

# Dielectric Interactions and the Prediction of Retention Times of Pesticides in Supercritical Fluid Chromatography with CO<sub>2</sub>

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*Herrn Professor Robert H. Schuster zu seinem 60. Geburtstag herzlich gewidmet*

A thermodynamic model for the partition of a solute (pesticide) between two immiscible phases, such as the stationary and mobile phases of supercritical fluid chromatography with CO<sub>2</sub>, is developed from first principles. A key ingredient of the model is the result of the calculation made by Liptay of the energy of interaction of a polar molecule with a dielectric continuum, which represents the solvent. The strength of the interaction between the solute and the solvent, which may be considered a measure of the solvent power, is characterized by a function  $g = (\epsilon - 1)/(2\epsilon + 1)$ , where  $\epsilon$  is the dielectric constant of the medium, which is a function of the temperature  $T$  and the pressure  $P$ . Since the interactions between the nonpolar supercritical CO<sub>2</sub> solvent and the slightly polar pesticide molecules are considered to be extremely weak, a regular solution model is appropriate from the thermodynamic point of view. At constant temperature, the model predicts a linear dependence of the logarithm of the capacity factor ( $\ln k$ ) of the chromatographic experiment on the function  $g = g(P)$ , as the pressure is varied, with a slope which depends on the dipole moment of the solute, dispersion interactions and the size of the solute cavity in the solvent. At constant pressure, once the term containing the  $g$  (solvent interaction) factor is subtracted from  $\ln k$ , a plot of the resulting term against the inverse of temperature yields the enthalpy change of transfer of the solute from the mobile (supercritical CO<sub>2</sub>) phase to the stationary (adsorbent) phase. The increase in temperature with the consequent large volume expansion of the supercritical fluid lowers its solvent strength and hence the capacity factor of the column (or solute retention time) increases. These pressure and temperature effects, predicted by the model, agree excellently with the experimental retention times of seven pesticides. Beyond a temperature of about 393 K, where the liquid solvent densities approach those of a gas (and hence the solvent strength becomes negligible), a dramatic loss of the retention times of all pesticides is observed in the experiments; this is attributed to desorption of the solute from the stationary phase, as predicted by Le Châtelier's principle for the (exothermic) adsorption process.

**Key words:** Dielectric Interactions; Supercritical Fluid Chromatography with CO<sub>2</sub>; Thermodynamic Model; Regular Solution; Activity Coefficients of Pesticides; Adsorption; Le Châtelier's Principle.

## 1. Introduction

The separation of substances by chromatography is one of the milestone achievements of chemistry. The underlying principle of this process is the equilibrium partition of the solute between a stationary (adsorbent) phase and a mobile (solvent) phase. In a variant of this technique [1], the mobile phase consists of a supercritical fluid, usually carbon dioxide (CO<sub>2</sub>). This fluid solvent, which does not contaminate the environment and has a low critical temperature  $T_C = 304.5$  K and critical pressure  $P_C = 73.9$  bar is particularly useful in the

separation of thermally labile substances such as natural products for the pharmaceutical and food industries and in the analysis of substances such as pesticides in the environment. Its advantages are to be weighed against its limited scope as a nonpolar solvent, which dissolves only up to slightly polar solutes, although this aspect can be improved by the addition of polar modifiers such as methanol [2].

One important aspect of the application of the technique of supercritical fluid chromatography is the effect of pressure and temperature on the retention times or times needed for the different solutes to traverse

the chromatographic column. Increasing the pressure, that is the density, of the solvent increases the (favorable) interaction of the solvent with the solute, and this means that more solute dissolves in the mobile phase. Since the solute spends more time in the mobile phase than in the stationary phase, its retention time is lowered. Increasing the temperature, on the other hand, lowers enormously the density of the (supercritical) solvent and thus its solvent power; hence, retention times of the solute in the column should increase without limit with increasing temperature. However, since all adsorption processes are exothermic, at high temperatures the adsorbent loses its adsorbent power (by Le Châtelier's principle), the solute desorbs from the stationary phase and consequently the retention times then decrease with further increase in temperature. The desorption process follows the equilibrium (and kinetic) laws of any gas reaction  $A + B = AB$ , where  $A$  is the adsorbate,  $B$  the adsorbent substrate and  $AB$  the adsorbate-adsorbent complex. Other examples of this same gas reaction besides adsorption chromatography are the binding of oxygen by myoglobin and the formation of ammonia from molecular nitrogen plus molecular hydrogen [3]. This desorption process will not be studied in detail in what follows.

