# Molecular theory of chromatographic selectivity enhancement for blocklike solutes in anisotropic stationary phases and its application

**ARTICLE** *in* ANALYTICAL CHEMISTRY · JUNE 1992

Impact Factor: 5.64 · DOI: 10.1021/ac00035a010



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# Molecular Theory of Chromatographic Selectivity Enhancement for Blocklike Solutes in Anisotropic Stationary Phases and Its Application

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**An equation, based on a lattice-fluid model and applicable to gas, liquid, and supercritical fluid chromatographies, is derived to describe the selectivity enhancement (SE) experienced by structural isomers of comparable van der Waals volume, when an isotropic stationary phase is replaced by an anisotropic (orientationally ordered) one. The equation has the form ln (SE) = $A_{min}c_1 + A_{sur}c_2 - c_4$, where $A_{min}$ and $A_{sur}$ are, respectively, the (scaled) minimum cross-sectional area and total surface area of the solute isomer, and the coefficients, $c_1$, $c_2$, and $c_4$, depend on solvent geometric parameters, solute-solvent interaction energies, and state variables (temperature, $T$, and mobile-phase density, $\rho$). It is shown that, for planar PAH isomers, the equation reduces to ln (SE) = $A_{min}c_1 + c_5$. Using our SFC data on two polymeric stationary phases (one, isotropic, and the other, smectic), the predicted linear dependence of ln (SE) on $A_{min}$ and the general dependence of $c_1$ on $T$ and $\rho$ are confirmed. Plots of ln (SE) vs $T^{-1}$ at fixed $\rho$ are constructed, and the slopes and intercepts of the plots are interpreted on a molecular level. A decent linear correlation between ln (SE) and $A_{min}$ is also observed from published GC results for five-ring PAH isomers, including nonplanar ones.**

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), which can be modeled as blocks,[1] are relatively rigid molecules with a three-dimensional structure (viz., length, breadth, and thickness). The chromatographic separation and identification of PAHs, especially PAH isomers, are not only challenging but also important tasks because of their known or suspected mutagenic and carcinogenic activity[2,3] and the difficulty of their analysis using conventional stationary phases.

However, liquid-crystalline stationary phases[4] and other stationary phases with some anisotropic characteristics[5,6] have shown unique selectivities for PAH compounds in gas,[7,8] liquid[9-12] and supercritical fluid chromatography[13,14] (GC, LC and SFC, respectively).

A liquid-crystalline or mesomorphic state is a thermodynamically stable state intermediate in properties between the solid state and the isotropic liquid state. Such mesophases are formed, in general, by elongated, rodlike molecules with rigid central cores and more flexible, hydrocarbon pendant groups. Among the three major types of liquid-crystalline phases, viz., smectic, nematic, and cholesteric, the smectic phase is the most highly structured one in which the molecules are arranged in layers and within each layer the long axes of the molecules are preferentially aligned in one direction.

Side-chain, liquid-crystalline polymers, widely used as stationary phases,[5,13,14] contain a flexible spacer linking the main chain (backbone) to the mesogenic group. Such polymers often show a greater ability to form a mesophase than polymers lacking a spacer, when other factors are the same.[15] Talrose et al.[16] synthesized a homologous series of such side-chain polymers, which they studied by X-ray crystallography. The polymers were observed to be smectic with comblike (or brushlike) structure.

The retention mechanism and selectivity of blocklike solutes (such as PAHs and steroids) on anisotropic and isotropic phases have been the subjects of much discussion and research,[17-20] and many attempts have been made to understand the selectivity enhancement (SE) due to the orientational order of the anisotropic phase. The most noteworthy effort was made by Wise et al.,[21] who, based on observations of shape selectivity for liquid-crystalline phases in GC by Janini et al.[22,23] and Radecki et al.,[24] described a relationship between the length-to-breadth ratio (L/B) of PAHs and their retention. Although the empirical treatment

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0003-2700/92/0364-1246$03.00/0 

met with reasonable success in correlating L/B to the retention data, there are some exceptions.[5,21] Later, Wise and Sander proposed a "slot" model[25] to explain the retention behavior of blocklike solutes (planar and nonplanar PAHs) in anisotropic phases.

Martire and Boehm[26] in their LC study concluded that chemically bonded phases exhibit shape selectivity which increases as the chains become more fully extended, and that rigid-rod solutes have greater retention than globular ones. Later, Martire[1] developed a molecular theory, based on a lattice model, addressing the SE experienced by structural isomers from the orientational order of nematic phases in gas chromatography (GC). A molecular-structural descriptor for the SE of conformationally rigid isomers, $g = 3\ (v_R - a_R)$, emerged from the theory, where $v_R$ is a reduced molecular volume and $a_R$ is a reduced molecular area. However, the theory is limited to GC, and attractive interaction-energy terms were not explicitly included in the formulation (a cancellation of such terms, between the anisotropic phase and a reference isotropic phase, was assumed).

Recently, we developed a molecular theory of chromatography for blocklike solutes in both anisotropic and isotropic phases.[27-29] The theory was applied successfully to the interpretation and analysis of our supercritical fluid (SFC) experimental data[28,29] and GC, liquid chromatography (LC), and SFC data published by other groups.[27,28]

In the present paper, we use the expressions obtained for absolute retention[27,28] to derive an equation for the retention of blocklike solutes in an anisotropic phase relative to that in an isotropic phase at the same temperature. This equation is phrased in terms of the ratio of the solute distribution coefficient in the two phases, which we shall still refer to as the selectivity enhancement. (It will be shown that, for practical purposes, the presently defined SE is equivalent to the previously defined[1] SE.) We will test the SE equation using our SFC data obtained from two parallel experimental studies (mimicking the anisotropic and isotropic phases, respectively) and also apply it to the analysis of experimental data found in the literature.[5,6]

## THEORY

In this section, we derive an equation for the logarithm of selectivity enhancement, ln (SE), using the retention equations for blocklike solutes in anisotropic[27] and isotropic[29] stationary phases. For those details of the model and derivation not presented here, the interested reader is referred to our previous studies.

The model is a three-dimensional, mean-field, simple cubic lattice with $M$ cells or sites of volume, $v_o$, for blocklike solutes in an isotropic mobile phase with (a) an anisotropic stationary phase composed of blocklike molecules or (b) an isotropic stationary phase composed of chainlike molecules.

The model system for the mobile phase is identical for both chromatographic systems. It consists of $N_o$ holes (each occupies a unit cell of volume $v_o$), $N_m$ mobile-phase molecules (dimensions $qqr$) and $N_t$ solute molecules (dimensions $abc$). All of them are assumed to be isotropically distributed among the $M$ sites ($M = N_o + qqrN_m + abcN_t$).

