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Journal of Chromatography A, 715 (1995) 267–278

JOURNAL OF CHROMATOGRAPHY A

Derivation of solubility parameters of chlorinated dibenzofurans and dibenzo[*p*]dioxins from gas chromatographic retention parameters via SOFA

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First received 24 March 1995; revised manuscript received 24 May 1995; accepted 24 May 1995

Abstract

Molar heat of vaporization, molar liquid volume and Scatchard–Hildebrand solubility parameters of chlorinated dibenzofurans (PCDFs) and dibenzo[*p*]dioxins (PCDDs) were derived from (semi-)empirical values of heat of vaporization, (subcooled) liquid density and gas chromatographic Kovats retention indices. To this end a thermodynamic prediction model (SOFA), recently developed, was extended by an exchange entropy contribution representing molecular orientational disorder. The parameters derived were validated using experimental values of relative retention times on stationary phases of different polarities.

Accurate to extremely accurate results were obtained with standard errors of regression close to experimental inaccuracy and high correlation coefficients comparing favourably to existing methods of prediction. The parameters derived performed quite well for apolar to moderately polar stationary phases. For polar phases inaccuracy increased significantly. The method has several advantages compared to other methods used for the prediction of chromatographic retention.

1. Introduction

Due to their high accuracy, rapid obtainability, versatility and to the low amounts of substances required, chromatographic retention parameters are being used for the determination and estimation of partition constants and other physico-chemical properties of organic compounds. The pertinents methods may be suited to individual compounds and, as often occurs in environmental chemistry, to series of structurally related or congeneric compounds. A basic requirement is a theoretical model connecting the chromatographic retention parameter to the partition constant. In its most simple form this model may be a monolinear Collander-type regression relationship as used for the determination of the partition coefficient between *n*-octanol and water (K_{ow}) and the HPLC reverse-d-phase capacity factor (k') for series of compounds [1].

In order to obtain a more accurate and general relationship we have recently proposed the SOFA (solubility parameters for fate analysis) thermodynamic model [2]. This model has proved capable to accurately predict K_{ow}, Kovats

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SSDI 0021-9673(95)00623-0

GC retention indices (I) on different columns, (subcooled) liquid vapour pressure (P), aqueous solubility (S_w), Henry's law constant (H) and k' of methylchlorobenzenes. Predictions were isomer specific. Chromatographic retention parameters were predicted at a level of accuracy that compared favourably to experimental accuracy. In the SOFA model, which will be summarized in the Method section, the first step is the derivation of the compound's key descriptors, i.e. its heat of vaporization (ΔH/cal mol^{-1}), molar liquid volume (V/cm^3 mol^{-1}) and calculated from these: its Scatchard–Hildebrand solubility parameter [δ/(cal cm^{-3})$^{1/2}$] [3]. The latter is an energy density of the liquid defined by ΔH, V, gas constant (R/cal mol^{-1} K^{-1}) and absolute temperature (T/K):

$$\delta = [(\Delta H - RT)/V]^{1/2} \quad (1)$$

For the derivation of key descriptors accurate experimental data of descriptors, chromatographic retention parameters or other partition constants have to be used. Once the key descriptors have been derived they can be applied to the prediction of in principle all other partition properties.

Here we derive the key descriptors of the environmentally relevant compound series of the polychlorinated dibenzofurans (PCDFs) and dibenzo[p]dioxins (PCDDs) in order to use them elsewhere for the prediction of partition constants such as bioconcentration factors and sediment sorption constants [4]. Simultaneously we would like to find out the model's potential to accurately predict GC retention of these compounds on stationary phases of varying polarity. To this end it turns out to be necessary to extend the SOFA model by the inclusion of a novel molecular orientational disorder entropy contribution. For the derivation of key descriptors we use Kovats retention indices (I) determined by Hale et al. [5] and Donnelly et al. [6] on apolar DB5 columns. The model is validated using relative retention times (RRT) determined by Ryan et al. [7] on columns of different polarity. The predictions are compared with the results obtained by other methods [6,8–12].

2. Method

2.1. The SOFA model equations of I and RRT

SOFA enables a consistent prediction of all types of partition constants, including chromatographic retention parameters [2]. The mixing process of a solute, i, in a solvent (stationary phase), s, is modelled as an exchange of molecules in similar lattices filled with just solute or solvent molecules. If solute and solvent molecules have approximately identical shapes and dimensions, only one lattice can describe liquid solute, solvent and solution. An exchange enthalpy contribution can be understood as the result of the energy gain from the formation of solute–solvent interactions and the energy loss from breaking solute–solute and solvent–solvent interactions. An exchange entropy contribution, deviating from the random-mixing ideal-solution expression, may result especially when strong solute–solvent interactions are present, which limit the number of accessible lattice configurations. If solute and solvent molecules are markedly dissimilar, a combinatorial entropy contribution may arise from the extra lattice space in solution available for the smaller molecule compared with the space in a lattice filled with just small molecules. Based on this model an expression can be derived for the logarithm of the activity coefficient of the solute in the solvent at infinite dilution: $\ln \gamma_{i,s} = H^{ex}_{i,s} + S^{ex}_{i,,s} + S^{co}_{i,s}$ (see Ref. [2] for details). In this expression i stands for the solute and s for the stationary phase or solvent. The exchange enthalpy contribution is $H^{ex}_{i,s} = V_i[\delta_i^2 + \delta_s^2 - 2\delta_i\delta_s c_{1,I,s}(c_{2,I,s}\delta_s + \delta_i)/(\delta_s + c_{2,I,s}\delta_i)]/RT$. Constants $c_{1,I,s}$ and $c_{2,I,s}$ occur in this contribution, which are characteristic for the class of compound, here denoted by I, and the solvent. The exchange entropy contribution reads $S^{ex}_{i,s} = X_{I,s} + c_{3,I,s} \ln A_i$, where $X_{I,s}$ represents the class-solvent specific effect of molecular substitutional disorder and $c_{3,I,s}$ that of orientational disorder. The latter implies an extension of an expression presented before [2]. The descriptor, A_i, stands for the maximum number of orientations a solute molecule can take at a lattice point [13]. In solution the maximum