## 2. Theory

The system consists of two immiscible liquid phases containing  $c$  solute components. The mobile phase, represented by a prime  $'$ , is supercritical CO<sub>2</sub> solvent 1 and solutes 2, 3, ... (the pesticides) dissolved in it. The stationary phase, denoted by a double prime  $''$ , is a fluid layer of the solvent and the solutes adsorbed on the chromatographic column support.

The chemical potential of component  $i$  in the mobile phase is  $\mu_i'$  and in the stationary phase  $\mu_i''$ . Both are given by [4]:

$$\mu_i = \mu_i^\bullet(T, P) + RT \ln x_i \gamma_i, \quad (1)$$

where  $\mu_i^\bullet(T, P)$  is a function only of the variables temperature  $T$  and pressure  $P$ , and the second term on the right gives the effect of the mole fraction  $x_i$  on the chemical potential  $\mu_i$ .  $\gamma_i$  is the activity coefficient of the component  $i$  in the nonideal solution.

The difference  $A_i = \mu_i' - \mu_i''$  or affinity of transfer of component  $i$  from the mobile phase to the stationary phase is

$$A_i = \mu_i' - \mu_i'' = \mu_i^{\bullet'} - \mu_i^{\bullet''} + RT \ln \frac{x_i' \gamma_i'}{x_i'' \gamma_i''} \quad (2)$$

$$A_i = RT \ln K_i(T, P) + RT \ln \frac{x_i' \gamma_i'}{x_i'' \gamma_i''}, \quad (3)$$

where

$$\mu_i^{\bullet'} - \mu_i^{\bullet''} = RT \ln K_i. \quad (4)$$

At equilibrium, the affinity of transfer of each component is zero ( $\mu_i' = \mu_i''$ ), and then

$$\frac{x_i'' \gamma_i''}{x_i' \gamma_i'} = K_i(T, P). \quad (5)$$

This is Nernst's distribution law. The ratio on the left depends solely on  $T$  and  $P$  and  $K_i$  is a true equilibrium constant, known as partition or distribution coefficient of component  $i$  between the two nonideal phases.

Recall the definition of partial molar volume  $v_i^\bullet$  and partial molar enthalpy  $h_i^\bullet$  of component  $i$  in the standard state,

$$v_i^\bullet = \left( \frac{\partial \mu_i^\bullet}{\partial P} \right)_T \quad (6)$$

and

$$-\frac{h_i^\bullet}{T^2} = \left[ \frac{\partial (\mu_i^\bullet/T)}{\partial T} \right]_P, \quad (7)$$

and replace these in the derivatives of (4) to obtain

$$\begin{aligned} \left( \frac{\partial \ln K_i}{\partial P} \right)_T &= \frac{1}{RT} \left[ \left( \frac{\partial \mu_i^{\bullet'}}{\partial P} \right)_T - \left( \frac{\partial \mu_i^{\bullet''}}{\partial P} \right)_T \right] \\ &= -\frac{v_i^{\bullet''} - v_i^{\bullet'}}{RT} \end{aligned} \quad (8)$$

and

$$\begin{aligned} \left( \frac{\partial \ln K_i}{\partial T} \right)_P &= \frac{1}{R} \left[ \frac{\partial (\mu_i^{\bullet'}/T)}{\partial T} \right]_P - \frac{1}{R} \left[ \frac{\partial (\mu_i^{\bullet''}/T)}{\partial T} \right]_P \\ &= \frac{h_i^{\bullet''} - h_i^{\bullet'}}{RT^2}. \end{aligned} \quad (9)$$

The standard enthalpy change of transfer  $\Delta_{tr} h_i^\bullet \equiv h_i^{\bullet''} - h_i^{\bullet'}$  and standard volume change  $\Delta_{tr} v_i^\bullet \equiv v_i^{\bullet''} - v_i^{\bullet'}$  are, like the quantities  $\mu_i^\bullet$ , from which they were obtained, independent of composition.