The model system for the anisotropic stationary phase consists of $N_o$ holes, $N_t$ solute molecules (dimensions $abc$), and $N_s$ blocklike stationary-phase molecules (dimensions $\omega\omega l$). The stationary-phase molecules are assumed to be arranged in parallel layers, and within each layer the long axes of the molecules are perfectly aligned in one direction.

We have already derived the retention equation for blocklike solutes fully aligned within the anisotropic stationary phase:[27]

$$\ln K = ab \ln\left[\frac{1-\theta_s}{1-\theta_s\left(1-\frac{1}{\omega}\right)}\right] - abc \ln\left[\frac{1-\theta_m}{1-\theta_m\left(1-\frac{2}{3q}-\frac{1}{3r}\right)}\right] - \left[\frac{2(ac+bc)\epsilon_{st}}{kT}\right]\left[\frac{\theta_s\left(\frac{1}{\omega}\right)}{1-\theta_s\left(1-\frac{1}{\omega}\right)}\right] + \left[\frac{2(ab+ac+bc)\epsilon_{mt}}{kT}\right]\left[\frac{\theta_m\left(\frac{2}{3q}+\frac{1}{3r}\right)}{1-\theta_m\left(1-\frac{2}{3q}-\frac{1}{3r}\right)}\right] - \ln 3 \quad (1)$$

where $K$ is the distribution coefficient of the solute, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $\theta_i$ is the occupied volume fraction (segmental density) of the $i$th component, $\epsilon_{i,j}$ (<0) is the attractive interaction energy between a segment of molecule i and a segment of molecule j, and the subscripts s, m, and t denote the stationary phase, the mobile phase, and the solute, respectively. Also, the product $ab$ is designated as the minimum cross-sectional area of the solute molecule. This molecular-structural parameter is instrumental in effecting shape-selective separations (see later).

The model system for the isotropic stationary phase consists of $N_0$ holes, $N_t$ solute molecules, and $N_s$ flexible, chainlike stationary-phase molecules, each occupying $m$ sites. We assume that the stationary-phase molecules and the solute molecules are isotropically distributed.

The following retention equation is derived for blocklike solutes in the isotropic, chainlike stationary phase:[29]

$$\ln K = abc \ln\left\{\left[\frac{1-\theta_s}{1-\frac{\theta_s}{3}\left(1-\frac{1}{m}\right)}\right]\left[\frac{1-\theta_m\left(1-\frac{2}{3q}-\frac{1}{3r}\right)}{1-\theta_m}\right]\right\} + \left[\frac{2(ab+ac+bc)}{kT}\right]\left[\frac{\theta_m\left(\frac{2}{3q}+\frac{1}{3r}\right)\epsilon_{mt}}{1-\theta_m\left(1-\frac{2}{3q}-\frac{1}{3r}\right)} - \frac{\theta_s\left(\frac{2}{3}+\frac{1}{3m}\right)\epsilon_{st}}{1-\frac{\theta_s}{3}\left(1-\frac{1}{m}\right)}\right] \quad (2)$$

Note that, with the isotropic phase, any shape selectivity for structural isomers having the same molecular volume ($abc$) would have to come from the second term on the right hand side of eq 2, i.e., from differences, if any, in the total surface area, $2(ab + ac + bc)$, of the solute molecules.

Let us here define the "selectivity enhancement" (SE) as

$$\mathrm{SE} = \frac{K_{an}}{K_{is}} = \frac{k'_{an}\phi_{an}}{k'_{is}\phi_{is}} \quad (3)$$

where $K$ is the solute equilibrium distribution or partition coefficient, $k'$ is the solute capacity factor, $\phi$ is the column phase ratio ($\phi = V_m/V_s$, where $V_m$ and $V_s$ are, respectively, the mobile-phase and stationary-phase volumes), and the subscripts an and is refer to the anisotropic and isotropic stationary phases, respectively. The defined SE is therefore the ratio of the net retention times for a given solute in two structurally different stationary phases contained in otherwise identical columns (same column phase ratio, same mobile phase, and same column "dead" or hold-up volume at the same temperature).

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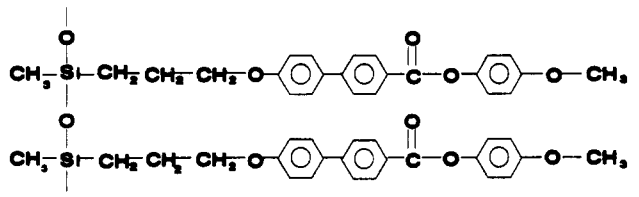
(a) Biphenyl carboxylate ester polysiloxane



(b) Octylmethylpolysiloxane

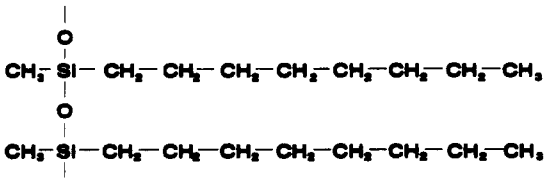


**Figure 1.** Structure of the stationary phases: (a) anisotropic phase, (b) isotropic phase.

Taking the logarithm of eq 3, one obtains

$$\ln (SE) = \ln K_{an} - \ln K_{is} = -\Delta G_{an/is}/RT \quad (4)$$

where $\Delta G_{an/is}$ is the molar free energy change in transferring the solute, at infinite dilution, from the isotropic to the anisotropic stationary phase.

Substituting eqs 1 and 2 into eq 4, we have

$$\ln (SE) = ab\left\{\ln\left[\frac{1-\theta_{s(a)}}{1-\theta_{s(a)}\left(1-\frac{1}{\omega}\right)}\right]+\frac{2\epsilon_{st(a)}}{kT}\left[\frac{\theta_{s(a)}\left(\frac{1}{\omega}\right)}{1-\theta_{s(a)}\left(1-\frac{1}{\omega}\right)}\right]\right\}+$$
$$\frac{2(ab+ac+bc)}{kT}\left[\frac{\epsilon_{st(i)}\theta_{s(i)}\left(\frac{2}{3}+\frac{1}{3m}\right)}{1-\frac{\theta_{s(i)}}{3}\left(1-\frac{1}{m}\right)}-\frac{\epsilon_{st(a)}\theta_{s(a)}\left(\frac{1}{\omega}\right)}{1-\theta_{s(a)}\left(1-\frac{1}{\omega}\right)}\right]-$$
$$abc\ln\left[\frac{1-\theta_{s(i)}}{1-\frac{\theta_{s(i)}}{3}\left(1-\frac{1}{m}\right)}\right]-\ln 3 \quad (5)$$

which is independent of the common mobile phase, and where the subscripts (a) and (i) distinguish the anisotropic and isotropic phases, respectively. Equation 5 can be written in the following form:

$$\ln (SE) = A_{min}c_1 + A_{sur}c_2 - V_w c_3 - \ln 3 \quad (6)$$

where $A_{min} = ab$, $A_{sur} = 2(ab + ac + bc)$, and $V_w = abc$ are the scaled minimum area, total surface area, and van der Waals volume, respectively, of the solute molecule.[27,28] (The scaled dimensions are with respect to the volume of a single cubic cell in the lattice (for $V_w$) or the area of one face of the cell (for $A_{min}$ and $A_{sur}$)).[27,28] The constants $c_j$ ($j$ = 1, 2, 3) in eq 6 are, respectively, the coefficients of $A_{min}$, $A_{sur}$, and $V_w$ in eq 5.