number will be reduced by molecular interaction, represented by $c_{3,I,s}$. The combinatorial entropy contribution, $S^{co}_{i,s} = \ln(V_i/V_s) - V_i/V_s + 1$.

In addition the SOFA model relates the vapour pressure, P_i, of the solute with its heat of vaporization: $\ln P_i = a_I - b_I \Delta H_i/RT$ (see Ref. [2] for details), where a_I is a class-specific constant for the entropy of vaporization and b_I for the contribution of ΔH_i. Finally, we remark that numerical values of a, b, c and X constants have to be derived by fitting to experimental data as described in sections below.

In this way a model equation for ln RRT is obtained from the specific retention volume, V_g, of congener i and the reference compound (r), where $V_{g,i}$ is a function of the congener's vapour pressure, its activity coefficient and the molecular mass of the stationary phase (M_s) [14]. After substitution of our model expression for the vapor pressure and activity coefficient one obtains:

$$\begin{aligned}\ln \mathrm{RRT}_{i,s} &= \ln V_{g,i,s} - \ln V_{g,r,s} \\ &= -\ln P_i - \ln \gamma_{i,s} + \ln(298.12R/M_s) \\ &\quad -\ln V_{g,r,s} = b_I \Delta \mathrm{H}_i \\ &\quad -V_i\left[\delta_i^2 + \delta_s^2 - 2\delta_i\delta_s c_{1,I,s}(c_{2,I,s}\delta_s + \delta_i)\right. \\ &\quad \left./(\delta_s + c_{2,I,s}\delta_i)\right]/RT \\ &\quad -a_{0,I} - a_{1,I}(T - 298.15) \\ &\quad - a_{2,I}(T - 298.15)^2 - X_{I,s} - c_{3,I,s}\ln A_i \\ &\quad -\ln(V_i/V_s) + V_i/V_s \\ &\quad +\ln(298.15R/M_s) - \ln V_{g,r,s} \end{aligned} \tag{2}$$

In Eq. 2 the entropy contribution to the vapour pressure (a_I) is approximated by a second order polynomial function of temperature, as we would like to obtain an accurate expression for the temperature dependence of RRT. This temperature dependence further requires the knowledge of the temperature at which a certain congener, i, is eluted during a linearly programmed gas chromatographic run. This temperature, T, is calculated from the boiling point temperatures, T_{bp}, of the pertinent (i), the first (b) and last (e) eluting congeners, and the elution temperatures of b and e according to Eq. 3:

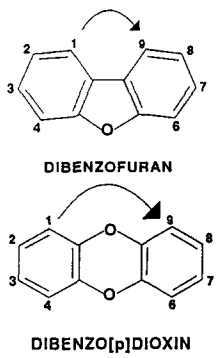
$$T = T_b + (T_e - T_b)(T_{bp,i} - T_{bp,b})/(T_{bp,e} - T_{bp,b}) \tag{3}$$

The elution temperatures T_b and T_e can be inferred from experimental data and the boiling points are estimated from the heat of vaporization (at 298.15 K) by the inverse of the semi-empirical Hildebrand rule [15]:

$$\Delta H = -2950 + 23.7T_{bp} + 0.02T_{bp}^2 \tag{4}$$

In a similar way a model equation, Eq. 5, is obtained for Kovats retention index $I_{i,s}$ from the activity coefficients $\gamma_{i,s}$, $\gamma_{z,s}$, $\gamma_{z+1,s}$ and vapour pressures P_i, P_z, P_{z+1} of the solute, i, and the n-alkanes with z or $z+1$ carbon atoms eluting just before and after i, respectively (see Ref. [2], Eq. 13). In this equation the entropy of vaporization constants a_I and a_Z, with Z denoting the class of n-alkanes, were considered to be independent of temperature. $\Delta X_{I,Z,s}$ represents a difference of substitutional exchange entropy effects between the classes I and Z. Eq. 5 holds for an isothermal chromatographic run. In case of a linearly programmed run the mean temperature can be taken as an approximation.

