Thermodynamic Interpretation of Retention Equilibrium in Reversed-Phase Liquid Chromatography Based on Enthalpy−Entropy Compensation

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The fundamentals of the retention equilibrium in reversed-phase liquid chromatography (RPLC) are studied on the basis of enthalpy−entropy compensation (EEC). First, retention data were acquired and the influence of the nature of the compounds, organic solvent modifier, and temperature on these data was assessed. Then, the data were analyzed according to the four different methods proposed by Krug et al., and an EEC was formally established. Linear correlations were observed between the logarithm of the adsorption equilibrium constants under the different RPLC conditions, suggesting linear free energy relationships (LFERs). Finally, the variations of the retentions with the experimental conditions are shown to be quantitatively explained by a new model based on EEC. This model affords a comprehensive interpretation of the variations of retention originating from changes of either one parameter alone or several simultaneously. The slope and intercept of the LFER that relates two equilibrium systems are accounted for by the new model. The parameters of this model are the changes of enthalpy and entropy associated with the retention, the compensation temperatures, and the experimental conditions.

Peak profiles in chromatography depend primarily on the thermodynamic characteristics of the phase equilibrium considered.[1] Numerous studies on retention behaviors and separation mechanisms in reversed-phase liquid chromatography (RPLC) have been made on the basis of the dependence of a retention parameter on the experimental conditions. It is relatively easy to make precise measurements of retention parameters, such as the retention factor (k') and the adsorption equilibrium constant (K).[2−4] The analysis of retention equilibrium data has the support of a strong theoretical basis, i.e., the thermodynamics of phase equilibria. For instance, the logarithm of the equilibrium constant is proportional to the change in the Gibbs free energy (ΔG) associated with the passage from the mobile to the stationary phase. Other thermodynamic parameters, i.e., the changes in enthalpy (ΔH) and entropy (ΔS), can be estimated from the temperature dependence of K or k', according to the van't Hoff equation. These are the main reasons for the wide variety of fundamental studies of separation mechanisms in RPLC that were made from the viewpoint of retention equilibrium.

Retention mechanisms in RPLC have also been discussed from an extrathermodynamic point of view. Mechanistic similarities of retention behaviors in RPLC were discussed on the basis of the enthalpy−entropy compensation (EEC) between ΔH and ΔS. Numerous publications demonstrated experimentally an EEC[5−18] or supported the possibility of EEC on theoretical bases.[19−23] Compensation temperatures (T_c) between about 500 and 1000 K were reported under different experimental conditions involving the mobile-phase solvents, the sample compounds, and the

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temperature range.[6,7,13,15−18,24] That an EEC exists suggests that the retention behavior is governed by a single mechanism. EEC was also found in normal-phase LC systems (NPLC), using a polar stationary phase (e.g., Permaphase ETH) and a nonpolar solvent (e.g., hexane with 1% ethanol). However, the retention process in NPLC systems was shown to be mechanistically different from that in RPLC because T_c in NPLC ($\sim$140 K) is quite different from that in RPLC (between about 500 and 1000 K).[6] Similarly, compensation behavior was confirmed for retention equilibria in other systems such as ion-pair RPLC,[24,25] ion-exchange LC,[26] and gas chromatography.[27,28]

On the other hand, Krug et al.[19−21] demonstrated that, for statistical reasons, a linear correlation could be expected between values of ΔH and ΔS that are derived from a van't Hoff plot, even when there is no real EEC effect. When that happens and the linear correlation originates only from the random errors made in the measurements of the two thermodynamic functions, the slope and the correlation coefficient of the linear plot between ΔH and ΔS are respectively equal to the harmonic mean of the experimental temperatures (T_{hm}) and close to unity. Krug et al. proposed four different methods to clarify whether a linear correlation between ΔH and ΔS results from an actual physico-chemical effect or from the statistical compensation of the experimental errors.[19−21] There are many publications concerning the establishment of EEC for the retention equilibrium in RPLC. In most cases, however, the thermodynamic parameters (ΔH and ΔS) were derived from van't Hoff plots but were not discussed according to the procedures proposed by Krug et al., leaving the validity of their conclusions in doubt.

The goal of this paper is to show how the use of EEC relationships permits a clarification of the thermodynamic background of the characteristic features of equilibrium parameters. We take retention equilibria in RPLC as a concrete example and develop a new model based on the use of EEC in order comprehensively to interpret the changes in retention behavior properties that are due to changes of some of the experimental conditions. First, retention equilibrium data for compounds belonging to a few homologous series were measured under different sets of experimental conditions. Second, these data were analyzed by following the four approaches proposed by Krug et al.,[19−21] in order to determine whether an EEC does exist for retention in RPLC or not. Then, a new model was derived that explains the influence of some experimental conditions on retention equilibria. Finally, we demonstrated that the model was effective for a comprehensive interpretation of the changes in retention behavior accompanying changes in different experimental conditions of RPLC.

EXPERIMENTAL SECTION

Reagents and Column. Pulse response experiments (i.e., elution chromatography) were carried out using an RPLC system consisting of a column packed with C_{18}-silica gel particles. Table

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Table 1. Physicochemical Properties of C_{18}-Silica Gel Particles and the RPLC Column

average particle diameter (μm)	45
particle density, ρ_p (g cm^{-3})	0.86
particle porosity, ϵ_p	0.46
carbon content (wt %)	17.1
column size (mm)	6 × 150
column void fraction, ϵ	0.42

1 lists some of the physicochemical properties of the packing material and of the column used (YMC, Kyoto, Japan). Two aqueous solutions of organic modifiers, methanol and tetrahydro-furan (THF), were used as the mobile-phase solvents. Their compositions were methanol/water (70:30, v/v) and THF/water (50:50, v/v). Several homologous series having different structures and chemical properties were used as sample compounds, *n*-alkylbenzenes, *p*-alkylphenols, *n*-alkanes, *n*-alkanols, and a group of aromatic hydrocarbons (benzene, biphenyl, naphthalene, bi-naphthyl). All the compounds used were reagent grade. They were used without further purification. Sample solutions were prepared by dissolving the sample compounds into the mobile phase. The concentration of the sample compound in these solutions was $\sim$0.1 wt % in most cases. Uracil and sodium nitrate were used as inert tracers.

Apparatus. The measurements of the elution peak profiles were made using a high-performance liquid chromatograph system (LC-6A, Shimadzu, Kyoto, Japan). A valve injector (model 7125, Rheodyne, Cotati, CA) was used for injecting small volumes of the sample solution into the stream of mobile phase. The column temperature was kept constant, using a thermostated water bath. The ultraviolet detector of the HPLC system (SPD-6A) was used for monitoring the concentration of the sample compound at the exit of the column.

Procedure. A small sample of solution (i.e., a concentration perturbation pulse) was introduced into the mobile-phase stream at the inlet of the column. In this study, the retention factors were measured at six different flow velocities of the mobile-phase solvent in order to determine the flow rate dependence of the retention behavior. The compounds studied here have all small molecules and fast mass-transfer kinetics. Not surprisingly, their retention factors are independent of the mobile-phase flow velocity (and practically independent of the pressure). The injection volume depended on the solubility and sensitivity of the sample compound and ranged between 0.5 and 300 μL. The elution peaks were measured at near-zero surface coverage of the sample compounds. The column temperature was adjusted between 288 and 308 K. The superficial velocity (u_0) of the mobile phase was adjusted between 0.06 and 0.12 cm s^{-1}, in order accurately to measure the experimental retention data, although the retention equilibrium is essentially independent of the mobile-phase flow rate. The measurements showed the retention factors to be independent of the flow rate, confirming that the column temperature is radially uniform and that the influence of the pressure on k' is negligible (at constant flow rate, the average column pressure changes with the column temperature, in inverse proportion to the mobile-phase viscosity).[29] The retention param-

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eters of the sample compounds were measured at least six consecutive times at each temperature. As described earlier, the precision of the retention data obtained is high. For instance, the relative standard deviation of the retention factor of toluene was 0.24% for seven data points. The retention behavior was found to be sufficiently sensitive to changes of the experimental conditions in the ranges investigated. The internal porosity (ϵ_p) of the C_{18}-silica gel particles and the void fraction (ϵ) of the RPLC column were calculated from the pulse response data measured using the inert tracers.