If we employ eq 6 to compare a set of structural isomers having the same molecular volume, $V_w$, then $V_w c_3$ becomes a constant within this set and

$$\ln (SE) = A_{min}c_1 + A_{sur}c_2 - c_4 \quad (7)$$

where $c_4 = V_w c_3 + \ln 3$. Accordingly, when the isotropic stationary phase is replaced by an anisotropic one, any enhancement in shape selectivity experienced by this group of isomers would be due to differences in $A_{min}$ and $A_{sur}$, as will be discussed.

Previously,[1] the selectivity enhancement, (SE)′, among a set of isomers was defined with respect to a (hypothetical) cubic reference solute (dimensions $ddd$) that has the same molecular volume as the set of isomers ($V_w = abc = d^3$). Using this definition,

$$\ln (SE)' = \ln (SE) - \ln (SE)_r \quad (8)$$

where $\ln (SE)_r$ for the reference solute is given by eq 5, with $a = b = c = d$ and *without* the −ln 3 term, which disappears because the cubic solutes are isotropically distributed in both phases.[27] From eqs 5 and 8 we obtain

$$\ln (SE)' =$$
$$(ab-d^2)\left\{\ln\left[\frac{1-\theta_{s(a)}}{1-\theta_{s(a)}\left(1-\frac{1}{\omega}\right)}\right]+\frac{2\epsilon_{st(a)}}{kT}\left[\frac{\theta_{s(a)}\left(\frac{1}{\omega}\right)}{1-\theta_{s(a)}\left(1-\frac{1}{\omega}\right)}\right]\right\}+$$
$$\left[\frac{2(ab+ac+bc)-6d^2}{kT}\right]\times$$
$$\left[\frac{\epsilon_{st(i)}\theta_{s(i)}\left(\frac{2}{3}+\frac{1}{3m}\right)}{1-\frac{\theta_{s(i)}}{3}\left(1-\frac{1}{m}\right)}-\frac{\epsilon_{st(a)}\theta_{s(a)}\left(\frac{1}{\omega}\right)}{1-\theta_{s(a)}\left(1-\frac{1}{\omega}\right)}\right]-\ln 3 \quad (9)$$

which can be written in the following form:

$$\ln (SE)' = A_{min}c_1 + A_{sur}c_2 - c'_4 \quad (10)$$

where $c'_4$ is equal to ln 3 plus the collection of terms involving $d^2$, and $c_4$ (eq 7) $\neq c'_4$ (eq 10). Therefore, eqs 7 and 10 have exactly the same form and differ only by a constant which, for present purposes, need not be specified.

Equations 3–7 will be applied here to analyze and interpret, at the molecular level, chromatographic results. For a given set of structural isomers, the *relative values* of the selectivity enhancement, as defined by eq 3, provide a valid means of assessing the effect of the orientational order of the anisotropic phase on the shape-selective separation of these isomers. Note that these equations are applicable to GC, LC, and SFC.

## EXPERIMENTAL SECTION

**Apparatus.** The chromatographic system consisted of a Model 501 Capillary Column Supercritical Fluid Chromatograph (Lee Scientific, Inc., Salt Lake City, UT) which is controlled by a computer (Model 45945A, Hewlett-Packard, Sunnyvale, CA). The syringe pump assembly has a capacity of 175 mL and is surrounded by a cooling jacket attached to a refrigerated circulating bath. The water temperature was maintained at about 10 °C during the filling process.

Injections were performed by a pneumatically operated injection valve (Valco Instrument Co., Inc., Houston, TX) with a 200-μL sample loop. A 35-cm length of 10-μm i.d. fused silica was used to split the sample upon injection. The split ratio was approximately 20:1, and the injection duration time was set at 0.01 s. A flame ionization detector (FID) was used for all experiments. The detector temperature was set at 325 °C. Hydrogen, air, and helium were obtained from common sources.

A chart recorder (Model 555, Linear Instruments Corp., Irvine, CA) was used to record the chromatograms. The mobile phase used was SFC-grade carbon dioxide (Matheson Gas Products, Baltimore, MD).

**Columns.** The capillary columns used were SB-Smectic and SB-Octyl-50 (Lee Scientific, Inc., Salt Lake City, UT). The first column, containing a smectic liquid-crystalline polysiloxane (Figure 1a), was 10 m long with a 50-μm internal diameter and a film thickness of 0.15 μm. It has been reported that this phase posssesses a glassy-to-smectic transition point at about 100 °C.[13] The second column, containing a 50% octyl- and 50% methylpolysiloxane (Figure 1b), was also 10 m long with a 50-μm internal diameter and a film thickness of 0.25 μm.

**Table I. Solutes**

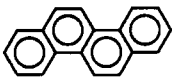
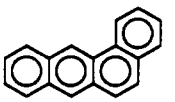
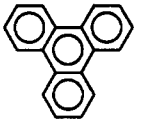
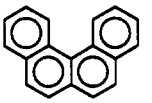
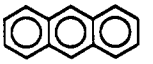
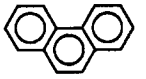
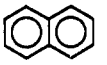
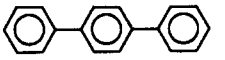
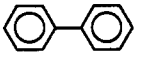
| name | molecular weight | chemical formula | structure | planarity |
|---|---|---|---|---|
| chrysene | 228.30 | $C_{18}H_{12}$ |  | planar |
| benz[*a*]anthracene | 228.30 | $C_{18}H_{12}$ |  | planar |
| triphenylene | 228.30 | $C_{18}H_{12}$ |  | planar |
| benzo[*c*]phenanthrene | 228.30 | $C_{18}H_{12}$ |  | nonplanar |
| pyrene | 202.26 | $C_{16}H_{10}$ |  | planar |
| anthracene | 178.24 | $C_{14}H_{10}$ |  | planar |
| phenanthrene | 178.24 | $C_{14}H_{10}$ |  | planar |
| naphthalene | 128.18 | $C_{10}H_8$ |  | planar |
| *p*-terphenyl | 230.31 | $C_{16}H_{14}$ |  | nonplanar |
| biphenyl | 154.21 | $C_{12}H_{10}$ |  | nonplanar |