$$\begin{aligned} I_{i,s} - 100z &= \{b_I\Delta H_i/RT - b_Z\Delta H_z/RT \\ &\quad - V_i\left[\delta_i^2 + \delta_s^2 - 2\delta_i\delta_s c_{1,I,s}(c_{2,I,s}\delta_s\right. \\ &\quad \left.+ \delta_i)/(\delta_s + c_{2,I,s}\delta_i)\right]/RT + V_z\left[\delta_z^2 + \delta_s^2\right. \\ &\quad \left.- 2\delta_z\delta_s c_{1,Z,s}(c_{2,Z,s}\delta_s + \delta_z)/(\delta_s\right. \\ &\quad \left.+ c_{2,Z,s}\delta_z)\right]/RT - a_I + a_Z - \Delta X_{I,Z,s} \\ &\quad - c_{3,I,s}\ln A_i + c_{3,Z,s}\ln A_z \\ &\quad - \ln(V_i/V_z) + (V_i - V_z)/V_s\} \\ &\quad \cdot 100/\{b_Z(\Delta H_{z+1} - \Delta H_z)/RT \\ &\quad - V_{z+1}\left[\delta_{z+1}^2 + \delta_s^2\right. \\ &\quad \left.- 2\delta_{z+1}\delta_s c_{1,Z,s}(c_{2,Z,s}\delta_s + \delta_{z+1})/(\delta_s\right. \\ &\quad \left.+ c_{2,Z,s}\delta_{z+1})\right]/RT + V_z\left[\delta_z^2 + \delta_s^2\right. \\ &\quad \left.- 2\delta_z\delta_s c_{1,Z,s}(c_{2,Z,s}\delta_s + \delta_z)/(\delta_s\right. \\ &\quad \left.+ c_{2,Z,s}\delta_z)\right]/RT - c_{3,Z,s}(\ln A_{z+1} \\ &\quad - \ln A_z) - \ln(V_{z+1}/V_z) + (V_{z+1} \\ &\quad - V_z)/V_s\} \end{aligned} \tag{5}$$



r	Inter-ring Cl-Cl interactions DD	DF
1	19,46	
2		19
3		46
4	18,29,36,47	36,47
5		18,29
6	17,39,26,48	17,39,26,48
7	16,49	16,49
8	28,37	28,37
9	27,38	27,38

Fig. 1. Skeleton structures of dibenzofuran (DF) and dibenzo[*p*]dioxin (DD). Skeleton numbers denote the positions of chlorine atoms. The inter-ring (r = 1–9) chlorine–chlorine interactions are denoted by the corresponding skeleton number pairs. If several pairs occur in an entry, e.g. entry 6 under heading DD and DF, it is meant that these pairs obtain equal x values in Eq. 6. As shown for interactions r = 1 (DD) and r = 2 (DF) between atoms 1 and 9, the pair interactions may differ for DD and DF.

2.2. Fragment parameters for ΔH, V and A

ΔH, V and A are descriptors for pure solutes or solvents. For solutes, ΔH_i and V_i ($=x$) are calculated in an extended fragment model. It includes the contribution of the parent compound ($x0_{DF,DD}$), dibenzofuran or dibenzo[*p*-]dioxin, the contribution of Cl atoms (xCl), of interactions between Cl atoms positioned *ortho* (o), *meta* (m) and *para* (p) to each other in the same ring ($x\mathrm{ClCl}_{o,m,p}$), between Cl atoms *ortho*, *meta* or *para* to the central CC bond in dibenzofuran ($x\mathrm{ClC}_{o,m,p}$), between Cl atoms *ortho*, *meta* or *para* to a central O atom ($x\mathrm{ClO}_{o,m,p}$) and between Cl atoms on different rings ($x\mathrm{ClCl}_r$). The latter (nine) interactions are defined in Fig. 1. By counting the number of times (nCl, $n\mathrm{ClCl}_{o,m,p}$ . . . . .) a certain interaction occurs within a congener molecule all 136 PCDFs and 76 PCDDs can be identified uniquely. In Table 2 the values for the identifiers of octachloro-DF/DD are included as an example.

The total value of ΔH_i or V_i is obtained by summation of the foregoing contributions multiplied by the number of times they occur in the molecule:

$$x = x0 + n\mathrm{Cl} \cdot x\mathrm{Cl} + \ldots\ldots + n\mathrm{ClCl}_9 \cdot x\mathrm{ClCl}_9 \quad (6)$$

As shown in Eq. 1, δ_i can be calculated directly from V_i, ΔH_i and RT. As shown in Table 1, for the stationary chromatographic phases estimated values of V_s and δ_s can be obtained from experimental values. The ΔH_z and V_z values of n-alkanes and the temperature dependencies of ΔH and V are approximated by simple empirical relationships as applied before [2].

A_i, the maximum number of molecular (congener) orientations at a lattice point, is approximated by the number of ways the C, H, O or Cl atoms in the molecule can be permutated in the molecular skeleton (n denotes the number of atoms):

$$A_i = [n\mathrm{C} + n\mathrm{H} + n\mathrm{O} + n\mathrm{Cl}]!/[n\mathrm{C}!n\mathrm{H}!n\mathrm{O}!n\mathrm{Cl}!] \quad (7)$$

Table 1
Molar liquid volume (V) and solubility parameter (δ) of gas chromatographic stationary phases at 298.15 K

Liquid phase (-silicone)[a]	V[b] ($\mathrm{cm^3\ mol^{-1}}$)	δ[c] [$(\mathrm{cal\ cm^{-3}})^{1/2}$]
DB1 (100% dimethyl-)	98.49	6.18
DB5 (5% phenyl-, 95% dimethyl-)	100.67	6.27
DB17 (50% phenyl-, 50% methyl-)	120.25	7.15
DB225 (50% methylcyanopropyl, 50% methylphenyl-)	139.00	8.34

[a] Composition taken from column supplier catalogues. V and ΔH values of mixed phases were estimated from the percentage contributions of the V and ΔH values of the single component phases.
[b] Estimated from liquid densities of corresponding silanes, obtained from Ref. [16].
[c] Calculated according to Eq. 1 from V and ΔH values estimated by Eq. 4 from boiling point temperatures of corresponding silanes, obtained from Ref. [16].

