solute partitions from the mobile to the stationary phase [8]. Eqn. 3 indicates that the solute retention depends upon the column temperature. An increase in the column temperature normally causes a decrease in the solute retention.

According to eqn. 3, the slope of the line that results from a plot of $\ln k'$ vs. $1/T$ is $-\Delta H^\circ/R$, and the intercept is $\Delta S^\circ/R + \ln \phi$. To obtain the entropy change, the phase ratio has to be known. Sentell and Dorsey [16] presented a method for calculating the volume of stationary phase with the following equation:

$$V_s = \frac{(\%C)(M)(W_\rho)}{(100)(12.011)(n_c)(\rho)} \quad (4)$$

where V_s is the stationary phase volume; %C is grams of carbon per 100 grams of bonded silica; n_c refers to the number of carbon atoms per mole of silane; the molecular weight of the silane is given by M ; the term W_ρ is the weight (g) of the bonded packing material in the column. The density of the bonded octadecylsilyl (ρ) is assumed to be equal to 0.8607 g/cm³ [17]. In this work, the mobile phase volume in the column was assumed to be the same as the retention volume of a non-retained solute, namely, potassium nitrite. The phase ratio was obtained from $\phi = V_s/V_m$, and the calculated value of ϕ was 0.426.

With β -CD in the mobile phase, the solute capacity factor will be affected by the extent of complex formation of β -CD with the solute in the mobile phase and other parameters [18]. As discussed earlier, the solute capacity factor with β -CD in the mobile phase can be defined by eqn. 5 [18].

$$1/k' = 1/k'_o + [(CD)_m]/k'_o K_D \quad (5)$$

where k'_o is the capacity factor with no β -CD present, $[(CD)_m]$ is the equilibrium

concentration of β -CD in the mobile phase, and K_D is the dissociation constant of the inclusion complex in the mobile phase. The earlier experimental data and data analysis indicated that the solute- β -CD complexes did not interact with or interacted very little with the stationary phase [18].

By solving eqn. 5 for k' and substituting $1/K_f$ for K_D , where K_f is the formation constant of the inclusion complex, eqn. 6 is obtained.

$$k' = k'_o \cdot 1/K_f / \{1/K_f + [(\text{CD})_m]\} \quad (6)$$

Taking the ln of both sides of eqn. 6, eqn. 7 is obtained.

$$\ln k' = \ln k'_o - \ln K_f - \ln \{1/K_f + [(\text{CD})_m]\} \quad (7)$$

Using eqns. 2 and 8, where ΔH_f° and

$$\ln K_f = -\Delta H_f^\circ/RT + \Delta S_f^\circ/R \quad (8)$$

ΔS_f° are the standard enthalpy and entropy changes of complex formation in the mobile phase, respectively, eqn. 9 can be acquired.

$$\ln k' = (\Delta H_f^\circ - \Delta H^\circ)/RT + (\Delta S - \Delta S_f^\circ)/R + \ln \varphi - \ln \{1/K_f + [(\text{CD})_m]\} \quad (9)$$

Eqn. 9 can be used in the calculation of ΔH_f° and ΔS_f° , and this will be discussed later.

Hydroxyl aromatics without β -CD in the mobile phase

The capacity factors for several hydroxyl aromatics (see Table I for structures) were obtained at 25, 30, 35 and 40°C with a C_{18} column. This is a limited temperature range and more work has to be performed to assess the effects of temperature on capacity factors at other temperatures. Fig. 1 shows that as the temperature is increased for the mobile phase without β -CD, the k' values of the compounds investigated decreased, and a linear relationship was obtained for all the hydroxyl aromatics. In the presence of β -CD, the same general graphs were obtained (see Fig. 2). The linear correlation coefficients with and without β -CD ranged from 0.956 to 0.996. At a given temperature, the presence of β -CD showed a decrease in the solute retention which was due to the formation of an inclusion complex between the solute and β -CD in the mobile phase [18]. It should be mentioned that Fujimura *et al.* [19] reported that β -CD and the β -CD complexes they studied did not show any interactions with a C_8 column. This is most likely due to the hydrophilic nature of the external part of the β -CD molecule. Also, we recently showed that interactions of β -CD hydroxyl aromatic complexes were not important for compounds 1–4 in Table I [18]. For compounds 5–7 in Table I, there was an indication that there may have been slight interactions of the complexes with C_{18} , but data analysis of the graphs of $1/k'$ vs. equilibrium concentration of β -CD indicated that the interactions were unimportant [18].