**Table II. Geometric Parameters of Solutes[a]**

| solute | $V_w'$ (Å$^3$) | dimensions (Å) | | | scaled parameters | | |
|---|---|---|---|---|---|---|---|
| | | *a* | *b* | *c* | $A_{min}$ | $A_{sur}/2$ | $V_w$ |
| chrysene | 207.77 | 2.57 | 6.66 | 12.13 | 5.16 | 38.90 | 34.29 |
| benz[*a*]anthracene | 207.77 | 2.57 | 7.38 | 10.95 | 5.71 | 38.54 | 34.29 |
| triphenylene | 207.77 | 2.57 | 8.53 | 9.48 | 6.60 | 38.29 | 34.29 |
| benzo[*c*]phenanthrene | 207.77 | 3.57 | 6.54 | 8.90 | 7.03 | 37.65 | 34.29 |
| pyrene | 181.01 | 2.57 | 7.38 | 9.54 | 5.71 | 34.31 | 29.87 |
| anthracene | 165.27 | 2.57 | 6.09 | 10.55 | 4.72 | 32.26 | 27.27 |
| phenanthrene | 165.27 | 2.57 | 6.51 | 9.88 | 5.04 | 32.06 | 27.27 |
| naphthalene | 122.77 | 2.57 | 5.97 | 8.01 | 4.62 | 25.21 | 20.26 |
| *p*-terphenyl | 218.79 | 3.35 | 4.76 | 13.74 | 4.80 | 38.33 | 36.10 |
| biphenyl | 149.45 | 3.65 | 4.47 | 9.15 | 4.92 | 27.31 | 24.66 |

[a] $V_w'$ is the van der Waals volume in Å$^3$, and $V_w = V_w'/v_0$, $A_{min} = ab/a_0$, and $A_{sur}/2 = (ab + ac + bc)/a_0$, where $v_0 = 6.06$ Å$^3$ and $a_0 = 3.32$ Å.[2,27-29]

**Solutes and Solvent.** The solutes used with both columns are PAHs and polyphenyls (Aldrich Co., Inc., Milwaukee, WI). They are differentiated by their retention order in the liquid-crystalline column as follows: naphthalene, biphenyl, phenanthrene, anthracene, pyrene, benzo[*c*]phenanthrene, triphenylene, *p*-terphenyl, benz[*a*]anthracene, and chrysene. Their relevant properties and geometric parameters are listed in Tables I and II, respectively.

Methylene chloride was used as the solvent (Fisher Scientific Inc.). Methane was injected as an "unretained" marker solute for determination of column void time (or hold-up time), $t_0$. The values of $t_0$ obtained from this method are in good agreement with those determined by the linearization of retention data for homologous series.[30] The concentration of each solute was approximately 2 mg/mL.

**Procedures.** The experiments consisted of performing triplicate injections of the solutes for each temperature–density combination. Five temperatures were chosen at 10 °C intervals from 107 °C to 147 °C. For each temperature, injections were made at 0.05 g/mL density intervals from 0.15 to 0.60 g/mL. Each setting point was determined by fixing the pressure at a given temperature to give the desired density, which was determined using a modification of the BWR equation of state.[31] Since the pressure drop across the capillary column and its effect on solute retention are essentially negligible when the state of the SF mobile phase is far from the critical point,[31] we assumed that $\rho_{inlet} \approx \langle \rho \rangle \approx \rho$.

The retention time was obtained from the average value of the retention distances measured on the chart paper or the retention

(30) Reister, R.; Yan, C.; Martire, D. E. *J. Chromatogr.* **1991**, *588*, 289–294.

(31) Martire, D. E.; Riester, R. L.; Bruno, T. J.; Hussam, A.; Poe, D. P. *J. Chromatogr.* **1991**, *545*, 135–147.

**Table III. Selectivity Enhancement (SE) of PAHs Due to Differences of Orientational Order and Interaction Energy between SB-Smectic and SB-Octyl-50 Phases**