This approximation is equivalent to the assumption that the number of orientations is proportional to the number of configurations of a mixture of free atoms at the lattice site. Note that, in addition to Eq. 6, Eq. 7 introduces systematic differences between PCDFs (nO = 1) and PCDDs (nO = 2). Moreover, A_i displays a maximum for PCDD/F at nCl = 4, whereas no maximum is found for A_z of n-alkanes with increasing nC = z.

2.3. Derivation of parameters

In order to derive x fragment parameters, Eqs. 5 and 6 have to be applied in a (non-)linear multiple regression and multi-response fit of the pertinent constants to experimental data of $I_{i,s}$, ΔH_i and V_i. The x fragment starting values have to be derived using Eq. 6 in a multilinear fit to experimental data or from fragment values obtained from previous calculations. Starting values for ΔX and c constants have to be obtained from theoretical considerations or from previous results. X starting values, e.g., correspond to Flory–Huggins contributions of ± 0.3, $c_1 = c_2 = 1$ holds for a simple Scatchard–Hildebrand solubility parameter model and c_3 has to be in the range of -1 to $+1$. Starting values of a and b constants may be obtained from experimental P_i and ΔH_i data or from previous results. If the starting values of the x fragment parameters are sufficiently close to their final values, these parameters can be fitted simultaneously with the ΔX, a, b and c constants.

2.4. Validation of the method

Once the x fragment parameters have been obtained, they can be used in Eq. 2 in order to calculate ln $RRT_{i,s}$ values. To this end the X, a, b and c parameters of this equation have to be fitted by a nonlinear regression procedure to experimental data of ln $RRT_{i,s}$. (Starting) values of b and c constants can be taken from the foregoing x parameter derivation, whereas starting values of $a_{1,I}$, $a_{2,I}$ and $a_{0,I}$ $[+\ln(298.15R/M_s) - \ln V_{g,r}]$ have to be found by trial and error. This type of calculation implies a validation of the x parameters derived and the model equations.

2.5. Statistics

All multilinear regression calculations were carried out by the MLINREG procedure of the STATPAK program (North-West Analytical, Portland, OR, USA). All nonlinear multiple, multiresponse, regression calculations were carried out by the SOFA program, developed previously [2]. This program is based on Simplex optimization with weighing of each type of property (t) by a factor of w_t, which is assumed to be inversely proportional to some measure for the experimental error (e_t). Using a pseudolinear approximation, the 95% confidence limits of the derived x parameters and constants can be calculated. The additional statistical data are the mean deviation $\langle \sigma_t \rangle$ of calculated from the N_t experimental values for each type of property, the corresponding correlation coefficient (r_t), not corrected for the number of parameters. All calculations can be carried out on a personal computer (minimum speed equivalent to a 486 Intel microprocessor with mathematical coprocessor).

2.6. Numerical example

A numerical example of the calculation of I of OCDF (after derivation of x parameters and a, b, c, X constants) is given in the Appendix.

3. Results

3.1. Derivation of x parameters

The x parameter derivation was performed using experimental values of heats of vaporization ($N_t = 16$), molar volumes ($N_t = 11$) (see Table 3), Kovats retention indices of PCDFs at a mean temperature of 510.65 K ($N_t = 115$) [5] and of PCDDs at a mean temperature of 528.15 K ($N_t = 41$) [6], both determined on a DB5 column with characteristics given in Table 1. Weights (w_t) were derived from various measures for

experimental inaccuracies and uncertainties (e_t) as reported in the literature. The latter were also reported for I ($e = 7$) by Robbat and Kalogeropoulos [9]. The results of this derivation are summarized in Tables 2, 3 and 4.

Table 2 shows the x parameters derived and their 95% confidence limits. It can be seen that all 42 parameters, except for h_{ClClo}, h_{ClOm}, v_{ClCo} and v_{ClCl2}, are statistically significant, in spite of their large number. With the help of Eqs. 6 and 1 all 212 ΔH, V and δ values were calculated. Some results are included in Table 3 together with their deviation of (semi-)empirical data and other statistics. Inaccuracies in calculations turn out to be equal to or less than experimental inaccuracies. The differences between PCDF and PCDD congeners with identical chlorine substitution pattern, as shown in Tables 2 and 3, are evident and explain their different chromatographic behaviour.

Table 4 summarizes the derived class and class-solvent constants. They turn out to be statistically significant without exception. Thus the introduction of molecular orientational exchange entropy, as shown by the c_3 values, substantially improved the prediction.

Additional statistical results are included in Table 6. Fig. 2 shows the excellent correspondence between calculated and experimental I data.