As explained above, the retention factors of the sample compounds were measured at different mobile-phase flow velocities. In practice, after the RPLC system had stabilized under constant flow rate and temperature, a series of the compounds were individually injected into the column and the corresponding elution peaks recorded. Then, the mobile-phase flow rate, the column temperature, or both were changed for the next experiment series. The volumetric flow rate of the mobile phase was measured at least three times during the measurements of the retention data of the sample compounds, at the beginning, the middle, and the end of the series. The relative standard deviation of the mobile-phase flow rate during the measurements of the retention factors of the alkylbenzenes varied between 0.20% and 0.68% for each of the six velocities. This shows that the control of the mobile-phase flow rate was sufficiently precise. Furthermore, the relative difference between the experimental flow rate and its intended level was between − 0.09% and + 0.86%, indicating that the accuracy of the flow rate was adequate.

On the other hand, the column temperature was checked after every sample injection. This showed how well the temperature was controlled around the intended levels. The deviation of the experimental temperatures from the intended ones was within ±0.1 K throughout the chromatographic measurements.

Data Analysis. According to the moment analysis method, the first absolute moment (μ_1) of the elution peak depends only on the equilibrium parameter, i.e., the adsorption equilibrium constant (K).

$$\mu_1 = (z/u_0)[\epsilon + (1 - \epsilon)(\epsilon_p + \rho_p K)] \tag{1}$$

The other symbols in this equation denote the physical properties of the C_{18}-silica gel particles and of the RPLC column and the experimental parameters. For instance, z and ρ_p are the column length and the density of the C_{18}-silica gel particles, respectively. Details on the moment analysis method were published earlier.[1,14−16,30−35] According to eq 1, K was calculated from the average value of the series of first moments, μ_1, of the elution peaks measured at different mobile-phase flow velocities.

The true value of μ_1 was derived by correcting the measured value for the retention time in the extracolumn tubes between
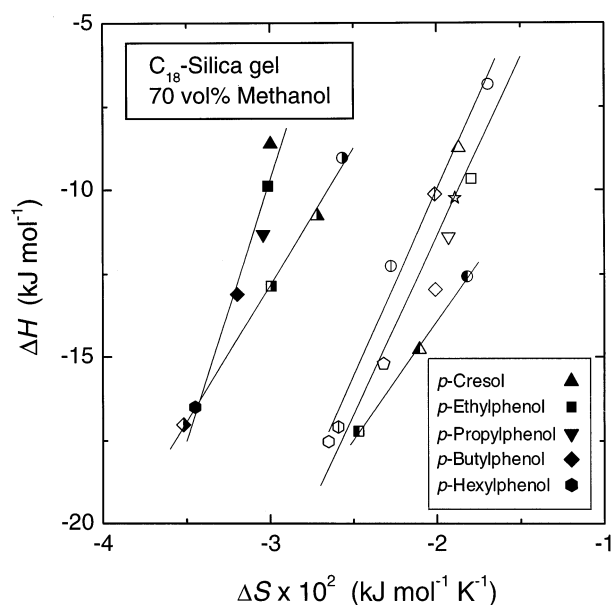
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Figure 1. Linear correlations between ΔH and ΔS for different homologous series. The correlation coefficients were 0.96 and 0.97 for *n*-alkylbenzenes and *p*-alkylphenols, respectively. Other symbols are as in Figures 2 and 3. Stationary phase, C_{18}-silica. Mobile phase, 70:30 (v/v) methanol/water.

the injection valve and the column and between the column and the detector. The additional residence time of the sample band in these tubes was measured by measuring the retention times of similar pulses injected without column. The influence of the width of the injected sample pulse on μ_1 was ignored due to the extremely small size of this pulse. As described above, the largest injection volume of sample solution was that for hexylbenzene, ∼300 μL, because of the low solubility of this compound in the mobile phase. This volume may be significant compared with the conventional sample volume in HPLC. However, the retention volume of hexylbenzene is 2 orders of magnitude larger than the sample volume, i.e., ∼30 mL. The retention of hexylbenzene is so large that the sample volume has little influence on the first moment analysis of its elution peaks.

As described above, the column temperature was changed between series of experiments, to derive the needed information on the thermodynamics of the retention equilibrium. Although u_0 was changed by a factor of 2, the same values of K were measured, irrespective of the value of u_0, suggesting that the temperature conditions in the column were adequately controlled. The particles of the material used are relatively large (see Table 1). This packing material is more suitable for preparative separations than for analytical purposes. However, the results and conclusions of this study concerning the characteristics of the retention behavior in RPLC are general because the retention equilibrium is essentially independent of the size and shape of the packing material used, as shown by eq 1, which includes no parameter related to the particle size.

RESULTS AND DISCUSSION

Enthalpy−Entropy Compensation for Different Series of Homologous Sample Compounds. Figure 1 shows linear correlations between ΔH and ΔS for different series of homologous compounds. The data for each compound were derived from
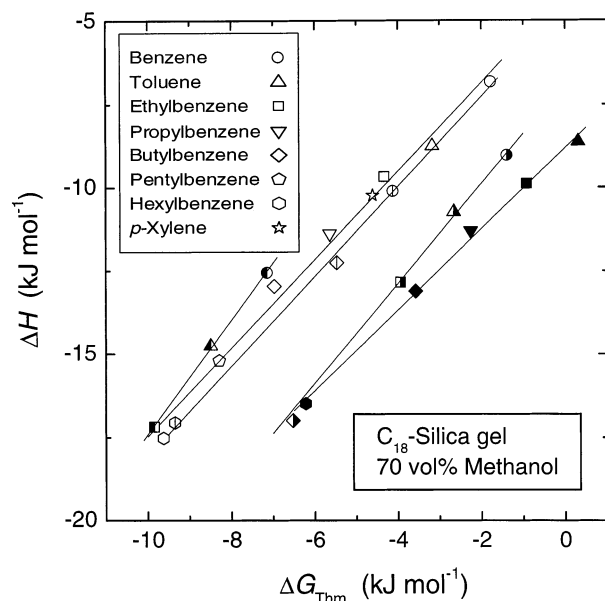
Figure 2. Linear correlations between ΔH and $\Delta G_{T_{hm}}$ for different homologous series. Other symbols as in Figures 1 and 3a,b.

the slope and intercept of the corresponding van't Hoff plot

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

where ΔH and ΔS are the enthalpy and entropy changes corresponding to the retention equilibrium, respectively, R is the gas constant, and T is the absolute temperature. Figure 1 suggests that there is probably an EEC for the retention equilibrium of these compounds in RPLC. Values of T_c ranging between 710 and 1560 K were calculated from the slopes of the straight lines in Figure 1. These results are consistent with those of previous studies made on EEC in RPLC.[6,7,13,15-18,24]

The most popular method for estimating ΔH and ΔS associated with the retention equilibrium is an analysis of the dependence of K or k' on the temperature, according to the van't Hoff equation. For instance, the values of $-\Delta H$ in Figure 1, i.e., $\sim 7-17$ kJ mol^{-1}, are of the same order of magnitude as other results previously reported.[5,36-44] As described earlier, however, Krug et al.[19-21] have shown that a statistical effect due to the measurement errors made on the slope and intercept of a linear regression, such as the van't Hoff plot, provides a linear correlation between the two thermodynamic parameters, even though no actual EEC is present. These authors showed that the slope of the linear correlation between ΔH and ΔS was equal to T_{hm} when the linear correlation resulted only from this statistical effect, whereas the correlation coefficient was close to unity even under such conditions. They also proposed four different methods to clarify whether the linear correlation

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observed between ΔH and ΔS results from a substantial physicochemical effect or from the statistical compensation due to the experimental errors.[19-21] In the following, the experimental retention equilibrium data in the RPLC system are analyzed on the basis of these four approaches.