| | density (g/mL) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 0.15 | 0.20 | 0.25 | 0.30 | 0.35 | 0.40 | 0.45 | 0.50 | 0.55 | 0.60 |
| | | | | | Temperature = 107 °C | | | | | |
| naphthalene | 0.30 | 0.30 | 0.28 | 0.32 | 0.37 | | | | | |
| biphenyl | 0.29 | 0.30 | 0.29 | 0.31 | 0.33 | | | | | |
| phenanthrene | | 0.57 | 0.58 | 0.58 | 0.62 | 0.68 | 0.70 | 0.67 | | |
| anthracene | | 1.08 | 1.09 | 1.11 | 1.20 | 1.24 | 1.28 | 1.28 | | |
| pyrene | | | | 0.70 | 0.78 | 0.82 | 0.80 | 0.82 | | |
| benzo[c]phenanthrene | | | | 0.68 | 0.67 | 0.70 | 0.71 | 0.70 | 0.67 | |
| triphenylene | | | | 0.77 | 0.81 | 0.82 | 0.83 | 0.81 | 0.84 | 0.90 |
| *p*-terphenyl | | | | 3.13 | 3.39 | 3.41 | 3.48 | 3.45 | 3.45 | |
| benz[*a*]anthracene | | | | | 2.09 | 2.19 | 2.16 | 2.14 | 2.15 | 2.29 |
| chrysene | | | | | 3.62 | 3.77 | 3.79 | 3.81 | 3.87 | 4.03 |
| | | | | | Temperature = 117 °C | | | | | |
| naphthalene | 0.41 | 0.39 | 0.41 | 0.45 | | | | | | |
| biphenyl | 0.39 | 0.39 | 0.39 | 0.41 | | | | | | |
| phenanthrene | | 0.73 | 0.78 | 0.84 | 0.81 | 0.79 | 0.87 | 0.89 | | |
| anthracene | | 1.31 | 1.38 | 1.49 | 1.50 | 1.45 | 1.51 | 1.52 | | |
| pyrene | | | 0.93 | 0.99 | 1.03 | 0.99 | 1.03 | 1.07 | 1.09 | 1.02 |
| benzo[c]phenanthrene | | | | 0.83 | 0.86 | 0.87 | 0.92 | 0.90 | 0.94 | 0.91 |
| triphenylene | | | | 1.02 | 1.11 | 1.03 | 1.06 | 1.01 | 1.15 | 1.30 |
| *p*-terphenyl | | | | 3.53 | 3.58 | 3.51 | 3.47 | 3.58 | 3.44 | |
| benz[*a*]anthracene | | | | 2.64 | 2.73 | 2.61 | 2.67 | 2.52 | 2.83 | 3.13 |
| chrysene | | | | | 4.53 | 4.40 | 4.45 | 4.51 | 4.74 | 5.21 |
| | | | | | Temperature = 127 °C | | | | | |
| naphthalene | 0.46 | 0.44 | 0.46 | 0.54 | | | | | | |
| biphenyl | 0.43 | 0.45 | 0.45 | 0.48 | 0.49 | | | | | |
| phenanthrene | | 0.88 | 0.90 | 0.94 | 0.97 | 1.01 | 1.00 | 1.07 | | |
| anthracene | | 1.52 | 1.56 | 1.63 | 1.64 | 1.70 | 1.73 | 1.83 | 1.93 | |
| pyrene | | | 1.09 | 1.15 | 1.20 | 1.26 | 1.28 | 1.37 | 1.36 | |
| benzo[c]phenanthrene | | | | 0.98 | 1.03 | 1.07 | 1.11 | 1.19 | 1.21 | |
| triphenylene | | | | 1.24 | 1.27 | 1.34 | 1.39 | 1.48 | 1.49 | |
| *p*-terphenyl | | | | 3.67 | 3.61 | 3.66 | 3.73 | 3.79 | 3.68 | |
| benz[*a*]anthracene | | | | 3.08 | 3.12 | 3.20 | 3.28 | 3.46 | 3.52 | |
| chrysene | | | | | 5.09 | 5.31 | 5.33 | 5.54 | 5.59 | |
| | | | | | Temperature = 137 °C | | | | | |
| naphthalene | 0.47 | 0.53 | 0.51 | | | | | | | |
| biphenyl | 0.48 | 0.42 | 0.52 | 0.51 | | | | | | |
| phenanthrene | 0.89 | 0.95 | 0.97 | 1.01 | 1.09 | 1.15 | 1.13 | | | |
| anthracene | 1.50 | 1.59 | 1.61 | 1.65 | 1.77 | 1.87 | 1.83 | 1.99 | | |
| pyrene | | | 1.21 | 1.30 | 1.38 | 1.44 | 1.47 | 1.56 | | |
| benzo[c]phenanthrene | | | | 1.11 | 1.19 | 1.24 | 1.26 | 1.34 | | |
| triphenylene | | | | 1.35 | 1.45 | 1.53 | 1.57 | 1.67 | | |
| *p*-terphenyl | | | 3.45 | 3.43 | 3.58 | 3.69 | 3.69 | 3.72 | | |
| benz[*a*]anthracene | | | | 3.13 | 3.32 | 3.47 | 3.53 | 3.70 | | |
| chrysene | | | | | 5.24 | 5.49 | 5.58 | 5.83 | | |
| | | | | | Temperature = 147 °C | | | | | |
| naphthalene | 0.52 | 0.55 | 0.56 | | | | | | | |
| biphenyl | 0.52 | 0.53 | 0.55 | 0.60 | | | | | | |
| phenanthrene | 0.95 | 1.02 | 1.10 | 1.13 | 1.17 | 1.24 | 1.35 | | | |
| anthracene | 1.53 | 1.64 | 1.73 | 1.79 | 1.84 | 1.96 | 2.02 | | | |
| pyrene | | 1.34 | 1.37 | 1.46 | 1.50 | 1.53 | 1.65 | | | |
| benzo[c]phenanthrene | | | 1.20 | 1.26 | 1.33 | 1.38 | 1.47 | | | |
| triphenylene | | | 1.46 | 1.55 | 1.61 | 1.66 | 1.77 | | | |
| *p*-terphenyl | | | 3.38 | 3.45 | 3.50 | 3.48 | 3.61 | | | |
| benz[*a*]anthracene | | | | 3.33 | 3.43 | 3.51 | 3.68 | | | |
| chrysene | | | | | 5.31 | 5.43 | 5.64 | | | |

time read from the computer clock for three chromatograms of the solutes.

**Results.** The capacity factor, $k'$, was obtained from $k' = (t_R - t_0)/t_0$, where $t_R$ is the retention time of the solute. Values of the natural logarithm of the capacity factor of the solutes for the two chromatographic systems have been reported elsewhere.[28,29] The values of selectivity enhancement (SE) are obtained from eq 3 using $\Phi_{an}/\Phi_{is} \approx 5/3$ and are reported in Table III.

## APPLICATION TO GC, LC, AND SFC

**Effect of Solute Characteristics.** Equation 5 describes a comparison of solute retention behavior between two stationary phases, one with long-range orientational order (anisotropic) and the other without such order (isotropic), contained in otherwise identical columns operated with the same mobile phase, at the same mobile-phase density ($\theta_m$) and temperature. It reduces to the form of eq 7 for a set of structural isomers having (roughly) the same van der Waals volume, $V_w$.

If we consider planar PAH isomers, for which the total surface areas ($A_{sur}$) are approximately the same (see Table II), eq 7 becomes

$$\ln (SE) = A_{min}c_1 + c_5 \quad (11)$$

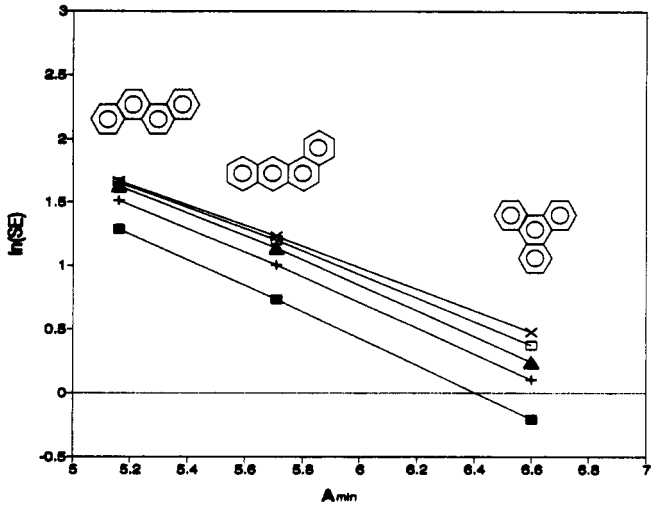



**Figure 2.** Plots of ln (SE) vs $A_{min}$ for planar four-ring PAH isomers at SF $CO_2$ density of 0.35g/mL and different temperatures: (■) 107 °C; (+) 117 °C; (▲) 127 °C; (□) 137 °C; (×) 147 °C.