3.2. Validation of the method

In order to validate the x parameters derived, Eq. 2 was used in a multiple nonlinear fit of the pertinent X, a and c constants to experimental ln RRT data of all ($N_t = 38$) tetrachlorobenzofurans (TCDFs) on four columns of different polarity (DB1, DB5, DB17, DB225) [7]. Column properties were those of Table 1, showing increasing

Table 2
Heat of vaporization (h) and molar volume (v) parameters for PCDD/Fs derived using model Eqs. 5 and 6 in a nonlinear fit to 183 experimental data

	$n_{...}$OCDF[a]	$n_{...}$OCDD[a]	h fragment (cal mol^{-1})	v fragment (cm^3 mol^{-1})
$x0_{DF}$	1	0	15558 (10)	140.40 (0.10)
$x0_{DD}$	0	1	17772 (44)	146.96 (0.20)
x_{Cl}	8	8	1854 (92)	15.76 (0.08)
x_{ClClo}	6	6	−5 (8)[b]	3.44 (0.11)
x_{ClClm}	4	4	−358 (10)	−0.52 (0.12)
x_{ClClp}	2	2	−296 (15)	−0.70 (0.17)
x_{ClCo}	2	0	−442 (62)	0.00 (0.14)[b]
x_{ClCm}	4	0	241 (111)	−4.50 (0.15)
x_{ClCp}	2	0	−117 (60)	−3.84 (0.14)
x_{ClOo}	2	4	−332 (59)	−0.66 (0.12)
x_{ClOm}	4	8	44 (112)[b]	−5.96 (0.13)
x_{ClOp}	2	4	−365 (58)	−3.66 (0.12)
x_{ClCl1}	0	2	273 (18)	−4.77 (0.19)
x_{ClCl2}	1	0	778 (20)	−0.05 (0.23)[b]
x_{ClCl3}	1	0	−29 (18)	−3.95 (0.21)
x_{ClCl4}	2	4	−163 (11)	0.57 (0.14)
x_{ClCl5}	2	0	80 (14)	−2.71 (0.17)
x_{ClCl6}	4	4	−216 (9)	0.93 (0.13)
x_{ClCl7}	2	2	−211 (13)	−0.20 (0.15)
x_{ClCl8}	2	2	−169 (12)	1.40 (0.14)
x_{ClCl9}	2	2	−323 (12)	3.58 (0.15)

[a] Identifiers of Eq. 6 for octachloro-DF/DD (OCDF/D) as an example.
[b] Parameter statistically not significant.
Values in parentheses represent the 95% confidence limits.

Table 3
Predicted values of heat of vaporization (ΔH), molar liquid volumes (V) and solubility parameters (δ) at 298.15 K, of PCDF/D, together with their deviations (exp. − calc.) from experimental data (given in parentheses)

Congener	ΔH[a] (cal mol^{-1})	V[b] (cm^3 mol^{-1})	δ[c] (cal cm^{-3})$^{1/2}$
DF	15558 (872)	140.40 (1.22)	10.325 (0.250)
36-	18939 (78)	157.53	10.792
248-	20038 (449)	168.01	10.758
2378-	21586 (232)[d]	184.35 (0.27)[d]	10.671 (0.051)
12346789-	25277 (−737)	230.50 (−1.63)[d]	10.348 (−0.119)
DD	17772 (−163)	146.96 (−4.10)	10.812 (0.102)
1-	19338 (−92)	156.10 (2.66)	10.959 (−0.119)
2-	19305 (180)	153.09 (2.46)	11.056 (−0.035)
23-	20833 (−444)	162.67	11.155
27-	20515 (137)	162.81 (0.92)	11.062 (0.007)
28-	20669 (1063)	160.63 (7.26)	11.180 (0.041)
124-	21778 (−386)	173.60	11.047
137-	21661 (595)	170.18	11.127
1234-	22943 (−365)	186.10	10.959
2378-	22910 (−173)	188.34 (−2.47)	10.886 (0.029)
234678-	24831	210.70 (−4.45)	10.726
12346789-	25738 (−1051)	231.27 (−1.15)	10.427 (−0.194)
r	0.982	0.995	0.926
$\langle\sigma\rangle$	439	2.60	0.095
e	375	3.00	0.176
N	16	11	10

[a] (Experimental) data inferred from Ref. [17] using an empirical $d\Delta H/dT = -13$ cal mol^{-1} K^{-1} value.
[b] Semi-empirical data calculated from the crystalline molar volume (V_c) according to $V = 13.05 + 0.98063V_c$ [18]. V_c obtained from crystalline densities from Refs. [19–25].
[c] Calculated by Eq. 1.
[d] Deviation from semi-empirical value estimated from (semi-)empirical values of DF, DD, 2378-D and 1234678-DD.

values of δ_s or increasing polarity; b_I and $c_{3,I,s}$ (PCDF) values were identical to those of Table 4. The experimental data were obtained applying different temperature programs from Ryan et al. [7], which were simulated by Eqs. 3 and 4. Experimental uncertainties were not reported by these authors; a value of $e = 0.001$ for ln RRT was inferred from their data. The results are included in Tables 5 and 6 and in Fig. 3.

DB1, DB5 and DB17 results are similar, DB225 (the polar cyanopropyl column) results showing clear deviation from these. The best results are obtained for DB5, the column which was also used for the derivation of x parameters, and are relatively poor for the polar DB225 column. Several a_1 and a_2 contributions are not significant from a statistical point of view. These results are in accordance with the additional statistical data of Table 6 and the scatter diagrams of Fig. 3.

