

# On the Relation between Retention Indexes and the Interaction between the Solute and the Column in Gas–Liquid Chromatography

Ola Engkvist,<sup>\*,†,§</sup> Piotr Borowski,<sup>§</sup> Agneta Bemgård,<sup>†</sup> Gunnar Karlström,<sup>§</sup> Roland Lindh,<sup>§</sup> and Anders Colmsjö<sup>†</sup>

Department of Theoretical Chemistry, Chemical Center, P.O.B. 124, S-221 00 Lund, Sweden, and Department of Analytical Chemistry, National Institute of Occupational Health, S-171 84 Solna, Sweden

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Gas–liquid chromatography retention indexes for organic molecules are determined by the interaction between the molecule and the column liquid phase. In this article, a model for calculating the interaction energy between a molecule and a dielectric wall is developed. The model is at least to our knowledge the first attempt to predict retention indexes from the interaction between the molecules and the column. This approach to predict retention indexes is radically different from methods proposed before. Earlier predictions of the retention indexes have been done by a large number of descriptors, which were linearly correlated to the retention indexes. The developed model has been tested for polycyclic aromatic hydrocarbons mainly with a molecular weight of 302. For the molecules with MW 302 the obtained correlation coefficient is 0.92. A somewhat simpler model is used to fit PAH with different MWs. A correlation coefficient of 0.998 is obtained if the retention indexes were fitted to the logarithm of the interaction energies between the PAHs and the column.

## INTRODUCTION

In order to identify and quantify chemical compounds, limitations in detector selectivity demand physical separation. This is widely performed with the aid of chromatographic techniques where the separation of compounds is based on individual differences in chemical interaction. This interaction takes place between the compounds in the mobile phase and the stationary phase. If the stationary phase in gas chromatography is considered as nonpolar, the compounds will elute in approximate order of boiling point. Introduction of polar functional groups in the stationary phase will alter the selectivity and thus the elution time of compounds that interact with the introduced groups. It is of utmost interest to understand the retention mechanisms in detail and be able to mathematically depict the separation process. From a practical point of view, it would be desirable to have a theoretical approach that makes it possible to predict retention times of chemical compounds, thus largely facilitating the identification process which otherwise would demand the availability of reference compounds.

In 1947, Wiener<sup>1</sup> determined the boiling points of paraffins with two topological indexes. Inspired by this work, topological indexes for several types of organic compounds have been developed. They have been used together with other descriptors such as polarizability, ionization potential, dipole moment, quadrupole moment, length, width, height, molecular weight, heat of formation, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), number of rings, and molecular weight to predict retention indexes. With the use of descriptors, retention indexes have been derived for a different type of organic compound groups such as alcohols and olefins,<sup>2–4</sup> polychlorinated biphenyls (PCBs), polychlorinated dibenzo-

dioxines (PCDDs) and polychlorinated dibenzofuranes (PCDFs),<sup>5–11</sup> hydrocarbons,<sup>1,12–15</sup> and polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs.<sup>9,16–26</sup> The descriptors are linearly correlated with multilinear regression to the retention indexes. Because of small prediction capability or colinearity only a handful of the descriptors is useful for predicting retention indexes. The results in these studies shows reasonable good correlation of descriptors versus gas chromatography retention indexes. However, the interpretation of the importance of a specific descriptor is often meaningless. As pointed out by some authors<sup>9,27</sup> there may be risks with this type of linear combinations such as random correlation resulting from too many descriptors used in the descriptor set. The standard deviation of the regression coefficients is usually large, in some cases even larger than the absolute values of the regression coefficients. This indicates that interpretation of which descriptors determine the retention indexes is more or less meaningless. One must, however, hold in mind that an equation predicting retention indexes with descriptors could have high predictive capacity even though interpretation of the regression coefficients is meaningless.

In this article a different approach to the problem of predicting retention indexes is proposed. The property which determines the retention indexes is the interaction energy between the solute and the liquid phase (assuming that all the solid support surface area in the column is covered with the liquid and no interaction between the solvated molecule and the solid support). Therefore a model for calculating the interaction energy between the solute and the liquid phase have been developed. In this article mainly correlation of retention indexes for PAHs with a molecular weight of 302 is presented.

The outline of the manuscript will be as follows. First an experimental section where the experimental determination of the retention indexes is described, then there is a theory section with three parts, first the description of a newly

<sup>†</sup> National Institute of Occupational Health.

<sup>‡</sup> Email: Ola.Engkvist@teokem.lu.se.

<sup>§</sup> Chemical Center.

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**Table 1.** Data for the PAHs

compound name	retention index	second virial coeff
dibenzo[ <i>a,e</i> ]pyrene	542.64	1032
dibenzo[ <i>a,h</i> ]pyrene	546.34	1093
dibenzo[ <i>a,e</i> ]pyrene	533.75	966
naphto[2,3- <i>a</i> ]pyrene	544.08	1047
naphto[2,3- <i>e</i> ]pyrene	539.87	984
dibenzo[ <i>a,e</i> ]fluoranthene	535.27	941
dibenzo[ <i>a,f</i> ]fluoranthene	541.57	1024
dibenzo[ <i>a,k</i> ]fluoranthene	535.60	973
dibenzo[ <i>b,e</i> ]fluoranthene	530.11	914
dibenzo[ <i>b,k</i> ]fluoranthene	534.10	944
dibenzo[ <i>j,l</i> ]fluoranthene	534.48	981
naphto[1,2- <i>k</i> ]fluoranthene	532.52	926
naphto[2,3- <i>b</i> ]fluoranthene	533.94	945
naphto[2,3- <i>j</i> ]fluoranthene	534.54	983
naphto[2,3- <i>k</i> ]fluoranthene	536.96	963
benzo[ <i>a</i> ]perylene	537.04	984
benzo[ <i>b</i> ]perylene	544.51	1011

developed direct SCF program, second the description of a model to calculate the interaction between a molecule and a dielectric medium, and finally a description of a model to predict the retention indexes. Thereafter follows sections with calculations, results, and conclusions.