Following Prigogine [4], we consider an infinitesimal change in the quantity  $A_i/T$ ; from (3)

$$\begin{aligned} \delta \left( \frac{A_i}{T} \right) &= R \left( \frac{\partial \ln K_i}{\partial T} \right)_P \delta T \\ &\quad + R \left( \frac{\partial \ln K_i}{\partial P} \right)_T \delta P + R \delta \ln \frac{x_i' \gamma_i'}{x_i'' \gamma_i''} \end{aligned} \quad (10)$$

and substituting (8) and (9) in (10), we obtain

$$\delta \left( \frac{A_i}{T} \right) = \frac{h_i^{\bullet\bullet} - h_i^{\bullet'}}{T^2} \delta T - \frac{v_i^{\bullet\bullet} - v_i^{\bullet'}}{T} \delta P + R \delta \ln \frac{x_i' \gamma_i'}{x_i'' \gamma_i''}. \quad (11)$$

Along a path of equilibrium of the system this expression must be zero.

A binary system consists of solvent A and solute B. Assuming that both are free to pass from one phase to the other, (11) applies to each component. For component B, (11) is integrated choosing, for convenience, an initial equilibrium state consisting of pure substance B in each of the phases at reference  $T_{\text{ref}}$  and  $P_{\text{ref}}$ , and with  $(x_B')^\circ = (x_B'')^\circ = 1$  for the pure phases. The final equilibrium state is at  $T, P, x_B', x_B''$  with  $A_B = 0$ . Since the reference state is pure B in each phase,  $(\gamma_B')^\circ = (\gamma_B'')^\circ = 1$ .

Integration of (11) from the initial equilibrium state  $A_B^\circ = 0$  to the final equilibrium state  $A_B = 0$  gives

$$\ln \frac{x_B'' \gamma_B''}{x_B' \gamma_B'} = \int_{T_{\text{ref}}}^T \frac{\Delta_{\text{tr}} h_B^\circ}{RT^2} dT - \int_{P_{\text{ref}}}^P \Delta_{\text{tr}} v_B^\circ dP; \quad (12)$$

superscript  $\bullet$  has been replaced by superscript  $\circ$ , since the reference state is pure substance B in each phase at  $T_{\text{ref}}$  and  $P_{\text{ref}}$ .

### 2.1. The Activity Coefficient

To complete the solution model, it is necessary to evaluate the activity coefficients of the solute,  $\gamma_B'$  and  $\gamma_B''$ , in each phase.

Integration of the fundamental equation of thermodynamics gives for the Gibbs energy per mole of the binary mixture

$$g = x_A \mu_A + x_B \mu_B. \quad (13)$$

The Gibbs energy of mixing  $g^M$  is the part in (13) due to mixing of the two components A and B. Using (2), this part is

$$g^M = RT (x_A \ln x_A \gamma_A + x_B \ln x_B \gamma_B). \quad (14)$$

The excess Gibbs energy  $g^E$  is the difference between the actual  $g^M$  and the corresponding ideal quantity  $g^{M,\text{id}}$ , which results from setting  $\gamma_i = 1$  in (1),

$$g^E = g^M - g^{M,\text{id}} = RT (x_A \ln \gamma_A + x_B \ln \gamma_B). \quad (15)$$

Other excess functions, such as the excess entropy  $s^E$  and the excess enthalpy  $h^E$ , are obtained from (15) by thermodynamic relations.