Plot of ΔH versus ΔG_{Thm}. Krug et al. claimed that ΔH should be linearly correlated with ΔG_{Thm} (ΔG at T_{hm}) if an actual EEC, based on a substantial physicochemical effect, takes place. Then, the two thermodynamic functions should be calculated from the slope and intercept of the linear correlation between $\ln K$ and $\{1/T - \langle 1/T \rangle\}$, respectively. The brackets ($\langle \rangle$) indicate an average value. Hence,

$$\Delta H = -R(\text{slope}) \qquad (3)$$

$$\Delta G_{T_{hm}} = -RT_{hm}(\text{intercept}) \qquad (4)$$

Figure 2 shows the linear correlations between ΔH and ΔG_{Thm}. T_c was calculated from the slope of the straight lines in Figure 2, after the following equation

$$T_c = \frac{T_{hm}}{1 - 1/(\text{slope})} \qquad (5)$$

The values of T_c obtained for the homologous series are listed in Table 2. They range between 710 (n-alkanes) and 1680 K (p-alkylphenols), so they are sufficiently different from T_{hm} ($= 298$ K) and are of the same order of magnitude as previous results on the same or similar series.[6,7,13,15-18,24] The linear correlations between ΔH and ΔG_{Thm} seem to belong to two different groups, the homologous series of hydrophobic (nonpolar) compounds and those of the polar compounds having a hydroxyl group.

Comparison of T_c with T_{hm} (Hypothesis Test). The values of T_c were compared with T_{hm} according to the t-test (Student's test). Krug et al.[19] proposed to test the null hypothesis, i.e., whether T_c is equal to T_{hm}, by calculating a minimum and a maximum value of T_c at an approximate $(1 - \alpha_s) \times 100\%$ confidence level using the following equations:

$$T_c \text{ (minimum)} = T_c - t_{m-2,1-\alpha_s}[V(T_c)]^{1/2} \qquad (6a)$$

$$T \text{ (maximum)} = T_c + t_{m-2,1-\alpha_s}[V(T_c)]^{1/2} \qquad (6b)$$

with

$$T_c = \frac{\sum(\Delta H - \langle \Delta H \rangle)(\Delta S - \langle \Delta S \rangle)}{\sum(\Delta S - \langle \Delta S \rangle)^2} \qquad (7)$$

and

$$V(T_c) = \frac{\sum(\Delta H - \Delta G_{T_c} - T_c \Delta S)^2}{(m-2)\sum(\Delta S - \langle \Delta S \rangle)^2} \qquad (8)$$

where m is the number of data pairs determined (ΔH and ΔS)

Table 2. Calculation Results of the Compensation Temperatures Concerning the Retention Equilibrium

	T_c (K)[a]	T_c (K)[b]	T_c (K)[c] min	T_c (K)[c] max	confidence level $(1 - \alpha_s) \times 100\%$
alkylbenzenes	1200	1070	320	1820	95
p-alkylphenols	1680	1560	330	2760	95
n-alkanes	710	710	350	1080	95
n-alcohols	820	820	340	1300	99
aromatic hydrocarbons	1140	1120	470	1770	95

[a] T_c calculated from the slope of the linear correlations between ΔH and $\Delta G_{T_{hm}}$. [b] T_c calculated by eq 7. [c] Range of T_c calculated by eqs 6-8 at $(1 - \alpha_s) \times 100\%$ confidence level.

and t is the value of the Student t for $m - 2$ data points and a confidence level of $100(1 - \alpha_s)\%$.

Table 2 lists the calculation results. The values of T_c derived from eq 7 agree well with those calculated from the slope of the straight plots of ΔH versus $\Delta G_{T_{hm}}$. Table 2 also lists the values of T_c (minimum) and T_c (maximum) derived from eqs 6a and 6b. The value of T_{hm} (= 298 K) is outside this range of T_c. According to the *t*-test based on the retention data, the hypothesis that T_c calculated from the slope of the plot between ΔH and ΔS is equal to T_{hm} can be rejected at a confidence level smaller than 5% in most cases, smaller than 1% in the case of the *n*-alcohols.

Convergence of the van't Hoff Plots at Each Corresponding T_c. Parts a and b of Figure 3 show the van't Hoff plots of (a) *n*-alkanes and *n*-alcohols and (b) the aromatic hydrocarbons, respectively. The linear regression lines tend to converge, although, in some cases, their intersections do not take place in a single point but in a small region of the plane. The distribution of the intersection points is probably due to the influence of the experimental errors. In this study, the values of K were measured in the temperature range between 288 and 308 K, which is far removed from the intersection points. The compensation temperatures estimated from the intersection points in Figure 3 are close to the values of T_c derived from the slope of the linear correlations between ΔH and $\Delta G_{T_{hm}}$. Similar results were observed for *n*-alkylbenzenes and *p*-alkylphenols.[17] The extrapolated van't Hoff plots for each sample series tend to converge. The coordinates of the intersection points correspond well to the T_c values estimated from the slope of the linear correlations between ΔH and $\Delta G_{T_{hm}}$.