### EXPERIMENTAL SECTION

Temperature programmed retention indexes (RI) with a molecular weight of 302 (Table 1) were obtained according to Lee *et al.*<sup>28</sup> and Vassilaros *et al.*,<sup>29</sup> on a Carlo-Erba Mega HRGC (Milan, Italy) equipped with a flame ionization detector and a 15 m × 0.28 mm XTI-5 column having a film thickness of 0.25 μm (Restek Corporation, Bellefonte, PA, U.S.A.). This stationary phase has a 5% phenyl substitution (the rest being methyl groups) and can be considered as equivalent to the home-made column used in ref 28. Phenanthrene, chrysene, picene, and benzo[*c*]picene were used as bracketing compounds. On-column injections were performed at an oven temperature of 70 °C, and after 2 min the oven temperature was programmed at 5 °C/min to 350 °C. Hydrogen was used as a carrier gas. The 17 PAHs, Table 1, were either purchased from Promchem (Wessel, Germany) or obtained from other laboratories (see Acknowledgment).

The retention indexes were recalculated and linerized by the use of two index determinators before further calculations. Phenanthrene was given RI = 300 and picene RI = 500. Thus for the GC system used, chrysene was adjusted to 407.50 and benzo[*c*]picene to 582.50 in order to achieve linearity between elution time and retention index. Only interpolated index values were used; bracketing standard must elute on each side of the compound to be determined. All chromatograms were registered by ELDSpro Lab data system, CDS AB, Kungshög, Sweden. The uncertainty is about 0.05 index units in the retention indexes for PAHs with MW 302 used in this article. In the fit with several different MWs the retention indexes used have been obtained with different columns so the uncertainty in RI will be a bit larger than for PAHs with MW 302.

### THEORY

As described in the introduction, there have been several quite successful attempts to correlate retention indexes to descriptors of PAHs. In this article the aim is to increase

the understanding of the physical phenomena that determine the retention index, and a model to predict retention indexes will be described. In the model the wall of the column is represented by a dielectric medium. The PAHs are described at the *ab initio* Hartree–Fock level of quantum theory. The PAHs are too large to be suitable for a conventional SCF calculation in which integrals are computed and stored on disk prior to the wave function optimization. The size of the PAHs leads to a prohibiting large number of integrals. A direct SCF program have been developed to circumvent this problem and is described in the following subsection. The calculation of the interaction energy between a molecule and a dielectric medium is thereafter described and in the final subsection a model to predict the retention indexes is presented.

### DIRECT SCF PROGRAM

For large systems, say more than 30 first row atoms (Li–Ne), the conventional SCF procedure is not practical. The inclusion of the polarization functions, using the DZP-quality basis set, results in the 400–500 basis functions and approximately 10<sup>9</sup>–10<sup>10</sup> two-electron integrals need to be computed which, if the calculation was carried out in the ordinary two-step fashion, would require 10–50 GB of the disk memory. In order to avoid the storage bottleneck the so-called direct SCF method has been proposed:<sup>30</sup> the integrals are recalculated when needed. In principle one is faced with the following challenges: (i) efficient integral evaluation and (ii) rapid convergency of the iterative procedure. Our implementation of the direct SCF program is based on the MOLCAS-3 program package.<sup>31</sup> The two-electron integrals are computed by the reduced multiplication scheme of the Rys–Gauss quadrature.<sup>32</sup> The present implementation is well suited for efficient calculation of the integrals over the generally-contracted and segmented-contracted basis sets. In order to further reduce the total time needed for the contraction of the density matrix with integrals we used a number of tricks recommended in the literature. First, we focused on integral prescreening; only integrals that significantly contribute to the Fock matrix are evaluated. Prescreening schemes are based on a rapid estimate of the largest integral in the given batch of integrals, scaled by the largest density matrix element that the integral could be contracted with ref 30. In this work an estimate, based on the Schwarz inequality proposed by Häser and Ahlrichs,<sup>33</sup> has been used to achieve this goal. A substantial time saving can also be obtained using a recursion relationship in the construction of the two-electron part of the Fock matrix.<sup>30</sup> In practice it means that the integrals are contracted with the density differences between subsequent iterations. Since the elements of that matrix vanish as the convergency is approached the integral prescreening becomes more efficient. An even more efficient prescreening was obtained by minimization of the density difference by linear combination as proposed by Häser and Ahlrichs.<sup>33</sup>

A good set of initial orbitals is essential for the rapid convergence of the iterative procedure. We have observed that the diagonalization of the core Hamiltonian, the common way of obtaining starting orbitals for small systems, gave poor convergence properties for the considered molecules. The steps taken by the first-order algorithm were random which sometimes led to positive total energies in the first

few iterations. A rapid convergence (usually within 10 iterations) was ensured by applying the "projection" technique as proposed by Cremer and Gauss.<sup>34</sup> In the first step we carried out the calculation in the conventional fashion using the minimal STO-3G basis set (134 basis functions for each of the investigated molecules). The orbitals were then "projected" on the space spanned by the DZP basis set according to

$$\mathbf{C}^{\text{DZP}} = (\mathbf{S}^{\text{DZP}})^{-1} \mathbf{S}^{\text{MIX}} \mathbf{C}^{\text{STO-3G}} \quad (1)$$

where  $\mathbf{C}^{\text{DZP}}$  and  $\mathbf{S}^{\text{DZP}}$  are the molecular orbital coefficients and overlap matrices in the DZP basis,  $\mathbf{C}^{\text{STO-3G}}$  are the molecular orbital coefficients in the STO-3G basis, and  $\mathbf{S}^{\text{MIX}}$  is the overlap matrix between those two bases, i.e.,  $(\chi^{\text{DZP}} | \chi^{\text{STO-3G}})$ . (Note, that from mathematical point of view projection from smaller to bigger space brings about arbitrariness.) This technique turned out to be very successful; the energy functional was brought close to the stationary solution in the first iteration, and the efficient use of the direct inversion in the iterative subspace (DIIS) extrapolation algorithm<sup>35,36</sup> was immediately possible.