Then, writing  $G^E = ng^E$  for the whole system of  $n$  moles,

$$\left( \frac{\partial G^E}{\partial n_i} \right)_{T,P} = RT \ln \gamma_i; \quad (16)$$

the Gibbs-Duhem Eqn.  $\sum_i n_i d \ln \gamma_i = 0$  has been used to obtain this result.

This formula is important because in what follows regular solutions for which

$$G^E \approx H^E, \quad (17)$$

where  $H^E = nh^E$  is the total excess enthalpy of the system, will be used to model the solutions of the (slightly polar) pesticides in the (nonpolar) solvent. Since  $h^{M,\text{id}} = 0$ ,

$$h^E = h^M = \frac{H^M}{n}; \quad (18)$$

it is necessary, then, to inquire into the heat of mixing  $h^M$  function, which by (17) gives  $G^E$ , and then to obtain from this the activity coefficient in the solution by (16). The solute activity coefficients in each phase will be needed to predict the capacity factor of the chromatographic column according to (12).

### 2.2. The Lattice Model

The heat of mixing  $H^M$  is identified with the interaction energy of the solution and calculated according to the lattice model of a liquid [4]. Molecules of both solvent and solute, assumed to be of the same size, occupy individual cells of a quasisolid lattice with coordination number  $z$  ( $z$  neighbors to a given molecule). A correction exists for the case where the molecules have different sizes.

If there are  $zX_{A,B}$  pairs of contacts between the molecules A and the B in the mixture, and the absolute value of the (attractive) potential for each pair is  $V_{A,B}$ , and similarly for A,A and B,B pairs, the total energy of interaction of all pairs of molecules, counting only nearest neighbor interactions, is

$$W = -zX_{A,A}V_{A,A} - zX_{B,B}V_{B,B} - zX_{A,B}V_{A,B}. \quad (19)$$

The following conservation relations apply between the different pairs of contacts in solution:

$$2X_{A,A} + X_{A,B} = N_A \quad (20)$$

and

$$2X_{B,B} + X_{A,B} = N_B. \quad (21)$$

$N_A$  and  $N_B$  are the numbers of A and B molecules in solution, resp. Substituting these in (19) gives

$$W = -N_A \Lambda_A - N_B \Lambda_B + X_{A,B} W_{A,B}, \quad (22)$$

where

$$\Lambda_A = \frac{z}{2} V_{A,A}, \quad \Lambda_B = \frac{z}{2} V_{B,B}, \quad (23)$$

$$W_{A,B} = \frac{z}{2} (V_{A,A} + V_{B,B} - 2V_{A,B}). \quad (24)$$

$\Lambda_A$  is the absolute value of the potential energy per molecule of pure liquid A, and similarly for  $\Lambda_B$ .  $\Lambda_A$  and  $\Lambda_B$  are also the vaporization energies per molecule of the two pure liquids.

The quantity

$$W + N_A \Lambda_A + N_B \Lambda_B = X_{A,B} W_{A,B} \quad (25)$$

is the change in energy of the system upon mixing the two pure liquids.  $X_{A,B}$  is a positive quantity, and thus  $W_{A,B} > 0$  corresponds to absorption of heat in the mixing process, while  $W_{A,B} < 0$  indicates evolution of heat.

Strictly,  $X_{A,B} W_{A,B} = U^E = H^E - PV^E$ , where  $U^E$  and  $V^E$  are the excess energy and excess volume, and  $P$  is the pressure, but the term  $PV^E$  can probably be neglected if, for example  $V^E = 10^{-6} \text{ m}^3$ ,  $P = 30 \text{ MPa}$ , giving  $PV^E = 30 \text{ J}$  for one mole of system, and typical  $h^E$  values are  $100 \text{ J mol}^{-1}$  or greater. Thus, formally