The thermodynamic parameters calculated from the slopes and intercepts of the $\ln k'$ vs. $1/T$ graphs for the hydroxyl aromatics in methanol–water (50:50) are listed in Table II. A comparison between the thermodynamic values of the structural isomers in methanol–water (50:50) is given in the following discussion. Enthalpy values can be

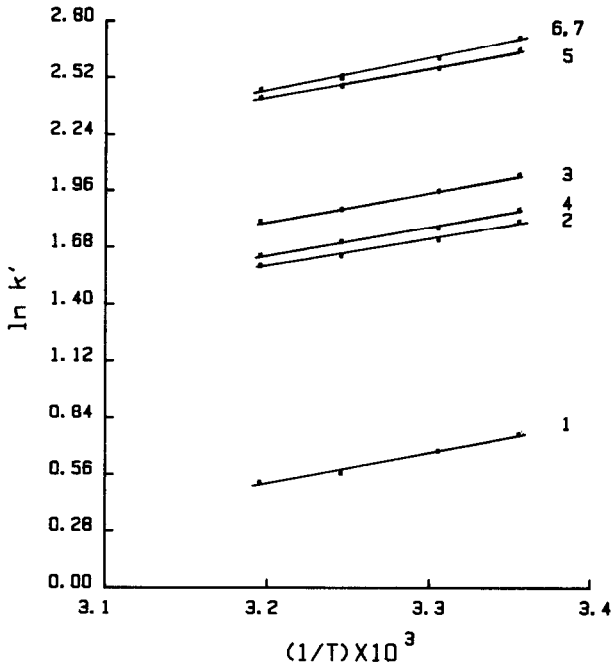


Fig. 1. Plot of $\ln k'$ vs. $1/T$ for several hydroxyl aromatics in methanol-water (50:50). See Table I for the names and structures of the compounds.

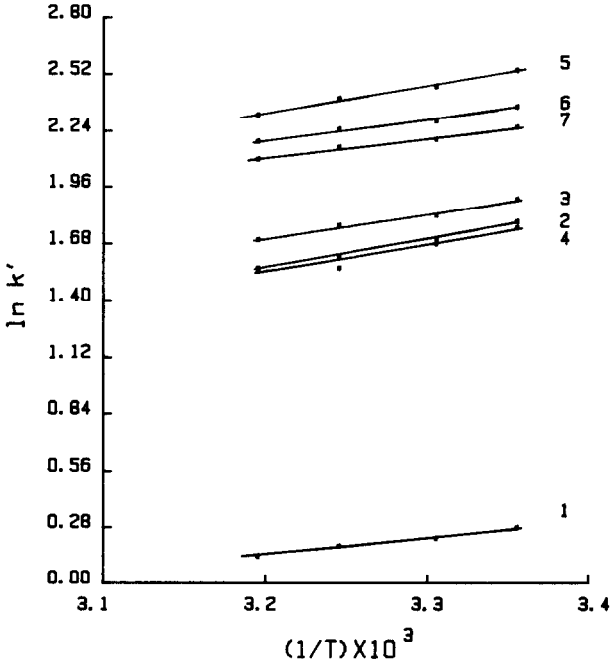


Fig. 2. Plot of $\ln k'$ vs. $1/T$ for several hydroxyl aromatics in methanol-water with 4.0 mM β -CD. See Table I for the names and structures of the compounds.

TABLE II

THE ΔH° , ΔS° , ΔH_f° , AND ΔS_f° VALUES OF SEVERAL HYDROXYL AROMATIC COMPOUNDS IN METHANOL-WATER (50:50) AND METHANOL-WATER (50:50) + 4.0 mM β -CD ON A C_{18} COLUMNS

The enthalpy and entropy units are kcal mol⁻¹ and cal mol⁻¹T⁻¹, respectively.