#### INTERACTION ENERGY BETWEEN A MOLECULE AND A DIELECTRIC MEDIUM

In the perturbation expansion of the intermolecular interaction energy, it is usually divided into four terms:<sup>37,38</sup>

$$E^{\text{tot}} = E^{\text{ele}} + E^{\text{ind}} + E^{\text{rep}} + E^{\text{disp}} \quad (2)$$

where  $E^{\text{ele}}$  is electrostatic interaction energy,  $E^{\text{ind}}$  is the induction energy,  $E^{\text{rep}}$  is the exchange repulsion energy, and  $E^{\text{disp}}$  is the dispersion energy. In this article the induction term is ignored since test calculations have shown that it has a negligible role in the model to predict retention indexes for nonpolar molecules. In principle, it can be included along the lines described below.

**Electrostatic Energy.** We approximate the charge distribution of the molecules with a multicenter multipole expansion.<sup>39-41</sup> A SCF wave function is constructed from a set of molecular orbitals. These orbitals are constructed from a set of basis functions

$$\psi_i = \sum_{\mu} c_{i\mu} \chi_{\mu} \quad (3)$$

where  $\psi_i$  is a molecular orbital,  $c_{i\mu}$  is an orbital coefficient and  $\chi_{\mu}$  is a basis function centered at a nucleus. A density matrix element  $D_{\mu\nu}$  is defined as

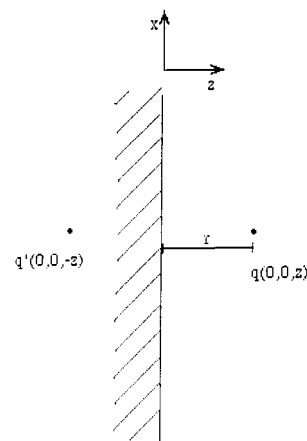
$$D_{\mu\nu} = \sum_i n_i c_{i\mu} c_{i\nu} \quad (4)$$

where  $n_i$  is the occupation number,  $\mu$  and  $\nu$  runs over basis functions, and  $i$  runs over orbitals.

The total molecular charge distribution could be expanded as

$$\rho = \sum_{\mu} \sum_{\nu} D_{\mu\nu} \chi_{\mu} \chi_{\nu} \quad (5)$$

We can divide the charge distribution into local contributions



**Figure 1.** The polarization of a dielectric medium from a charge  $q$  sited at  $(0,0,z)$  is modeled with a mirror charge  $q'$  sited at  $(0,0,-z)$ .

$\rho_{KL}$  where  $K$  and  $L$  are nuclei

$$\rho_{KL} = \sum_{\mu \in K} \sum_{\nu \in L} D_{\mu\nu} \chi_{\mu} \chi_{\nu} \quad (6)$$

A local charge center for each atom pair is calculated as

$$q_{KL} = \sum_{\mu \in K} \sum_{\nu \in L} D_{\mu\nu} \langle \chi_{\mu} \chi_{\nu} \rangle \quad (7)$$

In a similar way one can also define local dipole and quadrupole moments. For the higher moments we need a common origin for the expansion of these local moments. It is defined in the following way. Two centers of charge  $R_c$  are calculated, one for all positive charges and one for all negative charges.<sup>41</sup> The common origin is then obtained as the center of charge using the absolute values of these two charges. Local moments up to quadrupole moments are calculated for all atoms and bonds. With this choice of expansion centers the multicenter multiple expansion converges rapidly. The distributed moments add up to give correct molecular moments up to quadrupole moments, i.e., the distributed moments add up to give the expectation value of the SCF wave function for the corresponding moments. The distributed moments also include large parts of higher molecular moments.

The charges, dipoles, and quadrupoles of the molecule polarizes the dielectric media. This polarization could be modeled in the following way.<sup>42</sup> A charge  $q$  at a distance  $r$  from the dielectric media gives rise to a mirror charge  $q'$  sited at  $-r$  see Figure 1. The mirror charge is related to  $q$  by the following relationship

$$q' = -\frac{\epsilon_0 - 1}{\epsilon_0 + 1} q \quad (8)$$

where  $\epsilon_0$  is the dielectric constant for the medium at zero frequency. The interaction energy between a charge and its mirror charge is given by (in au)

$$E = \frac{1}{2} \frac{qq'}{2r} \quad (9)$$

where the factor  $1/2$  appears due to the energetical cost of polarize the media. In a similar way the local dipoles will give rise to mirror dipoles, and local quadrupoles will give rise to mirror quadrupoles. The electrostatic energy is then

equal to the interaction between all the local moments of the molecule and all the mirror moments in the dielectric media.

**Dispersion Energy.** The dipole–dipole term of the dispersion energy between two molecules could be written as<sup>43</sup>

$$E^{\text{disp}} = - \sum_{\alpha, \beta, \gamma, \delta}^3 T_{\alpha\beta} T_{\gamma\delta} \sum_{n_1 > 0, n_2 > 0} \frac{\langle 00 | \mu_{1,\alpha} \mu_{2,\beta} | n_1 n_2 \rangle \langle n_1 n_2 | \mu_{1,\gamma} \mu_{2,\delta} | 00 \rangle}{E_{n_1} - E_{0_1} + E_{n_2} - E_{0_2}} \quad (10)$$

where  $\mathbf{T} = \nabla \nabla (1/r)$ ,  $\mu$  is the dipole moment operator, and  $E_{n_i}$  is the  $n$ th excitation energy for molecule 1. From this expression of the dispersion energy we have derived a formula (see Appendix A) between a polarizability tensor sited at  $(0,0,z)$  and a dielectric medium as described in Figure 1.

$$E^{\text{disp}} = - \frac{(\epsilon_{\text{fast}} - 1)}{32(\epsilon_{\text{fast}} + 2)} E_{\text{die}} \sum_{\alpha}^3 \sum_i^{\text{atoms}} \frac{P_{i,\alpha\alpha}^{\text{disp}}}{r_i^3} \quad (11)$$

where  $P_{i,\alpha\alpha}^{\text{disp}}$  is the  $\alpha\alpha$  component of the polarizability tensor for atom  $i$  and  $\epsilon_{\text{fast}}$  is the dielectric constant in the high frequency region and  $E_{\text{die}}$  is the excitation energy for the dielectric medium.