Probability for the Intersection of the van't Hoff Plots. According to the variance analysis procedure (ANOVA) proposed by Krug et al.,[21] the probability that the straight lines in Figure 3 do intersect was assessed. Table 3 shows the calculation results for the five homologous series (i.e., the three series in Figure 3a and b, *n*-alkylbenzenes, and *p*-alkylphenols). In all cases, the mean sum of squares of the intersection (MS$_{con}$) is ~3 orders of magnitude larger than that of the nonintersection (MS$_{noncon}$). The ratio MS$_{con}$/MS$_{noncon}$ is much larger than the corresponding *F*-values. For instance, it is 1820 for the *n*-alcohol series, ~50 times larger than the *F*-value, $F(1, 2, 1 - \alpha_s = 0.975) = 38.5$, indicating that the probability for intersection is high compared with that for nonintersection, even accepting a low confidence level (2.5%) for nonintersection. On the other hand, the value of MS$_{noncon}$ is smaller than the absolute value of the mean sum of squares of the residuals (MS$_e$). For *n*-alcohols again, the ratio MS$_{noncon}$/MS$_e$
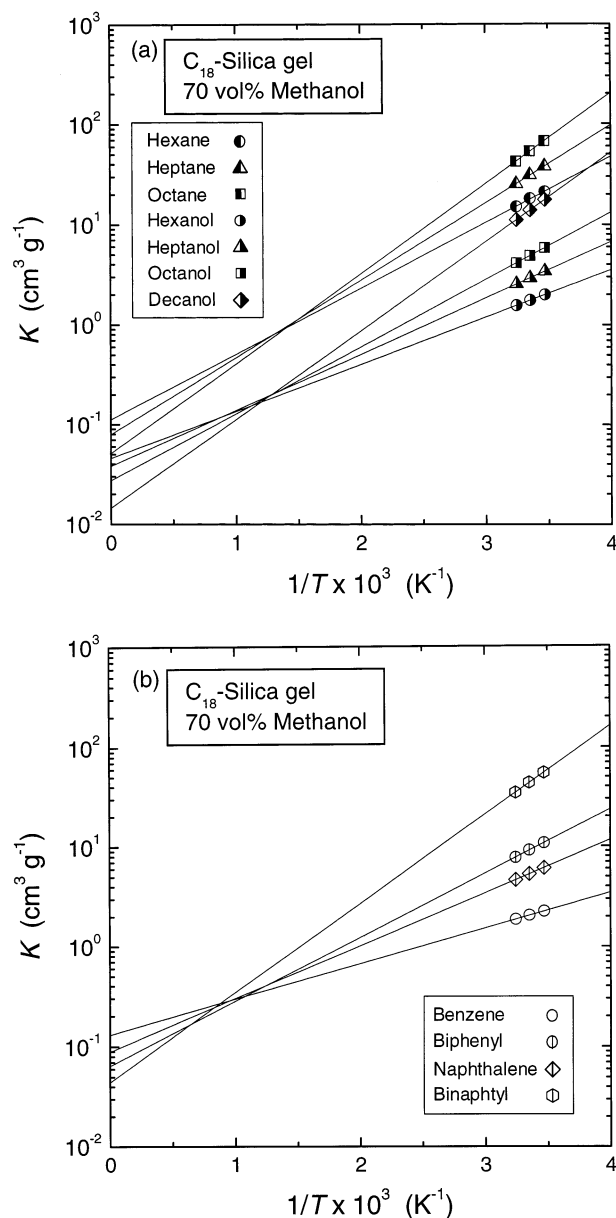
Figure 3. Van't Hoff plot for (a) *n*-alkanes and *n*-alcohols and (b) aromatic hydrocarbons.

(= 0.037) is sufficiently smaller than the corresponding *F*-value, $F(2, 3, 1 - \alpha_s = 0.975) = 16.0$. The probability for nonintersection is smaller than the precision of the experimental data. The variation due to nonconcurrence is not greater than that due to the measurement errors at the $100\alpha_s\%$ level of significance. Negative values of MS$_e$ are observed for a few series in Table 3. They suggest that the variation due to the measurement errors is quite small. The same conclusions are obtained for the other series.

On the basis of the results described above, we conclude that the linear correlations illustrated in Figure 1 account for an actual EEC, originating from true physicochemical effects that take place in the RPLC system studied and involve the retention equilibrium of the different series investigated.

It is worthwhile to consider the influence of the experimental conditions (i.e., the temperature range and the number of data points) and the manner in which the data analysis was performed on the accuracy of the values obtained for the thermodynamic

Table 3. ANOVA Table for the Retention Equilibrium of Different Homologous Series

source of variation	DF[c]	SS[d]	MS[e]	alkylbenzenes ($p^a = 8$, $q^b = 3$) DF[c]	SS[d]	MS[e]	p-alkylphenols ($p^a = 5$, $q^b = 3$) DF[c]	SS[d]	MS[e]
total	$pq-1$	SS_T	MS_T	23	2.4×10^1	1.0	14	1.3×10^1	9.1×10^{-1}
rows (samples)	$p-1$	SS_R	MS_R	7	2.4×10^1	3.4	4	1.2×10^1	3.1
columns (temps)	$q-1$	SS_C	MS_C	2	3.9×10^{-1}	2.0×10^{-1}	2	2.6×10^{-1}	1.3×10^{-1}
interactions	$(p-1)(q-1)$	SS_{RC}	MS_{RC}	14	2.8×10^{-2}	2.0×10^{-3}	8	1.3×10^{-2}	1.6×10^{-3}
slope	$p-1$	SS_S	MS_S	7	3.1×10^{-2}	4.5×10^{-3}	4	1.4×10^{-2}	3.5×10^{-3}
concurrence	1	SS_{con}	MS_{con}	1	3.1×10^{-2}	3.1×10^{-2}	1	1.4×10^{-2}	1.4×10^{-2}
nonconcurrence	$p-2$	SS_{noncon}	MS_{noncon}	6	3.8×10^{-4}	6.3×10^{-5}	3	4.0×10^{-5}	1.3×10^{-5}
residuals	$(p-1)(q-2)$	SS_e	MS_e	7	-3.0×10^{-3}	-4.3×10^{-4}	4	-7.3×10^{-4}	-1.8×10^{-4}

source of variation	n-alkanes ($p^a = 3$, $q^b = 3$) DF[c]	SS[d]	MS[e]	n-alcohols ($p^a = 4$, $q^b = 3$) DF[c]	SS[d]	MS[e]	aromatic hydrocarbons ($p^a = 4$, $q^b = 3$) DF[c]	SS[d]	MS[e]
total	8	2.0	2.5×10^{-1}	11	7.3	6.6×10^{-1}	11	1.5×10^1	1.4
rows (samples)	2	1.8	8.9×10^{-1}	3	7.1	2.4	3	1.5×10^1	4.9
columns (temps)	2	2.4×10^{-1}	1.2×10^{-1}	2	2.3×10^{-1}	1.1×10^{-1}	2	2.0×10^{-1}	9.8×10^{-2}
interactions	4	3.3×10^{-3}	8.2×10^{-4}	6	1.4×10^{-2}	2.3×10^{-3}	6	2.0×10^{-2}	3.3×10^{-3}
slope	2	3.9×10^{-3}	2.0×10^{-3}	3	1.3×10^{-2}	4.3×10^{-3}	3	2.0×10^{-2}	6.7×10^{-3}
concurrence	1	3.9×10^{-3}	3.9×10^{-3}	1	1.3×10^{-2}	1.3×10^{-2}	1	2.0×10^{-2}	2.0×10^{-2}
nonconcurrence	1	4.1×10^{-6}	4.1×10^{-6}	2	1.4×10^{-5}	7.1×10^{-6}	2	4.9×10^{-5}	2.4×10^{-5}
residuals	2	-6.4×-10^{-4}	-3.2×10^{-4}	3	5.8×10^{-4}	1.9×10^{-4}	3	-6.5×10^{-4}	-2.2×10^{-4}

[a] p is the number of sample compounds. [b] q is the number of experimental temperatures. [c] DF is the degree of freedom. [d] SS is the sum of squares. [e] MS is the mean sum of squares; MS = SS/DF for each source of variation.

parameters. As described earlier, the van't Hoff analysis of the temperature dependence of the retention parameters, such as k' or K, is the most usual method for estimating the change in the enthalpy (ΔH) and the entropy (ΔS) associated with the retention equilibrium. However, it is difficult accurately to estimate the value of ΔS from the intercept of the conventional van't Hoff plot, i.e., ln k' or ln K versus $1/T$.