Solute	Methanol-water		Methanol-water + 4.0 mM β -CD	
	ΔH°	ΔS°	ΔH_f°	ΔS_f°
1 ^a	-3.03	-6.92	-1.31	9.79
2	-2.72	-3.81	-	-
3	-2.87	-3.84	-0.49	10.4
4	-2.79	-3.91	-0.26	11.0
5	-2.98	-2.98	-0.34	10.7
6	-2.73	-3.73	-1.23	9.30
7	-3.20	-3.59	-1.29	9.53

^a See Table I for the name and structure of the compound.

considered as a measure of the efficiency of the transfer of the solute from the mobile phase to the stationary phase. The more negative the ΔH° value, the more effectively the solute is transferred to the stationary phase. The more negative ΔH° value of *p,p'*-biphenol compared to *o,o'*-biphenol indicated that the former interacted with the stationary phase more strongly than the latter in methanol-water (50:50). The ΔS° values in Table II can be rather difficult to interpret. A ΔS° value can be considered as the change in ordering of the solute as it partitions between the mobile phase and stationary phase. Also, changes in entropy of the mobile phase and changes in the entropy of the stationary phase as a result of the solute partitioning between these two phases are important considerations. There was no attempt in this work to distinguish all of these changes. Thus, only a general interpretation of the changes in ΔS° values is given. We considered the changes in the ΔS° values as the change in ordering of the solute as it partitions between the mobile phase and stationary phase. As Table II shows, there is a substantial difference between ΔS° values for *p,p'*- and *o,o'*-biphenol. The entropy values of *p,p'*- and *o,o'*-biphenol indicate better ordering of *p,p'*-biphenol on the stationary phase relative to the mobile phase than that of the *o,o'*-biphenol with methanol-water (50:50). The somewhat more negative ΔH° value of 1-naphthol compared with ΔH° value of 2-naphthol in Table II implies that 1-naphthol interacted more strongly with C_{18} than 2-naphthol. The difference in ΔS° values of 1- and 2-naphthol is small, namely, 0.07 cal mol⁻¹T⁻¹; thus the ordering of these compounds on the stationary phase relative to the mobile phase is approximately the same.

In the phenylphenol series, it is seen that the enthalpy change of 4-phenylphenol is the greatest, which indicated that 4-phenylphenol was more effectively transferred to the stationary phase than the other two isomers (Table II). 2-Phenylphenol had the smallest negative ΔS° value with methanol-water (50:50). This showed that 2-phenylphenol was less ordered on the stationary phase than in the mobile phase compared to 3- and 4-phenylphenol due to sorption [8]. The ortho position of the phenyl ring to the hydroxyl group in 2-phenylphenol resulted in intramolecular hydrogen bonding

between OH and π electrons of the phenyl ring [20]. This would cause the interaction of 2-phenylphenol with C_{18} to become less effective compared to the other two isomers in methanol-water (50:50).

Hydroxyl aromatics with β -CD in the mobile phase

The addition of β -CD to the mobile phase in the reversed-phase systems investigated resulted in the formation of inclusion complexes, if the solutes had the correct size and shape to fit into the cavity of β -CD [18]. We previously showed that in methanol-water mobile phases 1:1 complexes were formed with β -CD for the solutes listed in Table I [18]. In addition, the earlier experimental evidence indicated that generally the β -CD-solute complexes did not interact with the stationary phase. However, some of the data suggested the β -CD complexes of the phenylphenols interacted with the stationary phase, although we concluded that these interactions were weak [18]. Fig. 2 shows that linear relationships were obtained between $\ln k'$ and $1/T$ for the seven model compounds when the total concentration of β -CD was 4.0 mM in methanol-water (50:50). Close inspection of the data in Figs. 1 and 2 for *o,o'*-biphenol shows that at a given temperature the k' values for this compound changed very little. For example, the k' value was 6.22 at 25°C without β -CD and with β -CD it was 6.10. Because the reproducibility of the k' values for this compound was about ± 0.10 , the calculation of thermodynamic values for *o,o'*-biphenol with β -CD present was not considered accurate enough.