4. Discussion and conclusions

The nonlinear SOFA model has a thermodynamic basis extended with a relatively large number of extra-thermodynamic heat of vaporization and molar volume fragment parameters and with compound class and class-solvent constants. Temperature dependence of properties is included via empirical relationships. According to these characteristics the model allowed for the prediction of Kovats retention index and relative retention times of PCDF/Ds at different tem-

Table 4
Compound class and class-solvent constants derived using model Eqs. 5 and 6 in a nonlinear regression to 183 experimental data

Constant	I(PCDFs)	I(PCDDs)
$a_I + \Delta X_{I,Z,s}$	13.383 (0.210)	14.558 (0.274)
b_I	0.8162[a]	0.8162[a]
$c_{1,I,s}$	1.045 (0.110)	1.237 (0.161)
$c_{2,I,s}$	0.438 (0.018)	0.406 (0.021)
$c_{3,I,s}$	−0.142 (0.024)	−0.164 (0.032)
$c_{1,Z,s}$	0.607 (0.168)[b]	0.607 (0.68)[b]
$c_{2,Z,s}$	0.781 (0.154)[b]	0.781 (0.154)[b]
$c_{3,Z,s}$	0.15 (0.07)[b]	0.15 (0.07)[b]

[a] Not varied, but derived by monolinear fit of experimental ΔH_i data to experimental P_i data [17] via $\ln P_i = a_I - bI\Delta H_i$.
[b] Values for I(PCDFs) and I(PCDDs) forced to be identical. 95% Confidence limits are in parentheses; non-significant additional decimal figures are given in order to avoid rounding errors of data used in the Appendix.

peratures and, though less complete, on four columns of different polarity. In this way the SOFA model can assist in the choice of stationary phases and the identification of unknown compounds provided that sufficient data of the stationary phase are available in order to estimate its approximate molar volume and solubility parameter. In addition, heat of vaporization, (sub-cooled) molar liquid volume and solubility parameter were predicted (Table 3), which

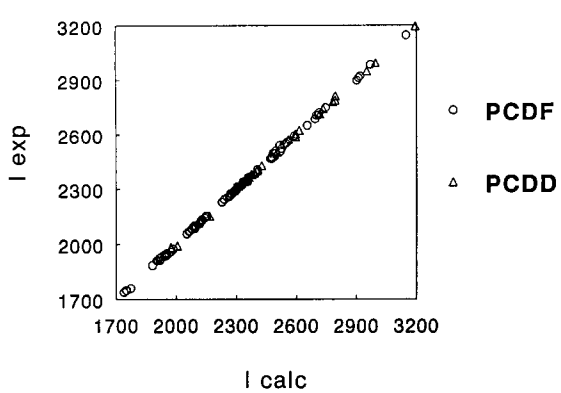


Fig. 2. Correlations between calculated (Eq. 2) and experimental data for Kovats retention indices (I) of polychlorodibenzofurans (510.65 K) and polychlorodibenzo[p-]dioxins (528.15 K) on DB5 columns.

was a main objective of this study. The different behaviour of PCDF and PCDD could be attributed to the presence of partly differing fragment parameters and maximum number of orientations on a lattice site in the two types of congeneric molecules. Moreover, though not shown here, values were obtained for the various enthalpic and entropic contributions to these properties (cf. Ref. [2]) and for boiling point temperatures (using Eq. 4). Table 6 shows that all predictions, with the exception of relative retention times on polar columns, are of the same order of accuracy as the experimental data. This accuracy allows for the physical discrimination of both isomer groups from each other and isomers within a group.

Other models have been used for the predictions of separate chromatographic properties of PCDFs and PCDDs. Their performance is summarized in Table 6 as well. Fragment models [6,8] dissect the retention property directly into contributions of molecular fragments (cf. the x parameters in the SOFA model, which dissect ΔH and V), turn out to be of equal accuracy compared to SOFA and require only simple mathematics and computer programs. The pertinent fragment parameters and their values, however, vary with type of property, compound series, column and temperature program. In addition, they do not provide much information on the chromatographic partitioning process.

Molecular connectivity [9] and mixed fragment-connectivity models [10] turn out to be of either equal or lower accuracy compared to SOFA. They have drawbacks similar to those of fragment models.

Models using molecular properties such as van der Waals surface [11], polarizability, ionization potential and dipole moment [12] do have, in contrast to the fragment and molecular connectivity models, a partly physical basis. The application of these molecular descriptors also has a scope more general than the latter. With respect to this they are similar to SOFA, though less complete. As they are of a computational simplicity intermediate to the fragment plus connectivity models and SOFA, they might have good perspectives for use. Currently, however, their

Table 5
Compound class and class-solvent constants as found by Eq. 2 for TCDFs on DB1, DB5, DB17 and DB225 columns

Constant	DB1	DB5	DB17	DB225
$-X_{1,s}\ldots$[a]	3.83 (3.14)	4.09 (2.05)	5.32 (4.17)	11.97 (0.80)
$c_{1,1,s}$	0.59 (0.01)	0.61 (0.01)	0.64 (0.02)	0.82 (0.05)
$c_{2,1,s}$	1.94 (0.06)	1.73 (0.06)	1.75 (0.29)	1.28 (0.28)
$a_{1,1}$	−0.01 (0.03)[b]	−0.01 (0.02)[b]	−0.03 (0.04)[b]	−0.045 (0.021)
$a_{2,1} \cdot 10^5$	9.28 (7.10)	6.93 (5.53)	−2.54 (10.6)[b]	−6.74 (5.42)

[a] $-X_{1,s} - a_{0,1} + \ln(298.15R/M_s) - \ln V_{g,r}$ was fitted as a sum.
[b] Contribution statistically not significant.
95% Confidence limits are in parentheses.

accuracy is very poor compared to all other models.

Finally, UNIQUAC and UNIFAC models have been used for the prediction of partition constants [26,27]. In order to solve the problem of finding values of intermolecular interactions each time a new molecule is introduced, in UNIFAC molecular interactions were composed out of interactions between functional groups of the pertinent molecules. In this thermodynamic model isomer differences are treated incompletely, however. Differences between *o*-, *m*- and *p*-substitution on ring systems are, e.g., not accounted for. In its current version UNIFAC, therefore, is not useful for chromatographic purposes requiring high accuracy. It has, however, to be mentioned that some common basis exists between the UNIQUAC model, underlying UNIFAC, and our SOFA model [2].

