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Solvation parameter model of comprehensive two-dimensional gas chromatography separations

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ABSTRACT

A solvation parameter model was used to generate comprehensive two-dimensional gas chromatography (GC × GC) retention diagrams for 54 solutes on four different stationary phase combinations. Retention diagrams are plots used to predict the relative position of solutes in GC × GC chromatograms. In this study, retention diagrams were based entirely on solute and stationary phase descriptors taken from the literature. The temperature-averaged values of the stationary phase descriptors were used to further simplify the model. The relative positions of the solutes in the retention diagrams were compared with experimentally obtained GC × GC chromatograms. Excellent agreement was observed for each column combination. The model was found to generate primary retention time predictions with standard errors that were approximately 1% of the range of the experimental values and secondary retention time predictions with standard errors that were approximately 5% of the range of the experimental values. It is concluded that the GC × GC solvation parameter model is sufficiently accurate to aid in the identification of optimal column combinations.

1. Introduction

Several research groups have developed models for predicting two-dimensional gas chromatography (GC × GC) retention times from single-column GC data [1–3]. These models have used solute retention indices or retention factors measured directly on the primary and secondary stationary phases as input data. The indices are combined with fluid mechanical calculations to produce GC × GC retention time predictions. Marriott and co-workers [4–7] have developed a related approach that maps GC × GC retention times to single-column retention indices.

We recently introduced a simple model [8] that converts single-column retention times (like those found in vendor catalogs) into retention indices. The retention indices are then combined to produce a retention diagram. Retention diagrams are a plot of the primary retention index I_1 along the horizontal axis and a constant near 1.6 rose to a power of ΔI (i.e., $1.6^{\Delta I}$) on the vertical axis where ΔI is the difference of the primary and secondary retention indices ($\Delta I = I_2 - I_1$). In this case, retention indices are defined to increase by 1.0 with the addition of a methylene group (as opposed to the increase of 100 used by Kovats retention indices). The main benefit of the retention diagram approach is that it provides a fairly accurate estimate of the *relative* positions of peaks within a GC × GC chromatogram without requiring the generation of specialized retention data (i.e., $\log k$ vs. $1/T$ plots, or temperature-dependent Kovats retention indices). Unfortunately, the retention diagram approach still requires the existence of retention data for each solute on both stationary phases.

Over the past 20 years, Abraham et al. [9,10] have developed a simple model for predicting retention factors for single-column, isothermal gas chromatography separations. Their model, when applied to GC stationary phases, employs a linear combination of 5 constants describing each solute and 6 constants describing the stationary phase. This model is most commonly represented as

$$\log k = lL + sS + aA + bB + eE + c \qquad (1)$$

where k is the retention factor of a solute; the parameters l, s, a, b, e, and c are system constants that characterize the selectivity of the stationary phase; and the parameters L, S, A, B, and E are solvation descriptors for the solute. A key benefit of this model is that each descriptor has physical meaning: L is related to solute size; S is related to solute dipolarity/polarizability; A is related to the hydrogen bond acidity of the solute; B is related to the hydrogen bond basicity of the solute; and E is the excess polarizability of the solute.

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Solute descriptors are determined through chromatographic measurements on a small set of stationary phases or theoretically predicted from molecular structure [11]. Stationary phase system constants are determined by monitoring the retention of a small set of probe solutes. Solute descriptors have been reported for nearly 4000 analytes [9] and system constants have been determined for nearly all types of commercially available GC stationary phases [12]. Poole and Poole recently revised the system constants for 50 modern capillary stationary phases and the solute descriptors for 112 organic compounds [13]. The revised values were shown to generate $\log k$ values that were 2.5 times more accurate than predictions based on the original descriptors. An advantage of using this solvation parameter model is that the retention of a specified solute on a particular stationary phase can be predicted without needing prior direct retention measurements of the solute on the stationary phase. This makes it possible to rapidly predict solute retention on numerous stationary phases without requiring an enormous database of retention information.

Arey et al. have previously used a solvation parameter model to relate GC × GC peak positions of petroleum hydrocarbons to their volatilities and aqueous solubilities [14]. Poole and Poole [15] have recently used the stationary phase system constants to identify column combinations that provide the greatest contrast in retention mechanisms. This article focuses on the use of a solvation parameter model to predict primary and secondary retention indices. These indices are then used to generate retention diagrams. The retention diagrams are compared with experimentally obtained GC × GC chromatograms. This approach is advantageous because it allows the relative retention of solutes to be predicted for numerous column combinations without requiring the availability of single-column retention indices.

2. Description of model

2.1. Calculating retention indices from solvation parameter

The solvation parameter model is normally used to calculate retention factors [12]. However, *retention indices* are required for the generation of GC × GC retention diagrams. Fortunately, the solvation parameter model can be transformed algebraically to an expression that directly calculates retention indices. This transformed equation (Eq. (2)) uses the original solute and stationary phase descriptors to generate a new set of solute descriptors labeled with primes (L', S', A', B', E') and a new set of stationary phase descriptors (s', a', b', and e')

$$I = L' + s'S' + a'A' + b'B' + e'E' \tag{2}$$

This modified form of the solvation parameter model is derived below.