There are two major problems in the conventional van't Hoff plot. One is the dependence of ΔS on ΔH. The value of the intercept (i.e., ΔS) of the extrapolated van't Hoff plot varies in connection with the change in the value of the slope (i.e., ΔH). The other one is the long distance between the intercept of the extrapolation and the data points plotted at the experimental temperatures. The potential for errors is extremely high when the intercept at $1/T = 0$ is far from the experimental data points. A very small fluctuation of the slope of the linear van't Hoff plot would lead to a large variation of its intercept. Chromatographic experiments in RPLC are usually carried out in the temperature range between about 273 and 323 K, and it is unusual to acquire data in a wider temperature range. It is difficult to determine accurately ΔS when it is estimated from the intercept of the plot at $1/T = 0$, in the conventional manner. The distance between the intercept and the data points is of the order of $1/298$, more than 5 times the experimental range ($1/273 - 1/323$). These are the reasons why Krug et al.[19-21] recommended using the plot of $\Delta G_{T_{hm}}$ versus ΔH for estimating the T_c values, instead of the plot between ΔH and ΔS.

According to the procedures proposed by Krug et al., the values of ΔH and $\Delta G_{T_{hm}}$ were calculated from the slope and intercept of the linear correlation between ln K and $\{1/T - \langle 1/T \rangle\}$ in this study. A parameter between brackets ($\langle \rangle$) indicates that we consider its average value, i.e., the arithmetic mean of its measurements. Because $T_{hm} = \langle 1/T \rangle^{-1}$, the value of the intercept is located close to the center of the range of experimental
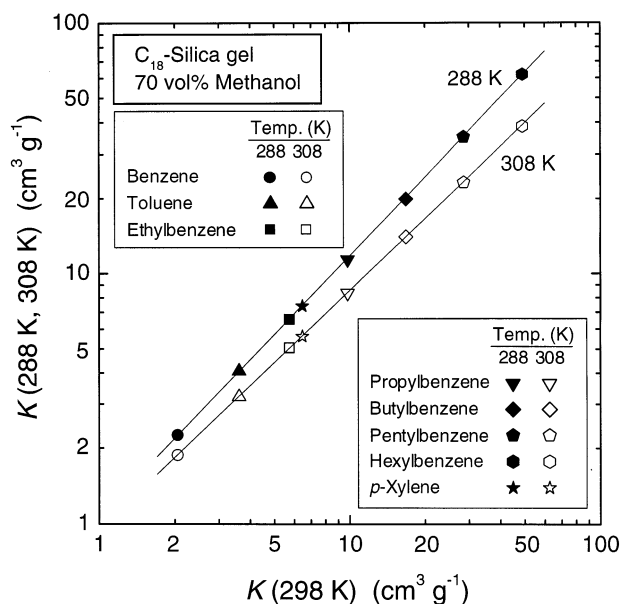
temperatures, in the middle of the set of experimental data points. When the values of ΔH and $\Delta G_{T_{hm}}$ are determined in such a way, it is likely that the influence of the experimental conditions (i.e., the narrow temperature range and the number of data points) on the estimate of T_c will be small, unless the plots are strongly scattered. Although the value of $\Delta G_{T_{hm}}$ still depends on that of ΔH, the magnitude of the error made in estimating ΔH influences the accuracy of the estimate of $\Delta G_{T_{hm}}$ much less than the error made on T_c when the conventional van't Hoff plot is used because the intercept of the extrapolated van't Hoff line is no longer far removed from the experimental data points.

Figure 3 also shows that the van't Hoff plots for the different sample compounds converge and that the coordinates of the intersection points correspond well to the T_c values. This self-consistency seems to prove the validity of the experimental data in this study. The existence of the real EEC was also demonstrated on the basis of two other statistical approaches. One is the comparison of T_c with T_{hm} according to the t-test. The other is the confirmation of the probability that the linear van't Hoff plots intersect according to the variance analysis.

The results in this study consistently indicate that the real EEC is established. For instance, Figure 3 graphically demonstrates the concurrence of the van't Hoff plots at the point corresponding to T_c. On the other hand, Table 3 statistically indicates the probability of the same convergence. In addition, the values of T_c calculated from the slope of the linear correlations of ΔH versus $\Delta G_{T_{hm}}$ in Figure 2 are fairly in agreement with those calculated by eq 7 as shown in Table 2, with those calculated by eq 17 as shown in Table 4, and with those calculated from the slope of the straight lines of ΔH versus ΔS in Figure 1. These consistencies between the results should prove the validity and accuracy of the experimental data and resulting values of the thermodynamic parameters derived in this study.
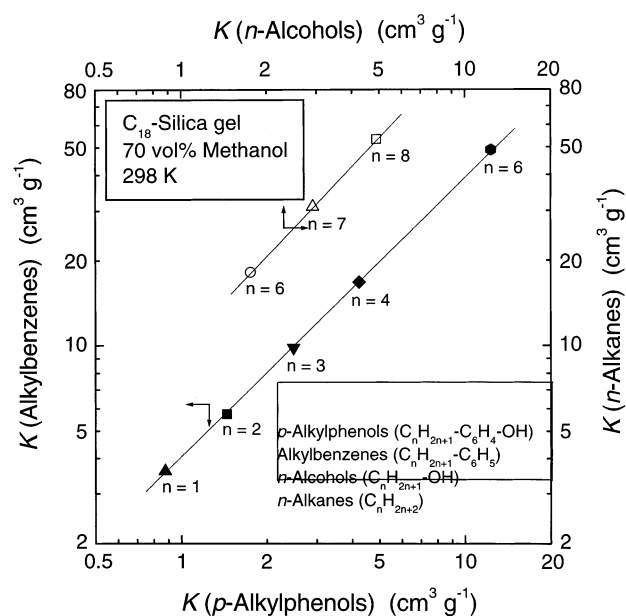
Table 4. Molecular Thermodynamic Parameters

	ΔH vs N_{m}		ΔS vs N_{m}		
	a_{h} (kJ mol^{-1})	b_{h} (kJ mol^{-1})	a_{s} (kJ mol^{-1} K^{-1})	b_{s} (kJ mol^{-1} K^{-1})	$a_{\mathrm{h}}/a_{\mathrm{s}}$ (K)
70 vol % methanol					
alkylbenzenes	-1.7	-6.6	-1.4×10^{-3}	-1.6×10^{-2}	1210
p-alkylphenols	-1.6	-6.8	-9.5×10^{-4}	-2.8×10^{-2}	1680
n-alkanes	-2.3	1.4	-3.3×10^{-3}	1.5×10^{-3}	710
n-alcohols	-2.0	3.2	-2.4×10^{-3}	-1.1×10^{-2}	820
50 vol % THF					
alkylbenzenes	-2.1	-9.1	-4.6×10^{-3}	-2.0×10^{-2}	460

Figure 4. Temperature dependence of K for alkylbenzenes.

Figure 5. Correlations between the values of K for alkylbenzenes and p-alkylphenols (solid symbols) and for n-alkanes and n-alcohols (open symbols). Mobile-phase composition, (70:30, v/v) methanol/water. Column temperature, 298 K.

Interpretation of the Retention Equilibrium in RPLC on the Basis of the Enthalpy−Entropy Compensation. The retention behavior in RPLC depends on various experimental parameters. In the following, we provide a comprehensive explanation of the variations of the retention equilibrium constant with the experimental conditions, i.e., the column temperature, the type of sample compounds, and the mobile-phase composition.