It would be useful to develop a method with a

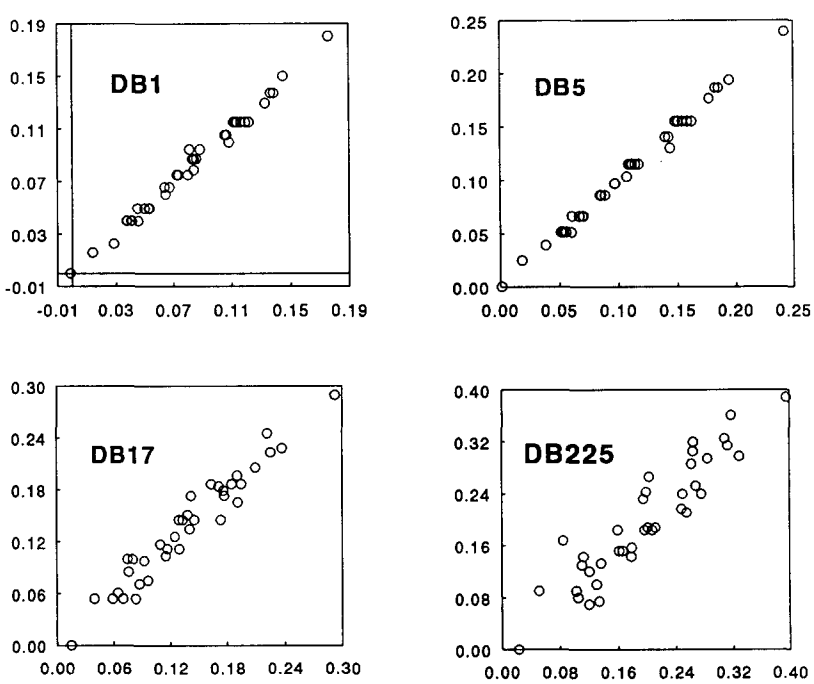


Fig. 3. Correlations between calculated (Eq. 3) values (on the horizontal axes) and experimental ln RRT data (on the vertical axes) for 38 TCDFs on DB1, DB5, DB17 and DB225 stationary phases.

Table 6
Comparison of statistical results obtained by the SOFA model and other prediction models for chromatographic retention of PCDF/Ds

Model	Property	Compounds	N	r	$\langle\sigma\rangle$	e
SOFA-Eq.5	I	PCDF	115[c]	0.9997	5.0	5.0
SOFA-Eq.5	I	PCDD	41[a]	0.9997	4.8	5.0
SOFA-Eq.2	ln RRT-DB1	TCDF	38[h]	0.994	0.003	0.001
SOFA-Eq.2	ln RRT-DB5	TCDF	38[h]	0.997	0.003	0.001
SOFA-Eq.2	ln RRT-DB17	TCDF	38[h]	0.970	0.012	0.001
SOFA-Eq.2	ln RRT-DB225	TCDF	38[h]	0.928	0.028	0.001
Fragment[a]	I	PCDD	41[a]	0.9998	3.5[k]	
Fragment[b]	I[b]	PCDF	110[c]	0.999	4.8[k]	
MC[d]	I	PCDF	115[c]	0.9944	16.0[k]	
MC/Fragment[e]	I	PCDD	34[a,e]	>0.9995	1.8	
SA[f]	I	PCDF	115[c]	0.984	30?[f,k]	
QC[g]	I	PCDF	69[c,g]	0.963	43[k]	
QC[g]	I	PCDD	37[c,g]	0.990	25[k]	

[a] Ref. [6]. Multilinear regression dissecting I into 11 fragment parameters.
[b] Ref. [8]. Multilinear regression dissecting I into 17 fragment parameters. Non-logarithmic I-index definition used.
[c] Ref. [5].
[d] Ref. [9]. Multilinear regression using 6 molecular connectivity (MC) indices.
[e] Ref. [10]. Multilinear regression using one molecular connectivity index and 6 fragment parameters. Selective use of experimental data.
[f] Ref. [11]. Monolinear regression using the molecular surface area (SA) as parameter. The reported error of 0.98 cannot be correct in view of other errors reported and the low correlation coefficient. The correct value is estimated to be about 30 retention index units.
[g] Ref. [12]. Multilinear regression using molecular polarizability, ionization potential and squared dipole moment as quantum chemical (QC) parameters. Selective use of experimental data.
[h] Ref. [7]. Only TCDF data selected, see text.
[k] If standard errors of regression were reported, the latter were divided by 1.3 in order to roughly estimate the mean error.

sound physical basis such as SOFA and with an equal accuracy, but using a reduced number of x fragment parameters or even without the latter. Work on this objective is in progress, in which ΔH and V are calculated from intermolecular interactions using the atom–atom pair potential approximation [28]. By this, it is simultaneously aimed at the improvement of the calculation of the interactions between solute and solvent molecules (the effect of column polarity).

5. Note

The calculated values of ΔH, V, δ, T_{bp} and I of all 212 PCDF/Ds and the calculated values of ln RRT (DB1, DB5, DB17, DB225) of all 38 TCDFs are available from the authors on request.