**Exchange Repulsion Energy.** For the exchange repulsion a very simple form was used. It was assumed that exchange repulsion between an atom in a molecule and a portion of the dielectric media had a Lennard-Jones form ( $C/r^{12}$ ). Accordingly integration over the dielectric media gives a simple  $C/r^9$  expression between the atoms in the PAHs and the dielectric medium

$$E^{\text{rep}} = \sum_i^{\text{atoms}} \frac{c_i}{r^9} \quad (12)$$

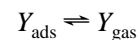
All carbon atoms have been assigned the same  $c_i$  ( $c_C$ ) and all hydrogens the same  $c_j$  ( $c_H$ ). The ratio between  $c_C$  and  $c_H$  is set to 50:1, which corresponds to 55% larger van der Waals radius for the carbon atoms than for the hydrogens.<sup>44</sup>

#### A MODEL FOR PREDICTING THE RETENTION INDEXES

The retention time is determined by the solutes adsorption to the liquid surface and to the solvation of the solutes in the liquid phase (assuming that all the solid surface area in the column is covered with liquid and that the solvated molecule does not interact with the solid support surface).<sup>45</sup> Recent experimental investigations by us have shown that for PAHs the retention is linear in the amount of liquid in the column, suggesting solvation being the dominating mechanism for the retention. In this work several solvation models have been tried, where the solvent have been treated as polarizable spheres. However the solvation models all failed to give good correlation. So therefore we turned our attention to adsorption models instead. It is noted that it is considerably more difficult to calculate accurate solvation energies than it is to calculate accurate adsorption energies. For instance in a solvation model one has to consider the

particular nature of the liquid, *e.g.*, the electrostatic problem could be solved exactly in an adsorption model with mirror charges, but this is not possible in a solvation model. A possible explanation for the failure of the solvation model will be discussed in the result section.

In the column there is an equilibrium between adsorbed molecules ( $Y_{\text{ads}}$ ) and molecules in the gas phase ( $Y_{\text{gas}}$ )



The column is divided into two parts, one bulk part ( $V_{\text{gas}}$ ) and one surface layer ( $V_{\text{ads}}$ ). The equilibrium constant at constant temperature is given by

$$K_e = \frac{(x_{\text{gas}}^Y/V_{\text{gas}})}{(x_{\text{ads}}^Y/V_{\text{ads}})} = \frac{x_{\text{gas}}^Y V_{\text{ads}}}{(1 - x_{\text{gas}}^Y) V_{\text{gas}}} \quad (13)$$

Thermodynamics gives the well-known relation

$$\Delta A = -k_b T \ln K_e \quad (14)$$

where  $A$  is the Helmholtz free energy and  $k_b$  is the Boltzmann constant. From these two relations one obtains

$$x_{\text{gas}}^Y = \frac{e^{-\Delta A/k_b T} V_{\text{gas}}}{V_{\text{ads}} + e^{-\Delta A/k_b T} V_{\text{gas}}} \quad (15)$$

The retention time for a substance is thus equal to

$$t_R = \frac{L}{x_{\text{gas}}^Y v_{\text{gas}}^Y} = \frac{t_0}{x_{\text{gas}}^Y} \quad (16)$$

where  $v_{\text{gas}}^Y$  is the velocity of the substance  $Y$  in the gas phase,  $L$  is the length of the column, and  $t_0$  is the retention time for the carrier gas. The retention index is defined as

$$\text{RI} = 100 \left( z + n \frac{\ln \left( \frac{t_R - t_0}{t_{R,z} - t_0} \right)}{\ln \left( \frac{t_{R,z+n} - t_0}{t_{R,z} - t_0} \right)} \right) = C_1 + C_2 \ln(t_R - t_0) = C_1' + C_2 \ln(1/x_{\text{gas}}^Y - 1) \quad (17)$$

where  $t_{R,z}$  is the retention time for a  $n$ -alkane with carbon number  $z$  and  $t_{R,z+n}$  is the retention time for a  $n$ -alkane with carbon number  $z + n$ . Accordingly the retention index can be described as a function of  $\Delta A$

$$\text{RI} = C_1' + C_2 \ln \left( \frac{[(V_{\text{ads}}/V_{\text{gas}}) + e^{-\Delta A/k_b T}]}{e^{-\Delta A/k_b T}} - 1 \right) \quad (18)$$

Most measurements of the retention indexes are performed with a temperature programmed gas chromatograph. Temperature programmed retention indexes are defined without the logarithm, thus

$$\text{RI} = C_1' + C_2 \left( \frac{[(V_{\text{ads}}/V_{\text{gas}}) + e^{-\Delta A/k_b T}]}{e^{-\Delta A/k_b T}} - 1 \right) = C_1'' + C_2 (V_{\text{ads}}/V_{\text{gas}}) e^{\Delta A/k_b T} \quad (19)$$