Influence of the Change in the Single Condition on the Retention Behavior. Figure 4 shows the temperature dependence of K for the alkylbenzenes. The values of K at 288 K (solid symbols) and those at 308 K (open symbols) are plotted versus those at 298 K (mobile phase 70% methanol, v/v). Only the column temperature was changed. Linear correlations are observed for the data at the two temperatures, suggesting that there is a linear free energy relationship (LFER). The solid lines in Figure 4 are correlations calculated by using a new model for the retention equilibrium that is described later. This model was derived in order quantitatively to explain the LFER observed under different experimental conditions. The methylene selectivity is constant at each temperature. However, the slope of the linear correlation at 288 K is slightly larger than that at 308 K. Thus, the lower the column temperature, the higher the methylene selectivity. Similar results were obtained for all the other sample series (not shown).

Figure 5 illustrates the linear correlations of the logarithmic values of K for two pairs of homologous series. The solid symbols correspond to the correlation between n-alkylbenzenes and p-alkylphenols, the open symbols that between n-alkanes and n-alcohols. As in Figure 4, the solid lines in Figure 5 show the calculated correlations. The slopes of the two straight lines are almost equal to unity, suggesting that the methylene selectivity is almost the same, irrespective of the chemical structure and the polarity of the sample molecules. The plots in Figure 5 also indicate that the retention of nonpolar compounds is stronger than that of the corresponding polar ones.

Figure 6 shows the influence of the mobile-phase composition on the retention behavior in RPLC. This figure compares the K values of four alkylbenzenes obtained with mobile phases made of 50:50 v/v THF/water and 70:30 v/v methanol/water at 298 K. In this comparison, only the mobile-phase composition was changed. A straight line with a slope smaller than unity is observed. The methylene selectivity is smaller for the THF than for the methanol-based aqueous mobile phase. Again, the solid line in Figure 6 shows the correlation calculated using our new model for retention equilibrium.

A Model Explaining the Change in Retention Behavior. Figures 4−6 show that the retention behavior in RPLC varies differently, depending on the experimental conditions, but that LFERs are observed under all these conditions. In the following, a comprehensive explanation of the change in the retention equilibrium is discussed.
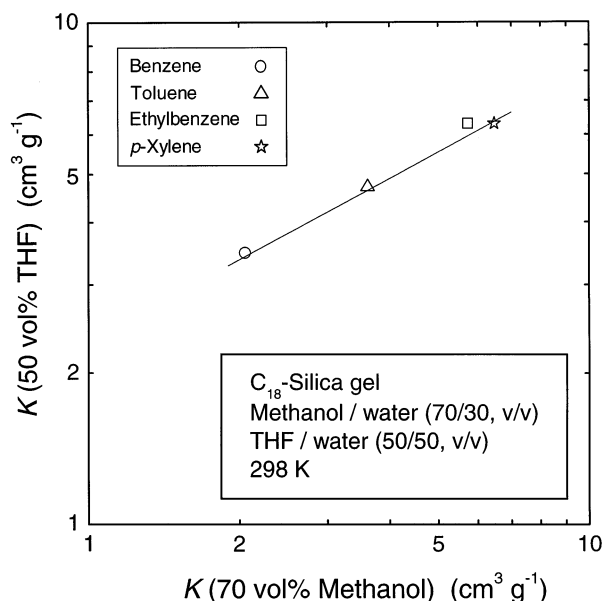
Figure 6. Correlation between the values of K for n-alkylbenzenes in 50:50 (v/v) THF/water and in 70:30 (v/v) methanol/water as the mobile phase.

The free energy change for retention equilibrium (ΔG) is related to K as follows.

$$\Delta G_{T_1}^{\mathrm{REF}} = - R_{T_1} \ln K_{T_1}^{\mathrm{REF}} \tag{9}$$

$$\Delta G_{T_2}^{\mathrm{SMP}} = - R_{T_2} \ln K_{T_2}^{\mathrm{SMP}} \tag{10}$$

where T_1 and T_2 denote the column temperatures and the superscripts REF and SMP denote the reference and the studied system, respectively. As described in Figures 4−6, the values of $\Delta G_{T_2}^{\mathrm{SMP}}$ are linearly correlated with those of $\Delta G_{T_1}^{\mathrm{REF}}$. The existence of a LFER is confirmed between the different RPLC systems studied here. Hence,

$$\ln K_{T_2}^{\mathrm{SMP}} = A \ln K_{T_1}^{\mathrm{REF}} + B \tag{11}$$

Substituting eqs 9 and 10 into eq 11 gives,

$$\Delta G_{T_2}^{\mathrm{SMP}} = A(T_2/T_1)\Delta G_{\mathrm{T_1}}^{\mathrm{REF}} - RT_2 B \tag{12}$$

Equation 12 formulates the LFER under the conditions considered.

On the other hand, ΔG is related to the enthalpy (ΔH) and the entropy changes (ΔS) according to the Gibbs−Helmholtz relationship.

$$\Delta G = \Delta H - T\Delta S \tag{13}$$

The following equation was proposed to correlate ΔG of a molecule involved in hydrophobic interactions with a certain molecular property value (X_{m}).[23,45]

$$\Delta G = a_{\mathrm{g}} X_{\mathrm{m}} + b_{\mathrm{g}} \tag{14}$$

where a_{g} and b_{g} are molecular thermodynamic parameters. The value of a_{g} is ΔG per unit value of the molecular property X_{m} and that of b_{g} is ΔG at $X_{\mathrm{m}} = 0$. Various molecular properties can be taken for X_{m}, for instance, the nonpolar surface area or reoccurring structural elements such as the methylene group. In this study, the number of methylene groups (N_{m}) was used as X_{m}. Figure 7a shows the linear correlations (solid lines) of ΔG at $T = T_{\mathrm{hm}}$ (298 K) with N_{m}. The four straight lines obtained with 70:30 methanol/water as the mobile phase are parallel, suggesting again that the methylene selectivity is independent of the chemical properties and molecular structures of the sample compounds. With 50:50 THF/water, the slope of the linear correlation (dotted line) is different from that of the solid lines. The good linear behavior of the straight lines in Figure 7a demonstrates the validity of eq 14.

Equations similar to eq 14 may be written for the enthalpy and entropy changes, using corresponding molecular thermodynamic parameters (a_{h}, b_{h}, a_{s}, b_{s}).[23,45]

$$\Delta H = a_{\mathrm{h}} X_{\mathrm{m}} + b_{\mathrm{h}} \tag{15}$$

$$\Delta S = a_{\mathrm{s}} X_{\mathrm{m}} + b_{\mathrm{s}} \tag{16}$$

Figure 7b shows the values of ΔH as a function of N_{m}. Although the plots for 50:50 THF/water exhibit some scattering, linear correlations are observed between ΔH and N_{m}, suggesting the validity of eq 15. Similarly, Figure 7c shows the correlation of ΔS and N_{m}. Although Figure 7c shows more scatter than parts a and b, it is probable that ΔS is linearly correlated with N_{m} since both ΔG and ΔH are. Table 4 lists the values of the slope (a) and the intercept (b) calculated. With the slopes of the straight lines in Figure 7b and c (a_{h} and a_{s}), T_{c} is represented as[23]

$$T_{\mathrm{c}} = a_{\mathrm{h}}/a_{\mathrm{s}} \tag{17}$$

Table 4 lists the ratios of a_{h} to a_{s}, which are consistent with the values of T_{c} in Table 2. The ratio $a_{\mathrm{h}}/a_{\mathrm{s}}$ for the alkylbenzenes in the system using 50:50 THF/water is also in agreement with the value of T_{c} (= 430 K) previously reported with this solvent.[18]

Differentiating both sides of eq 12 with respect to N_{m}, we obtain

$$\frac{\partial \Delta G_{T_2}^{\mathrm{SMP}}}{\partial N_{\mathrm{m}}} = A\left(\frac{T_2}{T_1}\right)\frac{\partial \Delta G_{T_1}^{\mathrm{REF}}}{\partial N_{\mathrm{m}}} \tag{18}$$