For eqn. 9, it was assumed that $\ln \varphi$ and $\ln \{1/K_f + [(CD)_m]\}$ changed very little with temperature, and thus a plot of $\ln k'$ vs. $1/T$ would give a straight line with a slope of $(\Delta H_f^\circ - \Delta H^\circ)/R$. These aspects are supported by the linear plots in Fig. 2. Also, the K_f values were calculated for all four temperatures for solutes 1 and 3-7 using eqn. 5 with a value of $8.04 \cdot 10^{-4}$ M for the equilibrium concentration of β -CD and appropriate values of k' and k'_0 [18]. The equilibrium concentration of β -CD was not expected to change much with temperature because it was present in considerable excess compared to the solutes. With the K_f values and the equilibrium concentration of β -CD, $\ln \{1/K_f + [(CD)_m]\}$ values were calculated for solutes 1 and 3-7 at the four temperatures. The percentage changes in $\ln \{1/K_f + [(CD)_m]\}$ from 25 to 40°C for solutes 1 and 3-7 were 1.1%, 4.5%, 4.8%, 2.8%, 1.6% and 1.2%, respectively. Thus, the percentage changes in $\ln \{1/K_f + [(CD)_m]\}$ values were considered small enough so that reasonable estimates of ΔH_f° could be made from the slopes. Additional data would have to be acquired for highly accurate values of ΔH_f° .

From the slopes of the lines in Fig. 2 and assuming $\ln \{1/K_f + [(CD)_m]\}$ changed little with temperature, it was then possible to calculate ΔH_f° because ΔH° values were calculated earlier (Table II). Once ΔH_f° values were acquired then ΔS_f° values could be calculated from eqn. 8. The K_f values for the solutes needed for the calculation of ΔS_f° values were obtained from ref. 18. Table II lists the calculated ΔH_f° and ΔS_f° values. As shown in Table II, all the ΔH_f° values are negative indicating favorable conditions for complex formation. However, the respective ΔH° value in Table II for a given compound is more negative than the corresponding ΔH_f° value indicating that there was more of a tendency for the hydroxyl aromatics to interact with the stationary phase relative to β -CD molecules in the mobile phase.

In Table II, the ΔS_f° values are all positive which indicates that upon complex formation in the mobile phase a more disordered state results relative to the solute that

is uncomplexed. This is in contrast to the ΔS° values in Table II with no β -CD present in the mobile phase where all of the ΔS° value were negative. It should be mentioned that Lewis and Hansen [21] reported values of $-2.6 \text{ kcal mol}^{-1}$ (ΔH_f°) and $7 \text{ cal mol}^{-1}\text{T}^{-1}$ (ΔS_f°) for the binding of phenol with β -CD in aqueous solution using calorimetry. These values correlate, in general, with the ΔH_f° and ΔS_f° values for the hydroxyl aromatics in Table II. It is beyond the scope of this work to define all the interactions that result in positive ΔS_f° values. For example, hydrogen bonding interactions between the solute and solvent are involved in addition to interactions between water and methanol molecules in the binary mobile phase.

Of primary interest in this work were the effects of the enthalpy and entropy values on the capacity factors of the hydroxyl aromatics with β -CD present in the mobile phase. By subtracting eqn. 9 from eqn. 3, one obtains eqn. 10.

$$\ln k'_o - \ln k' = -\Delta H_f^\circ/RT + \Delta S_f^\circ/R + \ln\{1/K_f + [(CD)_m]\} \quad (10)$$