In our model we guess a reasonable temperature taking into consideration the temperature-programming performed (Test

calculations show that the predicted retention indexes are insensitive to the chosen temperature). For a particle in the canonical ensemble we may write

$$\Delta A(V, T) = A_{\text{gas}}(V_{\text{gas}}, T) - A_{\text{ads}}(V_{\text{ads}}, T) = k_b T [\ln Q_{\text{ads}}(V_{\text{ads}}, T) - \ln Q_{\text{gas}}(V_{\text{gas}}, T)] \quad (20)$$

where  $Q(V, T)$  is the partition functions described below. The interaction energy between a dielectric medium and a molecule is a function of the  $z$  coordinate of the center of gravity for the molecule and the two Euler angles  $\alpha$  and  $\beta$  of the molecule. The Euler angles are defined as in ref 46. A rotation of the third Euler angle  $\gamma$  does not affect the  $z$  coordinates of the atoms in the molecule, and, consequently, the interaction energy is independent of  $\gamma$ . In the model, the partition function for the adsorbed molecule is calculated as

$$Q_{\text{ads}}(V_{\text{ads}}, T) = 2\pi \int_0^Z dz \int_0^\pi d\beta \sin(\beta) \int_0^{2\pi} d\alpha e^{-E^{\text{tot}}(z, \alpha, \beta)/k_b T} = V_{\text{ads}} + 2\pi \int_0^Z dz \int_0^\pi d\beta \sin(\beta) \int_0^{2\pi} d\alpha (e^{-E^{\text{tot}}(z, \alpha, \beta)/k_b T} - 1) \quad (21)$$

where  $Z$  is so distant from the dielectric medium that the interaction energy between the molecule and the dielectric medium is approximately zero. For  $Y$  in the gas phase, the interaction energy is zero, and, accordingly the partition function is equal to

$$Q_{\text{gas}}(V_{\text{gas}}, T) = V_{\text{gas}} \quad (22)$$

Helmholtz free energy then becomes

$$\Delta A(V, T) = k_b T \ln \frac{V_{\text{ads}} + 2\pi \int_0^Z dz \int_0^\pi d\beta \sin(\beta) \int_0^{2\pi} d\alpha (e^{-E^{\text{tot}}(z, \alpha, \beta)/k_b T} - 1)}{V_{\text{gas}}} \quad (23)$$

The temperature dependent retention index could be written as

$$\text{RI} = C_1'' + C_2' \int_0^H dz \int_0^\pi d\beta \sin(\beta) \int_0^{2\pi} d\alpha (e^{-E^{\text{tot}}(z, \alpha, \beta)/k_b T} - 1) \quad (24)$$

where the integral is the second virial coefficient.

## CALCULATIONS

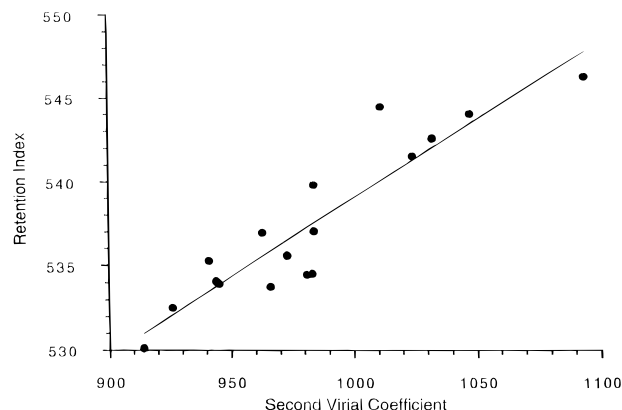
The geometry optimization of the PAHs was performed with the molecular mechanics program (MM2) in the MacMimic program package (InStar Software, Lund, Sweden). The optimized bond lengths for aromatic C–C bonds were between 1.38 and 1.46 Å, and for C–H bonds about 1.1 Å. Bond angles (C–C–C) were between 117.6° and 124.3°, and the H–C–C angles varied between 116.1° and 122.4°. The C–C–C angle in a five-membered ring varied between 104.6° and 135.7°. Three of the PAHs are nonplanar due to overlap of the van der Waals radius between hydrogen atoms of different rings. In this work we have focused on planar PAHs, although most PAHs are nonplanar.<sup>47</sup> Also when intuition suggest that PAHs are planar, usually they are not.<sup>47</sup> The MM2 geometries were used in the

calculation of the closed shell Hartree–Fock wave function with the direct SCF program implemented in MOLCAS-3 quantum chemical software.<sup>31</sup> As a compromise between accuracy and computational effort a small Dunning–Hay basis set<sup>48</sup> was used. For carbon atoms a primitive set of 9s5p1d was contracted to 4s2p1d, while for hydrogen atoms a primitive set of 4s1p was contracted to 2s1p. Test calculations on naphthalene and some PAHs were performed in order to deduce a reasonable partition of  $P_{\text{mol}, \beta \delta}^{\text{disp}}$  for the carbons and the hydrogens. All carbons in a molecule were given the same polarizability ( $P_{\text{mol}, \beta \delta}^{\text{C}}$ ), and similarly also all hydrogens in a molecule were given the same polarizability ( $P_{\text{mol}, \beta \delta}^{\text{H}}$ ).  $P_{\text{mol}, \beta \delta}^{\text{C}}/P_{\text{mol}, \beta \delta}^{\text{H}}$  was set to 2.6 except for the  $zz$  term which was set to 7.1. The liquid phase in the column was XTl-5, which is a derivative of silicon oil ((CH<sub>3</sub>)<sub>3</sub>SiOSi(CH<sub>3</sub>)<sub>3</sub>). We estimated  $\epsilon$  for the liquid phase from silicon oil,  $\epsilon_0 = 2.18$ ,  $\epsilon_{\text{high}} = 1.89$ .  $E_{\text{die}}$  in eq 11 was estimated to be 0.30 Hartree. The temperature was chosen to be 473 K. Numerical integration in the  $z$  direction is performed up to 21.2 Å ( $Z = 21.2$ ) away from the wall. The grid for the Euler angles is 5° up to 14 Å away from the wall and thereafter 10°. Calculations with smaller grids and larger  $Z$  were performed, but the accuracy of the predicted retention indexes did not increase significantly. The only parameter that was not determined is the exchange repulsion parameters. The ratio between these is fixed, but the magnitude is fitted.