The following equation is derived by combining eqs 13, 15, and 16.

$$\Delta G = \Delta H - T\Delta S = (a_{\mathrm{h}} N_{\mathrm{m}} + b_{\mathrm{h}}) - T(a_{\mathrm{s}} N_{\mathrm{m}} + b_{\mathrm{s}}) \tag{19}$$

Substituting eq 19 into eq 18 and rearranging gives

$$A = \frac{a_{\mathrm{s}}^{\mathrm{SMP}} T_1 (T_{\mathrm{c}}^{\mathrm{SMP}} - T_2)}{a_{\mathrm{s}}^{\mathrm{REF}} T_2 (T_{\mathrm{c}}^{\mathrm{REF}} - T_1)} \tag{20}$$

where $a_{\mathrm{s}}^{\mathrm{REF}}$ and $a_{\mathrm{s}}^{\mathrm{SMP}}$ are the increments of ΔS for one methyl-

(45) Lee, B. Proc. Natl. Acad. Sci. U.S.A. **1991**, 88, 5154.
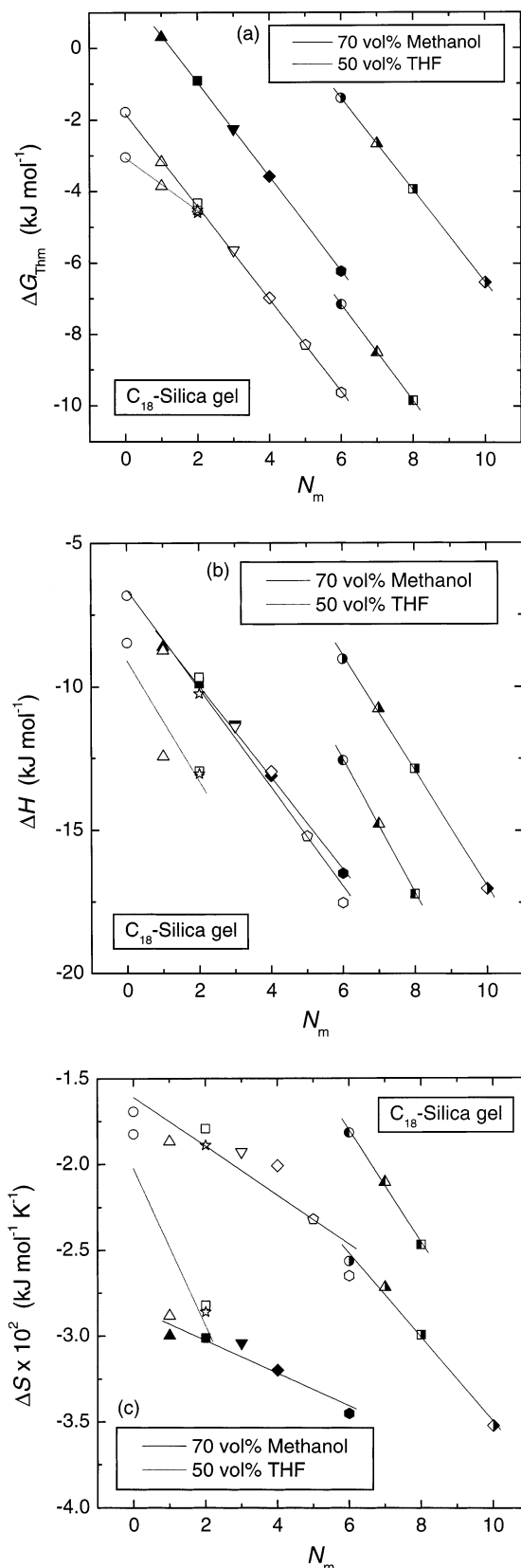
Figure 7. Correlations between (a) ΔG_{Thm} and N_m, (b) ΔH and N_m, and (c) ΔS and N_m. Symbols as in Figures 1−3.

ene unit in the reference and the sample system, respectively. Equation 20 indicates that A depends on the temperature and that this temperature dependence is correlated with T_1, T_2, T_c^{REF}, and T_c^{SMP}. On the other hand, by substituting eq 19 into eq 12, we

obtain B as

$$B = \frac{1}{RT_2}\left[A\left(\frac{T_2}{T_1}\right)(b_{\text{h}}^{\text{REF}} - T_1 b_{\text{s}}^{\text{REF}}) - (b_{\text{h}}^{\text{SMP}} - T_2 b_{\text{s}}^{\text{SMP}})\right] \quad (21)$$

Together, eqs 20 and 21 should explain the correlation of the retention behaviors in two chromatographic systems. Equations 20 and 21 account for the dependence of the slope and intercept of the LFER in eq 12 on the molecular thermodynamic parameters (a and b) in eqs 15 and 16, the compensation temperatures (T_c), and experimental temperatures (T).

Interpretation of the Change in Retention Behavior due to the Variation of One RPLC Parameter, on the Basis of the Model. When only the temperature is changed, eqs 20 and 21 should be modified as follows.

$$A = \frac{T_1(T_c - T_2)}{T_2(T_c - T_1)} \quad (22)$$

$$B = \frac{1}{RT_2}\left[A\left(\frac{T_2}{T_1}\right)(b_{\text{h}} - T_1 b_{\text{s}}) - (b_{\text{h}} - T_2 b_{\text{s}})\right] \quad (23)$$

The solid lines in Figure 4 were calculated according to eqs 22 and 23 for alkylbenzenes, taking $T_1 = 298$ K and $T_2 = 288$ or 308 K. Comparison of the experimental data (symbols) and the model prediction (straight lines) demonstrates the validity of the model (hence of eqs 20 and 21).

At constant temperature, eqs 20 and 21 can be written as follows.

$$A = \frac{a_{\text{s}}^{\text{SMP}}(T_c^{\text{SMP}} - T)}{a_{\text{s}}^{\text{REF}}(T_c^{\text{REF}} - T)} \quad (24)$$

$$B = \frac{1}{RT}[A(b_{\text{h}}^{\text{REF}} - T b_{\text{s}}^{\text{REF}}) - (b_{\text{h}}^{\text{SMP}} - T b_{\text{s}}^{\text{SMP}})] \quad (25)$$

The two straight lines in Figure 5 were calculated by taking the *p*-alkylphenols and the *n*-alcohols as the reference and the alkylbenzenes or the *n*-alkanes as the studied system, respectively. The solid line in Figure 6 was calculated by taking the systems using 70:30 methanol/water and 50:50 THF/water as the reference and the studied system, respectively. In both Figures 5 and 6, the experimental data are compared with the straight lines calculated by using eqs 24 and 25.

The comparison of experimental data (symbols) and the results calculated from eqs 20 and 21 in Figures 4−6 show that these equations allow the correct prediction of the changes in the retention equilibrium constant due to variations of the experimental conditions such as the temperature, the nature and size of the sample molecules, the nature of the organic modifier, and the composition of the mobile phase.