where, from eq 5

$$c_1 = \text{slope} = \ln\left[\frac{1-\theta_{s(a)}}{1-\theta_{s(a)}\left(1-\frac{1}{\omega}\right)}\right] + \frac{2\epsilon_{st(a)}}{kT}\left[\frac{\theta_{s(a)}\left(\frac{1}{\omega}\right)}{1-\theta_{s(a)}\left(1-\frac{1}{\omega}\right)}\right] \tag{12}$$

and

$$c_5 = \text{intercept} = -V_w \ln\left[\frac{1-\theta_{s(i)}}{1-\frac{\theta_{s(i)}}{3}\left(1-\frac{1}{m}\right)}\right] - \ln 3 + \frac{(A_{sur})}{kT}\left[\frac{\epsilon_{st(i)}\theta_{s(i)}\left(\frac{2}{3}+\frac{1}{3m}\right)}{1-\frac{\theta_{s(i)}}{3}\left(1-\frac{1}{m}\right)} - \frac{\epsilon_{st(a)}\theta_{s(a)}\left(\frac{1}{\omega}\right)}{1-\theta_{s(a)}\left(1-\frac{1}{\omega}\right)}\right] \tag{13}$$

According to eq 11, ln (SE) should be a linear function of $A_{min}$ at constant temperature for any given set of planar PAH isomers. It is evident that both the slope and the intercept of eq 11 are temperature dependent. Since the first and the second terms in eq 12 are both negative, the slope should always be negative. Also, the slope is predicted to become less negative with increasing temperature. Figure 2 shows plots of ln (SE) vs $A_{min}$ for the planar PAH isomers at constant mobile-phase density and different temperatures, constructed using the SE values in Table III and the $A_{min}$ values in Table II. The correlation coefficients are about 0.99, and the slopes indeed become less negative with increasing temperature.

Note that the slope of ln (SE) vs $A_{min}$ should be the same at different mobile-phase densities if, as assumed in the theoretical model, (a) absorption of the mobile phase molecules by the stationary phase (swelling effect) can be neglected and (b) relatedly, $\theta_s$ and $\epsilon_{st}$ in both the anisotropic and isotropic phases are independent of mobile-phase density. Shown in Figure 3 are plots of ln (SE) vs $A_{min}$ at different mobile-phase densities. As can be seen, the slopes are essentially the same (see later).

Lochmüller et al.[6] synthesized a 4,4′-dipentylbiphenyl–dimethylsiloxane (55B) phase and an octadecyldimethylchlorosilane (ODS) phase to mimic an extended state (anisotropic) and a collapsed state (isotropic), respectively. The two columns were used to study shape selectivity in LC and to test the unified molecular theory proposed by Martire and Boehm.[26] They calculated the selectivity factor, $\alpha$, as the ratio of the capacity factor of the solute to that of benzene

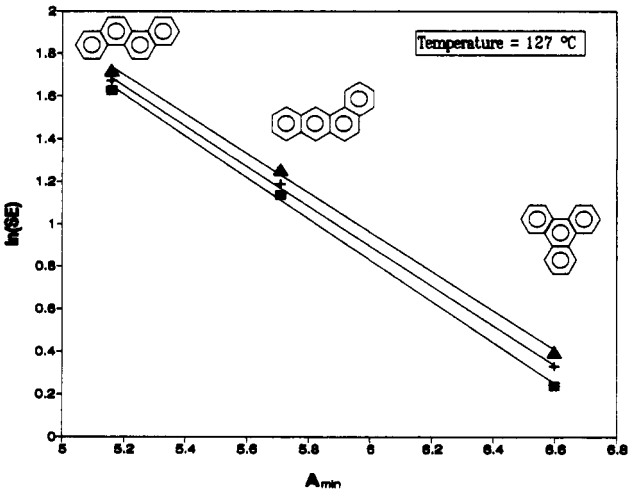



**Figure 3.** Plots of ln (SE) vs $A_{min}$ for planar four-ring PAH isomers at 127 °C and different mobile-phase densities: (■) 03.5 g/mL; (+) 0.45 g/mL; (▲) 0.55 g/mL.

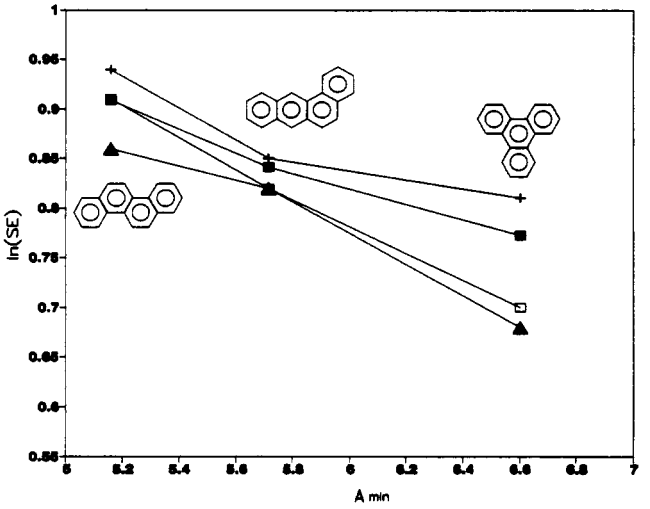



**Figure 4.** Plots of ln (SE) vs $A_{min}$, using data generated from ref 6 for four-ring PAH isomers at different volume fractions of methanol in the mobile phase: (■) 0.70 (benzene as reference solute); (+) 0.70; (▲) 0.80; (□) 0.90 (mesitylene as reference solute).

or mesitylene (reference solute). Using their data we generated the logarithm of selectivity enhancement, ln (SE)

$$\ln (SE) = \ln\left(\frac{\alpha_{55B}}{\alpha_{ODS}}\right) \tag{14}$$

The results for four-ring PAH isomers are shown Figure 4, as plots of ln (SE) vs $A_{min}$. Although there is scatter of the limited data, the general trend is clear: ln (SE) decreases with increasing $A_{min}$.

Wise and co-workers[5] obtained retention data for PAHs and methyl-substituted PAHs on both a liquid-crystalline phase (SB-Smectic) and a methylpolysiloxane phase (SB-Methyl-100) in GC. In order to determine whether similar retention mechanisms and the physical nature of the stationary phases are responsible for the unique shape selectivity in both GC and LC, they also obtained LC retention data on both polymeric and monomeric $C_{18}$ phases. Using their relative retention data on the smectic liquid–crystalline phase (anisotropic) and the methylpolysiloxane phase (isotropic), values of ln (SE) were generated. The structures and minimum areas of the five-ring PAH isomers[27] are illustrated in Figure 5.