From eqn. 10, it is seen that the change in capacity factor with the addition of β -CD is a function of T , ΔH_f° , ΔS_f° , $1/K_f$, and the equilibrium concentration of β -CD. The three major terms in eqn. 10 ($-\Delta H_f^\circ/RT$, $\Delta S_f^\circ/R$, and $\ln\{1/K_f + [(CD)_m]\}$) were calculated for solutes 1 and 3-7 at 25°C and are listed in Table III. The K_f values were taken from ref. 18. The data in Table III shows that solutes 1, 6, and 7 have similar numerical values for the sets of major terms and 3, 4, and 5 have similar sets of numerical values. The clustering of solutes indicates that the differences in the \ln of the capacity factors without and with β -CD for the solutes in a given cluster would be similar. This conclusion is supported by the k' values reported earlier for the solutes in Table III [18]. The grouping of solutes that appear in Table III implies similar interactions for these compounds in a given group. The $\ln\{1/K_f + [(CD)_m]\}$ terms have the greatest absolute values and thus determine to a large extent the magnitude of $\ln k'_o - \ln k'$. Because the equilibrium concentration is the same for β -CD for all the solutes the different values for the $\ln\{1/K_f + [(CD)_m]\}$ terms are a result of the unequal values obtained for K_f for the various solutes. For solutes 3, 4, and 5 the $\Delta H_f^\circ/RT$ terms make relatively smaller contributions compared to the $\Delta S_f^\circ/R$ terms. This is also indicated by comparing the appropriate ΔH_f° and ΔS_f° values in Table II. For solutes 1, 6 and 7 the same general conclusions can be made by comparing the data in Tables II and III. However, the entropy contribution is somewhat less, while the enthalpy contribution is somewhat greater.

TABLE III

COMPARISON OF THE MAJOR TERMS IN EQN. 10 AT 25°C FOR SIX SOLUTES

Solute ^a	$\Delta H_f^\circ/RT$	$\Delta S_f^\circ/R$	$\ln\{1/K_f + [(CD)_m]\}$
1	-2.21	4.93	-6.44
3	-0.83	5.23	-5.79
4	-0.43	5.54	-5.69
5	-0.57	5.38	-5.71
6	-2.08	4.68	-6.23
7	-2.18	4.80	-6.36

^a See Table I for names and structures of compounds.

Using data reported earlier for solutes 1 and 3–7, the percentage changes in k' values were calculated in going from 0.0 mM β -CD to 4.0 mM β -CD [18]. Percentage changes of 71.0, 39.3, 33.0, 33.9, 60.0, and 66.3 were obtained for solutes 1, 3, 4, 5, 6, and 7, respectively. By plotting $\ln \{1/K_f + [(CD)_m]\}$ vs. percentage change of the k' values a linear relationship was obtained with a correlation coefficient of 0.999. Linear relationships were also obtained for $-\Delta H_f^\circ/RT$ vs. percentage change of k' values and $\Delta S_f^\circ/R$ vs. percentage change of k' values for solutes 1, 6, and 7 with both plots showing positive slopes. In addition, graphs of $-\Delta H_f^\circ/RT$ vs. percentage change of k' values and $\Delta S_f^\circ/R$ vs. percentage change of k' values gave linear relationships for solutes 3, 4, and 5, but the enthalpy plot had a positive slope and the entropy plot had a negative slope. These various relationships show that the major terms in eqn. 10 can be combined in a linear fashion to yield the change in capacity factors with the addition of β -CD. However, opposite trends were obtained for the enthalpy and entropy terms for solutes 1, 6, and 7 compared to solutes 3, 4, and 5.

CONCLUSIONS

Without β -CD in the mobile phase, the negative ΔH° values for the solutes gave a measure of the effectiveness of the transfer of the solute from the mobile phase to the stationary phase. Because all of the entropy values were negative without β -CD in the mobile phase, this implied that the solutes were more ordered in the stationary phase relative to the solutes in the mobile phase. The less negative ΔH_f° values relative to the ΔH° values implied that the hydroxyl aromatics favored interaction in the stationary phase relative to the β -CD cavity. Because all the ΔS_f° values were positive a more disordered state resulted in the mobile phase as a result of complex formation.

It was shown that the change of the capacity factors with β -CD in the mobile phase was a function of several parameters, but these parameters could be grouped into three major terms and the quantitative contribution of each term to the change in capacity factor was evaluated. The model compounds fell into two groups with one group showing the same trend for the ΔH_f° and ΔS_f° values, while the other group of compounds showed opposite trends for the ΔH_f° and ΔS_f° values. The different trends in the ΔH_f° and ΔS_f° values for a given group of compounds showed that different interactions were operative with the two groups of hydroxyl aromatics.

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