Interpretation of a Change in Retention Behavior due to the Simultaneous Variations of the Three RPLC Parameters. As described above, the variation of K due to a change in only one of the experimental parameters, e.g., the column temperature, the nature of the sample compounds, or the mobile-phase composition,
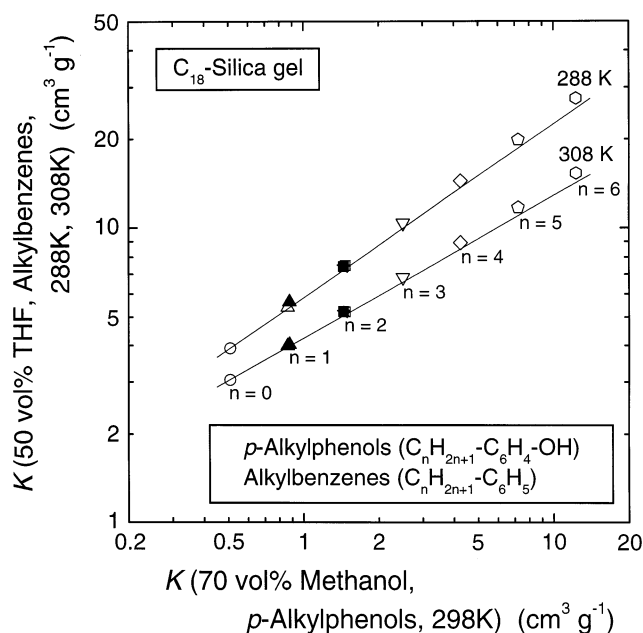
Figure 8. Correlation between the values of K for n-alkylbenzenes at 288 or 308 K in 50:50 (v/v) THF/water as the mobile-phase solvent and those of p-alkylphenols at 298 K in 70:30 (v/v) methanol/water. The solid symbols show the experimental data, the open symbols the values derived from Figure 9.
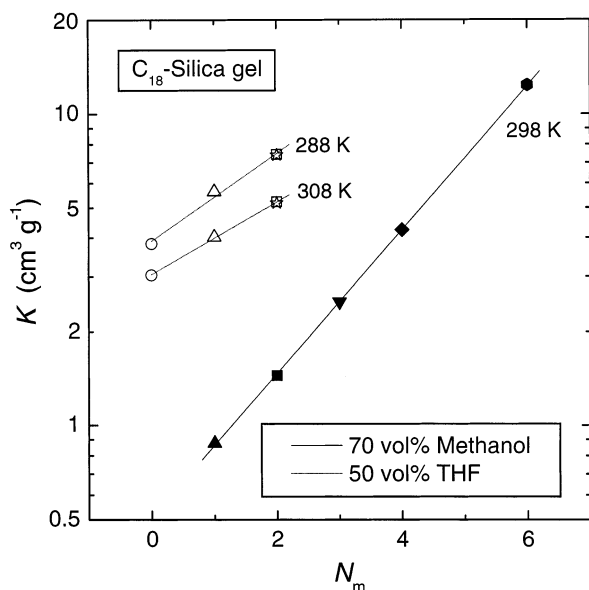

Figure 9. K as a linear function of N_m. Same symbols as in Figures 1 and 2.

is properly accounted for by eqs 20 and 21. Now we consider the effect of simultaneous variations of the three parameters.

In Figure 8, the values of K obtained under a set of experimental conditions are plotted versus those obtained with an entirely different set. In the abscissa are the values of K for the p-alkylphenols at 298 K, using 70:30 methanol/water as the mobile phase (REF). In the ordinate are the values of K for the alkylbenzenes at 288 or 308 K, using 50:50 THF/water as the mobile phase (SMP). The solid symbols show the experimental data. Toluene corresponds with p-cresol and ethylbenzene with p-ethylphenol. The open symbols were derived from the linear correlations in Figure 9. Figure 9 shows that the logarithm of K

is a linear function of N_m in the two RPLC systems considered (REF and SMP), at the different temperatures. The three straight lines in this figure were derived from the experimental data (plots) using a least-squares linear regression. The open symbols at $n = 1$ and 2 agree well with the corresponding data points in Figure 8. The two solid lines in Figure 8 were calculated according to eqs 20 and 21, using the results listed in Table 4. There are slight discrepancies between the open symbols and the solid lines at large values of n in Figure 8. However, the solid lines explain reasonably well the profiles of both the experimental and the calculated plots in Figure 8. We may conclude that eqs 20 and 21 provide an effective strategy for a comprehensive interpretation of how the retention equilibrium constant changes upon variations of the experimental conditions in RPLC, the column temperature, the nature and the size of the sample compounds, and the nature and composition of the organic modifier in the mobile phase.

CONCLUSION

Analyses of experimental retention data on the basis of the four approaches proposed by Krug et al. allows us to conclude that there is an EEC for retention equilibrium in RPLC. (1) Linear correlations were confirmed between ΔH and ΔG_{Thm}. Although T_c depends on the nature of the homologous series, it varies between 710 and 1560 K. (2) The Student t-test shows that the hypothesis that T_c is equal to T_{hm} should be rejected at confidence level as low as 1% or 5%. (3) The straight lines obtained as linear regressions of the van't Hoff plots tend to converge. The position of these intersection points corresponds to T_c calculated from the slope of the linear correlations between ΔH and ΔG_{Thm}. (4) According to the variance analysis procedure (ANOVA), the probability of the intersection of the van't Hoff plots was confirmed.

Linear correlations were observed between the logarithmic values of K under different experimental conditions, suggesting the establishment of LFER involving the column temperature, the chemical properties and the molecular structure of the sample compounds, and the nature and the concentration of the organic modifier in the mobile phase. A new model based on the EEC was developed for explaining the variation in the retention behavior due to changes in these experimental conditions. The manner in which the value of K changes can be analyzed quantitatively by using this new model whether only one experimental parameter is changed or several of them are altered simultaneously. Equations 20 and 21 relate the slope and intercept of the LFER and the molecular thermodynamic parameters relating ΔH and ΔS, T_c, and the temperatures of two equilibrium systems. It is expected that the new model could also be applied to fundamental thermodynamic studies of some of the characteristics of other chemical equilibria.

NOMENCLATURE

a	slope of the linear correlation between a thermodynamic property and X_m
A	slope in eq 11
b	intercept of the linear correlation between a thermodynamic property and X_m
B	intercept in eq 11
ΔG	free energy change (kJ mol^{-1})
ΔH	enthalpy change (kJ mol^{-1})

k'	retention factor
K	adsorption equilibrium constant ($cm^3\ g^{-1}$)
m	number of (ΔH and ΔS) data pairs
MS	mean sum of squares
N_m	number of m ethylene group
R	gas constant ($J\ mol^{-1}\ K^{-1}$)
ΔS	entropy change ($J\ mol^{-1}\ K^{-1}$)
SS	sum of squares
T	absolute temperature (K)
T_c	compensation temperature (K)
T_{hm}	harmonic mean of experimental temperatures (K)
T_1	temperature condition 1 (K)
T_2	temperature condition 2 (K)
u_0	superficial velocity ($cm\ s^{-1}$)
$V(T_c)$	defined in eq 8
X_m	property of molecule
z	column length (cm)

Greek Symbols

α_s	statistical level of significance
δ	void fraction of column
ϵ_p	porosity of stationary-phase particles
μ_1	first moment (s)
ρ_p	particle density ($g\ cm^{-3}$)

Superscripts

REF	reference
SMP	studied system

Subscripts

con	concurrence
e	referring to measurement errors
g	free energy change
h	enthalpy change
noncon	nonconcurrence
s	entropy change
T_c	compensation temperature
T_{hm}	harmonic mean of experimental temperatures
T_1	temperature condition 1
T_2	temperature condition 2

NOTE ADDED AFTER ASAP

This article was inadvertently posted ASAP before final corrections were made. The corrected version was posted on November 6, 2002.