Appendix: calculation of I (OCDF)

As an example of a detailed calculation, performed by computer in SOFA, the calculation of the Kovats retention index of octachlorodibenzofuran (OCDF) on a DB5 column at a mean temperature of 510.65 K (237.5°C) is given.

Molecular identifiers, $n\ldots$, and fragment contributions, $h\ldots$ and $v\ldots$, of OCDF are found in Table 2. After application of Eq. 6 one obtains: ΔH (298.15 K, OCDF) = 25277 cal mol^{-1} and V (298.15 K, OCDF) = 230.50 cm^3 mol^{-1}. Using Eq. 1 the solubility parameter is obtained: δ (298.15 K, OCDF) = 10.348 [cal cm^{-3}]$^{\frac{1}{2}}$. For the calculation of combinatorial entropy effects an approximated volume V^{co} (298.15 K, OCDF) = $v_o + 8v_{Cl}$ = 140.40 + 8 × 15.76 = 266.48 cm^3 mol^{-1} was used in order to

account for the non-isomer specific behaviour of S^{co} (see Ref. [2]).

Heat vaporization, molar liquid volume and solubility parameter of the stationary phase (DB5) at 298.15 K were obtained from model compounds (see also Table 1). DB5 is approximated by a mixture of 5% phenyl- and 95% dimethyl-silane and the corresponding parameters were found from the percentage contribution of the pure model compounds: ΔH (298.15 K, DB5) = 4550 cal mol^{-1}, V (298.15 K, DB5) = 100.67 cm^3 mol^{-1} and (via Eq. 1): δ (298.15K, DB5) = 6.27 [cal cm^3]$^{\frac{1}{2}}$. The use of model compounds may lead to deviation of δ values presented elsewhere.

The z and $z+1$ values of the corresponding n-alkanes, found by optimization in SOFA, turned out to be 31 en 32, respectively. The ΔH and V values of n-alkanes at 298.15 K are obtained from the empirical equation given in Table 3 of Ref [2]: ΔH (298.15 K, $z = 31$) = 25059 cal mol^{-1}, ΔH (298.15 K, $z = 32$) = 25516 cal mol^{-1}, V (298.15 K, $z = 31$) = 545.34 cm^3 mol^{-1}, V (298.15 K, $z = 32$) = 562.84 cm^3 mol^{-1}. Via Eq. 1 we find: δ (298.15 K, $z = 31$) = 6.598 [cal cm^{-3}]$^{\frac{1}{2}}$, δ (298.15 K, $z = 32$) = 6.551 [cal cm^{-3}]$^{\frac{1}{2}}$.

Parameters at 510.65 K are obtained from values at 298.15 according the expressions $\Delta H(T) = \Delta H$ (298.15 K) − 13 (T − 298.15) and $V(T) = V$ (298.15 K) [1 + 0.001237(T − 298.15)] (see Ref. [2]): ΔH (510.65 K, OCDF) = 22515 cal mol^{-1}, ΔH (510.65 K, DB5) = 1788 cal mol^{-1}, ΔH (510.65 K, $z = 31$) = 22297 cal mol^{-1}, ΔH (510.65 K, $z = 32$) = 22753 cal mol^{-1}, V (510.65 K, OCDF) = 291.09 cm^3 mol^{-1}, V^{co} (510.65 K, OCDF) = 336.53 cm^3 mol^{-1}, V (510.65 K, DB5) = 127.13 cm^3 mol^{-1}, V (510.65 K, $z = 31$) = 688.69 cm^3 mol^{-1}, V (510.65 K, $z = 32$) = 710.79 cm^3 mol^{-1}. From these result via Eq. 1: δ (520.65 K, OCDF) = 8.594 (cal mol^{-3})$^{\frac{1}{2}}$, δ (510.65 K, DB5) = 2.466 (cal cm^{-3})$^{\frac{1}{2}}$, δ (510.65 K, $z = 31$) = 5.559 (cal cm^{-3})$^{\frac{1}{2}}$ and δ (510.65 K, $z = 32$) = 5.530 (cal cm^{-3})$^{\frac{1}{2}}$.

The logarithm of the temperature independent orientational entropy descriptors, A, are obtained from Eq. 7 in a numerical approximation of ln $A(n\mathrm{Cl}) = -19.1131 + 0.26419(n_{\mathrm{Cl}} - 4)^2$ for OCDF and ln A(z) = −0.782 − 1.910 z for n-alkanes leading to ln A(OCDF) = −14.879, ln A ($z = 31$) = −59.996 and ln A ($z = 32$) = −61.906.

The temperature independent class constants $a_{\mathrm{I}} + \Delta X_{\mathrm{I,Z,s}} = 13.383$, $b_{\mathrm{I}} = 0.8162$, $c_{1,\mathrm{I,s}} = 1.045$, $c_{2,\mathrm{I,s}} = 0.438$, $c_{3,\mathrm{I,s}} = 0.142$, $c_{1,\mathrm{Z,s}} = 0.607$, $c_{2,\mathrm{Z,s}} = 0.781$, $c_{3,\mathrm{Z,s}} = 0.148$ obtained after derivation are given in Table 4. The temperature independent constants $a_{\mathrm{Z}} = 12.764$ and $b_{\mathrm{Z}} = 0.62335$ are obtained from experimental n-alkane data (See Ref. [2]).

Substitution of the appropriate data mentioned above into Eq. 5 leads to I (calc) = 3150, whereas the experimental value I (exp) = 3147.

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