Assuming that the five-ring PAH isomers have the same van der Waals volume and roughly the same contact area, eq

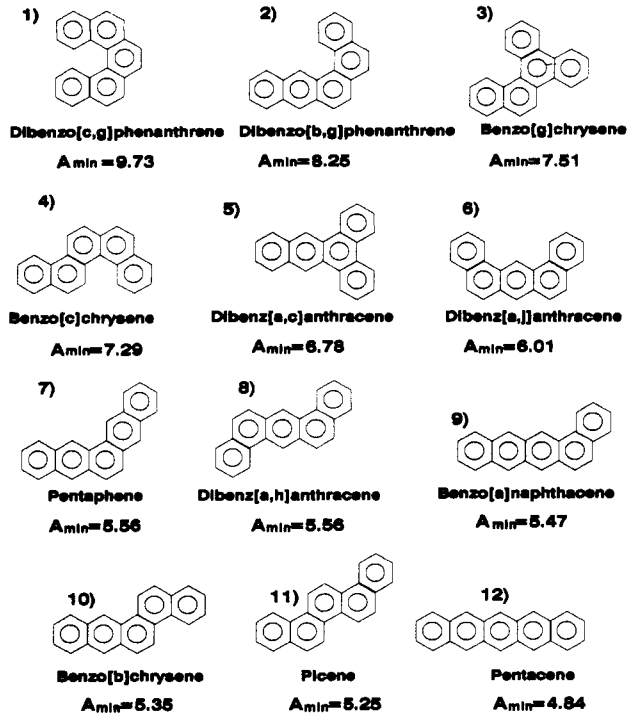



**Figure 5.** Structures and minimum areas of five-ring PAH isomers.

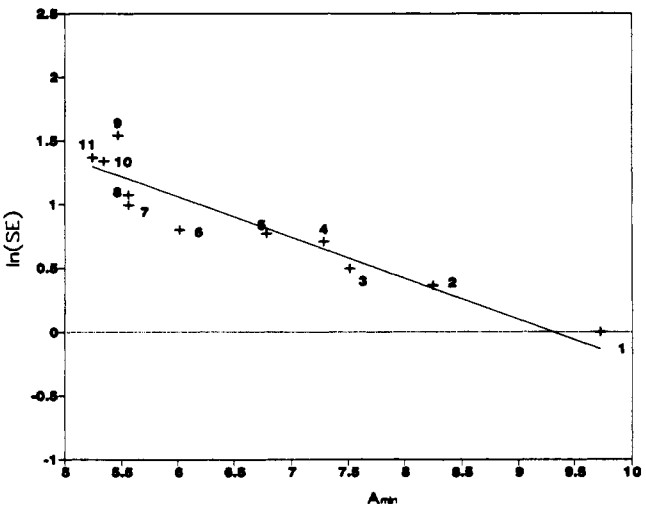



**Figure 6.** Plot of ln (SE) vs $A_{min}$ for 11 five-ring PAH isomers using data generated from ref 5: (+) experimental data; (—) best linear fit. (Order of the solutes is the same as that in Figure 5.)

11 predicts a linear relationship between ln (SE) and $A_{min}$. Shown in Figure 6 is the plot of ln (SE) vs the minimum area for five-ring PAH isomers.

**Effect of Mobile-Phase Parameters.** As mentioned earlier, according to our current model the mobile phase density does not influence the selectivity enhancement (see eq 5), because swelling effects are assumed to be negligible or to offset each other in the anisotropic and the isotropic systems. However, we do see in Table II and Figure 3 that there is some slight dependence of ln (SE) on the mobile-phase density. This interesting phenomenon will be analyzed and discussed in a subsequent paper.

**Effect of Stationary-Phase Parameters.** The key to the selectivity enhancement is the ordering of the anisotropic stationary phase: the better the stationary phase is aligned, the greater the selectivity enhancement. On the other hand, partial alignment of the "isotropic phase" would make the selectivity enhancement decrease. The stationary-phase density ($\theta_s$) also plays an important role. Higher anisotropic stationary-phase density ($\theta_{s(a)}$) would lead to an increase in selectivity enhancement. On the other hand, higher isotropic stationary-phase density ($\theta_{s(i)}$) acts in the opposite direction. Similarly, stronger solute–anisotropic phase interaction energy (more negative $\epsilon_{st(a)}$) makes the selectivity enhancement greater, while weaker solute–isotropic phase interaction is favorable to the selectivity enhancement.

**Effect of Temperature.** From eq 4

$$\ln (SE) = -\frac{\Delta G_{an/is}}{RT} = -\frac{\Delta H_{an/is}}{RT} + \frac{\Delta S_{an/is}}{R} \tag{15}$$

where $\Delta H_{an/is}$ and $\Delta S_{an/is}$ are, respectively, the molar enthalpy and entropy of solute transfer from the isotropic to the anisotropic stationary phase. Also

$$\Delta H_{an/is} = H_{s(a)} - H_{s(i)} \tag{16}$$

and

$$\Delta S_{an/is} = S_{s(a)} - S_{s(i)} \tag{17}$$

where $H$ and $S$ refer to solute partial molar quantities in the respective stationary phases, and from eq 5

$$H_{s(a)} = 2(ac + bc)\epsilon_{st(a)}L\left[\frac{\theta_{s(a)}\left(\frac{1}{\omega}\right)}{1 - \theta_{s(a)}\left(1 - \frac{1}{\omega}\right)}\right] \tag{18}$$

$$H_{s(i)} = 2(ab + ac + bc)\epsilon_{st(i)}L\left[\frac{\theta_{s(i)}\left(\frac{2}{3} + \frac{1}{3m}\right)}{1 - \frac{\theta_{s(i)}}{3}\left(1 - \frac{1}{m}\right)}\right] \tag{19}$$

$$\frac{S_{s(a)}}{R} = ab \ln\left[\frac{1 - \theta_{s(a)}}{1 - \theta_{s(a)}\left(1 - \frac{1}{\omega}\right)}\right] - \ln 3 \tag{20}$$

$$\frac{S_{s(i)}}{R} = abc \ln\left[\frac{1 - \theta_{s(i)}}{1 - \frac{\theta_{s(i)}}{3}\left(1 - \frac{1}{m}\right)}\right] \tag{21}$$

where $L$ is Avogadro's number.