2.2. Derivation of transformed solvation parameter equation

GC × GC retention diagrams require retention indices for both the primary and secondary stationary phases. It is convenient to define the retention indices relative to the isothermal retention of n-alkanes. Using such an approach, the retention indices are defined according to

$$I = \frac{I(\text{Kovats})}{100} = \frac{(\log k - \log k_n)}{(\log k_{n+1} - \log k_n)} + n \tag{3}$$

where I is the retention index, k is the retention factor for the solute, n is the number of carbon atoms for the largest n-alkane that has a retention factor smaller than k, k_n is the retention factor for the n-alkane with n carbon atoms, and k_{n+1} is the retention factor of the n-alkane with $n+1$ carbon atoms. This definition is identical to that developed by Kovats [16] with the exception that the retention indices increase by 1.00 with the addition of a methylene group to an n-alkane (as opposed to the Kovats-defined increase of 100).

The values of $\log k$, $\log k_n$, and $\log k_{n+1}$ can all be estimated from the solvation parameter model (Eq. (1)). The values of $\log k_n$ and $\log k_{n+1}$ are particularly simple as the values of S, A, B, and E for n-alkanes are by definition equal to zero. Thus, $\log k_n$ simplifies to

$$\log k_n = lL_n + c \tag{4}$$

where L_n is the solute size descriptor for the alkane with n carbon atoms. The values of L_n for the n-alkanes tabulated by Poole and Poole [13] are linearly dependent on n. A least squares fit of L_n plotted as a function of n for C_8–C_{13} generates a slope of 0.493, an intercept of −0.244, and an $R^2 = 0.9998$. This linear relationship can be substituted into Eq. (4) to generate

$$\log k_n = l(0.493n - 0.244) + c \tag{5}$$

$$\log k_{n+1} = l[0.493(n+1) - 0.244] + c \tag{6}$$

Eqs. (1), (5), and (6) can be substituted into Eq. (3) to generate

$$I = \frac{lL + sS + aA + bB + eE - l(0.493n - 0.244)}{0.493l} + n \tag{7}$$

This equation can be factored into solute terms and stationary phase terms

$$I = \left(\frac{L + 0.244}{0.493}\right) + \left(\frac{s}{l}\right)\left(\frac{S}{0.493}\right) + \left(\frac{a}{l}\right)\left(\frac{A}{0.493}\right) + \left(\frac{b}{l}\right)\left(\frac{B}{0.493}\right) + \left(\frac{e}{l}\right)\left(\frac{E}{0.493}\right) \tag{8}$$

Each quantity in parentheses can be defined as the following new solvation parameters

$$L' = \left(\frac{L + 0.244}{0.493}\right) \quad S' = \left(\frac{S}{0.493}\right) \quad A' = \left(\frac{A}{0.493}\right)$$

$$B' = \left(\frac{B}{0.493}\right) \quad E' = \left(\frac{E}{0.493}\right)$$

$$s' = \left(\frac{s}{l}\right) \quad a' = \left(\frac{a}{l}\right) \quad b' = \left(\frac{b}{l}\right) \quad e' = \left(\frac{e}{l}\right)$$

These parameters are combined to generate predictions of retention indices as shown in Eq. (2).

A GC × GC retention diagram is a plot of the primary column retention index I_1 on the horizontal axis and $1.6^{\Delta I}$ on the vertical axis where ΔI is the difference in the secondary and primary retention indices (i.e., $\Delta I = I_2 - I_1$) [8]. In terms of the solvation parameter model, the primary retention index is given by

$$I_1 = L' + s'_1S' + a'_1A' + b'_1B' + e'_1E' \tag{9}$$

where s'_1, a'_1, b'_1, and e'_1 are the system constants on the primary stationary phase. The difference in the retention indices is given by

$$\Delta I = I_2 - I_1 = \Delta s'S' + \Delta a'A' + \Delta b'B' + \Delta e'E' \tag{10}$$

where $\Delta s' = s'_2 - s'_1$, $\Delta a' = a'_2 - a'_1$, $\Delta b' = b'_2 - b'_1$, and $\Delta e' = e'_2 - e'_1$. A key result from this derivation is that the vertical position of each solute within the retention diagram is independent of L', that is, the value of $1.6^{\Delta I}$ only depends on the polarity descriptors of the solute (S', A', B', and E') and the difference in the polar selectivities of the primary and secondary stationary phases.

The preceding derivation included terms involving the hydrogen bond basicity of the solutes and the corresponding hydrogen bond acidity of the stationary phase (e.g., B, b, B', b', $\Delta b'$, etc.). It is important to note that most commercially produced capillary columns