## RESULTS AND DISCUSSION

In the theory section a model to calculate the interaction energy between a molecule and a dielectric medium was described. Here we will describe the results obtained when this model is used to predict the retention indexes for a set of 17 PAHs (14 of these were planar and the remaining three were nonplanar). Three different models are tested and discussed below. Finally a fit of PAHs with several different MWs will be performed. Before doing this, however, it is observed that there are at least four different physical processes responsible for the retention of the PAHs that can be identified. These are (i) adsorption of the molecule to the liquid–gas interphase, (ii) solvation of the molecule in the liquid, (iii) adsorption of the molecule to the liquid–solid interphase, and (iv) adsorption of the molecule to the gas–solid interphase. In this work the relative importance of the different processes will not be discussed. However it is noted that they all depend on the interaction between the molecule and another system. In this article it is assumed that interaction between the molecule and the solid support surface is negligible.

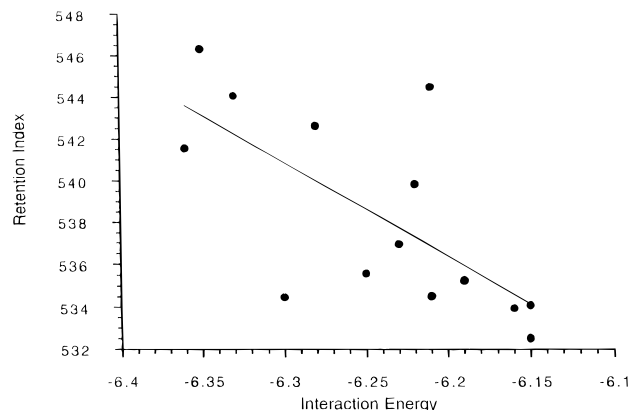
The proper way to evaluate the binding of a molecule to an interphase is to calculate the second virial coefficient. As was mentioned in the theory section the two parameters describing the repulsion between the wall and the molecule could not be determined from the first principle, and they were used as fitting parameters; however, in the prediction procedure, the ratio between the exchange repulsion parameters for carbon and hydrogen were kept fixed. Another problem is the balance between the electrostatic energy and the dispersion energy. Since the liquid phase is modeled as a dielectric medium, the quadrupole–quadrupole interactions will be excluded between the PAHs and the phenyl groups in the liquid phase. Further, in the model, many-body terms



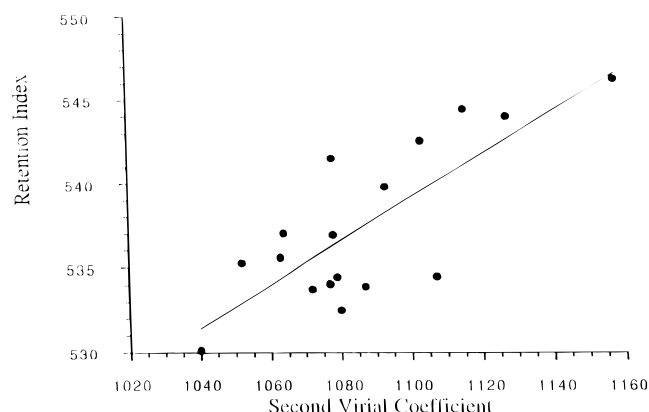
**Figure 2.** The second virial coefficient correlated to the experimental retention indexes for PAHs with MW 302. The correlation coefficient is 0.92. The equation of the straight line is  $RI = 444.73 + 0.009437 \cdot SVC$ .

in the dispersion is missing.<sup>49</sup> As will be described later, problems with the fitting of the nonplanar PAHs have led to the use of an artificially large distance between the liquid phase and the PAHs. Since the most important electrostatic term is the quadrupole–quadrupole interaction which decays as  $1/r^5$ , and since the dispersion term decays as  $1/r^3$  artificially large distances will favor the dispersion term. Given the reasons above it was decided to scale our dispersion term with a fitting factor  $X$ .  $X$  is fitted together with the repulsion parameters to give as high a correlation factor as possible for the retention indexes. The optimal value of  $X$  was found to be 0.3. The optimal values for the repulsion parameters were 0.745 au for the hydrogen atoms and 37.3 au for the carbon atoms. These values correspond to a maximum interaction energy of 3.5 kcal/mol between the studied PAHs and the dielectric medium. This is probably a large underestimation of the interaction energy, which is probably on the order of 15 kcal/mol. This will be discussed later in the text. In Figure 2 the experimentally determined retention indexes are plotted against the second virial coefficients. The correlation coefficient is 0.92.

A correlation coefficient of 0.92 indicates that the presented model is capable of picking up some essential features of the retention process. In order to understand what this may be, two other sets of calculations have been performed. If the exchange repulsion parameters are decreased until the minimum energy between the planar PAHs and the dielectric wall is 8 kcal/mol, the correlation coefficient for predicting the retention indexes decreases due to a poor fit of the three nonplanar PAHs. The reason for this behavior is that these three nonplanar PAHs will not have as attractive energy minima as the planar ones due to their nonplanarity and if the maximum interaction energy is large, the configurations with the largest attractive interaction energy will dominate the second virial coefficient. In the first of the above mentioned sets of calculations the 14 planar molecules were located in their optimal position relative to the dielectric wall, and the interaction energy was calculated (with  $X = 0.3$ ). The most favorable orientation was the configuration where the plane of the molecules was parallel to the surface of the medium approximately 2.0 Å from the dielectric medium. The obtained correlation is shown in Figure 3. The correlation coefficient is 0.69. If the three nonplanar PAHs had been included the correlation coefficient would have been even worse.