The above equations link the macroscopic thermodynamic properties to the microscopic parameters. Provided the stationary-phase densities ($\theta_s$) and interaction energies ($\epsilon_{st}$) and the orientational order of the anisotropic phase have only a relatively weak dependence on temperature, plots of ln (SE) vs $1/T$ at fixed mobile-phase density ($\theta_m$) should be linear, with a slope of $-\Delta H/R$ and an intercept of $\Delta S/R$.

Shown in Figure 7 are plots of ln (SE) vs $1/T$. The negative slopes reveal that the overall isotropic stationary-phase interaction with the solute molecule is stronger ($H_{s(i)}$ is more negative) than the overall anisotropic stationary-phase interaction with the solute, even though the segmental interaction energy in the anisotropic system ($\epsilon_{st(a)}$) is expected to be stronger than the one in the isotropic system ($\epsilon_{st(i)}$). Comparing eqs 18 and 19, we see that the "contact area" of the solute with the anisotropic stationary phase, $2(ac + bc)$, is much smaller than that with the isotropic phase, $2(ab + ac + bc)$; therefore, $\epsilon_{st(a)}$ is not negative enough to make up the loss due to the smaller contact area and $\Delta H_{an/is} = H_{s(a)} - H_{s(i)} > 0$, i.e., slope $< 0$. This slope becomes more negative with increasing solute size (see Figure 7).

Also, for a set of isomeric solutes having approximately the same $V_w$ ($= abc$) and $A_{sur}$ ($= 2(ab + ac + bc)$), such as planar PAH isomers, the one with the smallest $A_{min}$ ($= ab$) would have the largest value of $A_{sur} - 2A_{min}$ ($= 2(ac + bc)$). According to eqs 16, 18, and 19, then, it would have the most negative

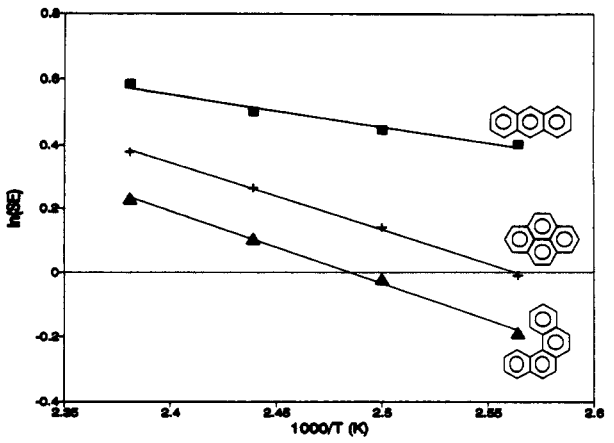



**Figure 7.** Dependence of ln (SE) on $1/T$ for PAH compounds at mobile phase (SF $CO_2$) density of 0.30 g/mL.

$H_{s(a)}$, the least positive $\Delta H_{an/is}$, and, hence, the most favorable (least negative) enthalpic contribution to ln (SE).

The interecepts of the plots in Figure 7 are clearly positive, indicating that $\Delta S_{an/is} > 0$ (eq 15). Since both $S_{s(a)}$ and $S_{s(i)}$ are negative (see eqs 20 and 21), it is also clear that $S_{s(i)}$ is more negative than $S_{s(a)}$, largely because $abc > ab$. Since the absolute entropies, $S_{s(a)}$ and $S_{s(i)}$, are "packing" entropies,[27,29] this indicates more efficient packing of the solutes with the anisotropic stationary phase, especially for solutes with small $A_{min}$. Therefore, for a set of planar PAH isomers, the one with the smallest $A_{min}$ would have the least negative $S_{s(a)}$, the most positive $\Delta S_{an/is}$, and, hence, the most favorable entropic contribution to ln (SE), as well.

Comparison of the relative SE values in Table III for the planar, four-ring PAHs having approximately the same $V_w$ and $A_{sur}$ values (see Table II) bears out the key role of $A_{min}$ in governing the magnitude of SE and, hence, shape-selective separations.

Note finally that the slope of plots of ln $k'$ vs $1/T$ at constant mobile-phase density (van't Hoff plot) has been commonly used in SFC to calculate the molar enthalpy of transfer of the solute from the mobile to the stationary phase,[32-35] and Martire and Boehm[36] have related the slope to the molar internal energy of solute transfer. Recently, Roth employed macroscopic thermodynamic analysis to show that, in general, the slope of ln $k'$ vs $1/T$ at constant mobile-phase density is related neither to the enthalpy nor to the internal energy of solute transfer between the two phases.[37]

According to our model, the slope of ln (SE) vs $1/T$ at constant mobile-phase density is related to the difference of the average interaction energy of the solute with the stationary phase in the two chromatographic systems. However, the slope of ln $k'$ vs $1/T$ is related to the difference of the average interaction energy of the solute with the mobile phase and the average interaction energy of the solute with the stationary phase in a given chromatographic system.

## CONCLUSIONS

A molecular theory, based on a lattice model, was developed to address the selectivity enhancement (SE) experienced by blocklike solutes in an anisotropic stationary phase relative to an isotropic one, due to differences in orientational order and interaction energy in the two phases.

According to the theory, three geometric descriptors, $V_w$, $A_{sur}$, and $A_{min}$ are, in general, required to characterize the selectivity enhancement of a given solute (eq 6). Within a set of structural isomers having about the same $V_w$, the number of descriptors for SE reduces to two (eq 7). Furthermore, with a set of planar PAH isomers, for example, $A_{sur}$ is approximately constant and a linear relationship between ln (SE) and $A_{min}$ is predicted at fixed temperature and mobile-phase density (eq 11).

The theory was tested primarily by using our ln (SE) data obtained from two parallel SFC experiments designed to mimic the anisotropic and the isotropic stationary phases of the model systems. The agreement between the theoretical predictions and experimental results is satisfactory and encouraging, particularly in the SFC and GC cases, for which more extensive data were available.

The present model is based on the assumption that the molecules in the anisotropic phase are perfectly aligned and the molecules in the isotropic phase are completely isotropic. However, virtually all anisotropic phases are only partially aligned due to thermal motion. In addition, possible absorption of the mobile-phase molecules by the stationary phase (swelling) was neglected. Therefore, a more complete model should allow for partial alignment of the anisotropic stationary phase and take swelling effects into account. A further refinement of the present model, along these lines, is in progress.

Finally, it should be noted that, in the application of the present theory, the solute molecules are assumed to meet the requirement of full alignment with the anisotropic stationary phase, although a distribution of orientations can also be considered.[38]

## ACKNOWLEDGMENT

This material is based upon work supported by the National Science Foundation under Grant CHE-8902735.

RECEIVED for review January 16, 1992. Accepted February 28, 1992.

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