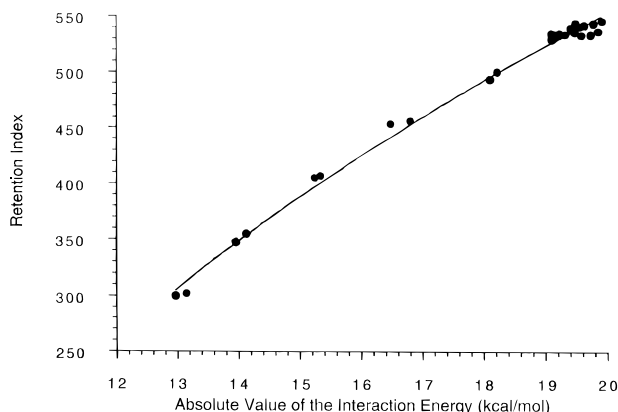
**Figure 3.** The maximal interaction energy between the 14 planar PAHs of MW 302 and the dielectric media correlated to the experimental retention indexes. The correlation coefficient is 0.69. The equation of the straight line is  $RI = 257.85 - 44.93 \cdot IE$ .



**Figure 4.** The second virial coefficient correlated to the experimental retention indexes for the PAHs with MW 302, when all the electrostatic moments for the PAHs are set to zero and all carbons in the PAHs are given the same polarizability and also all hydrogens in the PAHs are given the same polarizability, *i.e.*, the maximal interaction energy will be equal for all planar PAHs. The correlation coefficient is 0.79. The equation of the straight line is  $RI = 395.45 + 0.1307 \cdot SVC$ .

In another test calculation the electrostatic part of the interaction between the molecules and the medium was removed and identical values of the effective polarizability of carbon atoms in all molecules as well as of all hydrogen atoms in all molecules was assigned. This interaction potential mainly probes the importance of the shape of the molecules, since their maximum interaction with the medium, at least for the planar molecules, are the same. The correlation obtained by this approach is shown in Figure 4. The correlation coefficient is 0.79.

It is believed that this results partly explains why an adsorption model could correlate better than a solvation model in predicting retention indexes, even though the physical process in the column could be solvation. The high correlation coefficient (0.79) for the calculation described above indicates that the solvent could not penetrate into bay and fjord regions of the molecules. This result could explain the failure of the solvation model calculations since in this model the dielectric media would penetrate into bay and fjord regions of the molecules. It is also noted that the model is quite sensitive for errors in the polarizability. The molecule that is most difficult to correlate is benzo[*b*]perylene. If the polarizability of benzo[*b*]perylene is increased with 2%



**Figure 5.** The absolute value of the interaction energy (in kcal/mol) plotted against the experimental retention indexes for PAHs with six different MWs. The highest correlation coefficient was obtained when the retention indexes were correlated to the logarithm of the absolute value of the interaction energy. The correlation coefficient was equal to 0.998. The equation of the line is  $RI = -1168.5 + 1324.4 \cdot \ln[\text{abs(IE)}]$ .

keeping the polarizabilities for the other PAHs constant, then benzo[*b*]perylene will be on the fitted line given in Figure 2.

Finally a fit with six different MWs were performed. The 17 PAHs with MW 302 were fitted together with 10 PAHs of different MW [MW 178 (phenanthrene, anthracene), MW 202 (pyrene, fluoranthrene), MW 228 (chrysene, benz[*a*]-anthracene), MW 252 (benzo[*e*]pyrene, benzo[*a*]pyrene), and MW 276 (benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene)]. The difference in retention between PAH of different MW in a nonpolar column will be closely related to the difference in dispersion interaction between the PAH and the column. A problem with predicting retention indexes from temperature programmed gas chromatography is that the entropy and enthalpy of solvation will be a function of temperature leading to large difficulties in developing a model to predict retention indexes for substances with large differences in elution temperature. In the model for calculating the second virial coefficient described in the theory section it was assumed that the temperature is constant. The problem to develop a model that accounts for different elution temperature have led us to use a simpler model to predict retention indexes for PAHs with different MW. However, it must be emphasized that a fit with several different MWs will not include especially much information since an analytical chemist knows that the compounds will elute in the order of MWs. Therefore in the model used, the maximal interaction energy between the PAHs and the column was correlated to the retention indexes. The only parameter that was used as a fitting parameter was the repulsion parameter for carbons and hydrogens. However, the quotient between the two repulsion parameters was fixed precisely as in the fit with only PAHs with MW 302. The fitted optimal repulsion parameters were for carbon 80.95 and for hydrogen 1.62. The three nonplanar were made planar in the fit simply by setting the coordinate perpendicular to the plane to zero. In this fit the dispersion term was not scaled in relation to the electrostatic term. The obtained correlation coefficient was 0.991 if the retention indexes were fitted against the interaction energy and 0.998 if the retention indexes was fitted against the natural logarithm of the absolute value of the interaction energy (Figure 5).

## CONCLUSIONS

A new model for predicting gas-chromatography retention indexes is proposed. The difference between the proposed model and earlier models is that our model is based on the calculation of the interaction energy between the solute and the surface of the liquid phase in the column instead of as earlier models, where descriptors was used to predict retention indexes. A second virial coefficient was calculated for the solutes outside a planar dielectric wall and correlated to the experimental values of retention indexes for 17 PAHs with a molecular weight of 302. The obtained correlation coefficient is 0.92. A model where the solute is solvated in the liquid gave a considerably lower correlation coefficient than the adsorption model. This could be an indication of the existence of cavities in the liquid where the solute could reside. The number of cavities would probably be proportional to the amount of liquid phase in agreement with the experimental observation that the retention is proportional to the amount of liquid phase.

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## APPENDIX A

In a similar way to the dispersion interaction between two molecules we write the dispersion interaction between a molecule and one small sphere of the dielectric medium (assuming that only one characteristic excitation energy for the dielectric medium exists) as

$$E^{\text{disp}} = - \sum_{\alpha, \beta, \gamma, \delta} T_{\alpha\beta} T_{\gamma\delta} \sum_{n_{\text{die}} > 0} \frac{\langle 0 | \mu_{\text{die}, \alpha} | n_{\text{die}} \rangle \langle n_{\text{die}} | \mu_{\text{die}, \gamma} | 0 \rangle}{E_{n_{\text{mol}}} - E_{0_{\text{mol}}} + E_{\text{die}}} \sum_{n_{\text{mol}} > 0} \frac{\langle 0 | \mu_{\text{mol}, \beta} | n_{\text{mol}} \rangle \langle n_{\text{mol}} | \mu_{\text{mol}, \delta} | 0 \rangle}{E_{n_{\text{mol}}} - E_{0_{\text{mol}}} + E_{\text{die}}} \quad (25)$$

where  $\overline{E_{\text{die}}}$  is the characteristic excitation energy for the dielectric medium. The polarizability of a molecule could be written as

$$P_{\alpha\beta} = 2 \sum_{n > 0} \frac{\langle 0 | \mu_{\alpha} | n \rangle \langle n | \mu_{\beta} | 0 \rangle}{E_n - E_0} \quad (26)$$

For a small sphere of the dielectric medium  $P_{\alpha\beta}$  is given by

$$P_{\alpha\beta} = 2 \sum_{n > 0} \frac{\langle 0 | \mu_{\alpha} | n \rangle \langle n | \mu_{\beta} | 0 \rangle}{\overline{E_{\text{die}}}} \quad (27)$$

Accordingly we could write  $E^{\text{disp}}$  as

$$E^{\text{disp}} = -\frac{1}{2} \sum_{\alpha, \beta, \gamma, \delta} T_{\alpha\beta} T_{\gamma\delta} P_{\text{die}, \alpha\gamma} \overline{E_{\text{die}}} \\ \sum_{n_{\text{mol}} > 0} \frac{\langle 0 | \mu_{\text{mol}, \beta} | n_{\text{mol}} \rangle \langle n_{\text{mol}} | \mu_{\text{mol}, \delta} | 0 \rangle}{E_{n_{\text{mol}}} - E_{0_{\text{mol}}} + E_{\text{die}}} = \\ -\frac{1}{4} \sum_{\alpha, \beta, \gamma, \delta} T_{\alpha\beta} T_{\gamma\delta} P_{\text{die}, \alpha\gamma} \overline{E_{\text{die}}} P_{\text{mol}, \beta\delta}^{\text{disp}} \quad (28)$$

where we have defined  $P_{\text{mol}, \beta\delta}^{\text{disp}}$  as

$$P_{\text{mol}, \beta\delta}^{\text{disp}} = 2 \sum_{n_{\text{mol}} > 0} \frac{\langle 0 | \mu_{\text{mol}, \beta} | n_{\text{mol}} \rangle \langle n_{\text{mol}} | \mu_{\text{mol}, \delta} | 0 \rangle}{E_{n_{\text{mol}}} - E_{0_{\text{mol}}} + E_{\text{die}}} \quad (29)$$

The term  $P_{\text{mol}, \beta\delta}^{\text{disp}}$  is calculated (using SCF orbitals for the molecule) and partitioned out to the atoms. The extension of the dielectric medium is given in figure 1. With this extension of the dielectric media we multiply  $P_{\text{atom}, xz}^{\text{disp}}$ ,  $P_{\text{atom}, yz}^{\text{disp}}$ ,  $P_{\text{atom}, xz}^{\text{disp}}$ , and  $P_{\text{atom}, zy}^{\text{disp}}$  with 2 and  $P_{\text{atom}, zz}^{\text{disp}}$  with 4. The reason for this multiplication is given by the following argument. The fluctuating field outside the dielectric media could be described with a distribution function that is Gaussian<sup>50</sup>

$$X(f_x f_y f_z) = K e^{-c(f_x^2 + f_y^2 + 0.5f_z^2)} df_x df_y df_z \quad (30)$$

We perform the substitution  $f'_z = \sqrt{2}f_z$  which gives

$$X'(f_x f_y f'_z) = \frac{K}{\sqrt{2}} e^{-c(f_x^2 + f_y^2 + (f'_z)^2)} f_x df_y df'_z \quad (31)$$

The dispersion interaction between the electric media and an atom should be independent of which distribution function we use. The dispersion interaction will be

$$E^{\text{disp}} = -0.5 \vec{E} P \vec{E} = -0.5 \vec{E}' P' \vec{E}' \quad (32)$$

and accordingly

$$P'_{\alpha\beta} = P_{\alpha\beta} [1 + \delta_{\alpha z}] [1 + \delta_{\beta z}] \quad (33)$$

$P_{\text{mol}}^{\text{disp}}$  is thereafter diagonalized. If we change the polarizability tensor for the dielectric media to a spherical polarizability we will get

$$E^{\text{disp}} = -\frac{1}{4} P_{\text{die}} \overline{E_{\text{die}}} \sum_{\alpha} \sum_i^{\text{atoms}} \frac{P_{i, \alpha\alpha}^{\text{disp}}}{r_i^6} \quad (34)$$

The polarizability of the dielectric media is related to its dielectric constant through Clausius–Mossotti equation<sup>51</sup>

$$P_{\text{die}} = \frac{3(\epsilon_{\text{fast}} - 1)}{4N\pi(\epsilon_{\text{fast}} + 2)} \quad (35)$$

where  $N$  is the number density. Since the radiation is in the high frequency region Clausius–Mossotti equation should be accurate. In the high frequency region the dielectric constant is related to refraction index through the Maxwell relation

$$\epsilon_{\text{fast}} = n^2 \quad (36)$$

$E^{\text{disp}}$  is calculated between a point in the dielectric and a molecule. To calculate the total  $E^{\text{disp}}$  one has to perform an integration over the dielectric medium. Integration gives that  $E^{\text{disp}}$  is given by

$$E^{\text{disp}} = -\frac{(\epsilon_{\text{fast}} - 1)}{32(\epsilon_{\text{fast}} + 2)} \overline{E_{\text{die}}} \sum_{\alpha} \sum_i^{\text{atoms}} \frac{P_{i, \alpha\alpha}^{\text{disp}}}{r_i^3} \quad (37)$$

where  $r_i$  is the distance between atom  $i$  and the dielectric medium.

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