$$H^M = X_{A,B} W_{A,B}. \quad (26)$$

For a random mixture (regular solution) the probability that a given site is occupied by an A or B molecule is  $x_A$  and  $x_B$ , resp., and the same applies for an adjacent site. Hence the probability of an A, B contact is

$$2x_A x_B. \quad (27)$$

Multiplying this quantity by the total number of nearest neighbor contacts in the solution, which is  $zN/2$ , gives the total number of A,B contacts

$$zX_{A,B} = \left( \frac{1}{2} zN \right) (2x_A x_B) = zN x_A x_B, \quad (28)$$

and hence from (26)

$$H^M = N x_A x_B W_{A,B}. \quad (29)$$

### 2.3. Calculation of the Interaction Energy

Liptay [5] (and also others [6], [7]) has made thorough calculations of the change of energy ( $E - E^\circ$ ) per solute molecule of the system dissolved molecule plus surrounding solvent molecules relative to the molecules in the gas state  $E^\circ$ . The solute has a permanent electric dipole moment  $\boldsymbol{\mu}$  and polarizability  $\boldsymbol{\alpha}$ . The solvent is treated as a homogeneous and isotropic dielectric continuum with dielectric constant  $\varepsilon(T, P)$ , that is a function of the temperature and the pressure. The change of energy has two contributions. 1.) A cavity of size  $a$  must be made in the solvent in order to accommodate in it the solute molecule. An energy  $E_C$  is required for this process. 2.) The solute molecule is brought into the cavity. The energy of the system is lowered by (quantum mechanical) dispersion interactions by an amount  $E_D$ , and by interaction of the dipole  $\boldsymbol{\mu}$  with the surrounding dielectric (induction effect).

Excluded are specific interactions (orientation energy) such as electron-donor-acceptor complexes or hydrogen bond associations. This is done because in the systems considered (pesticides plus supercritical CO<sub>2</sub> solvent) there are no particular atoms in pairs of molecules with high concentrations of electrical charge, such that these electrostatic interactions can occur. Such effects would lead to the formation of new species in solution or at least to alterations of the spectrum of the dissolved molecule such as the apparition of new absorption bands. Liptay refers to this restriction to processes of solvation of "identical molecules".

(The above remarks refer to the pesticide solute supercritical CO<sub>2</sub> solvent interactions in the mobile phase of the chromatographic experiment. It is assumed that polar adsorption sites, which could be present in the stationary phase and cause hydrogen bonding to polar solutes, are capped by means of silanization reactions or even blocked by the introduction of suitable additives in the mobile phase [2]. These specific associations are the cause of the phenomenon of tailing, or asymmetry of the chromatographic peaks leading to degradation of the chromatographic separation [8].)

For the calculation of the interaction energy of the dipole with the surroundings, the total (permanent plus induced) dipole moment  $\boldsymbol{\mu}'$  of the solute is needed:

$$\boldsymbol{\mu}' = \boldsymbol{\mu} + \boldsymbol{\alpha} \cdot \mathbf{F}_R. \quad (30)$$

$\mathbf{F}_R$  is the effective electric field in the cavity or reaction

field (due to Onsager) caused by the dipole itself,

$$\mathbf{F}_R = f\boldsymbol{\mu}'. \quad (31)$$

$f$  is a positive quantity given to a first approximation by

$$f = \frac{1}{4\pi\epsilon_0} \frac{2}{a^3} \frac{\epsilon - 1}{2\epsilon + 1}; \quad (32)$$

$\epsilon_0$  is the permittivity of vacuum ( $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2\text{N}^{-1} \text{ m}^{-2}$ ) and  $a$  is the radius of the spherical cavity, in the middle of which the dipole moment, approximated by a point dipole, is located.

The work  $W$  due to the interaction of the dipole  $\boldsymbol{\mu}$  with the dielectric is divided in two parts: a contribution  $\boldsymbol{\mu}' \cdot \mathbf{F}_R/2$  is required to cause the polarization of the surrounding dielectric, such that the field in the cavity reaches  $\mathbf{F}_R$ ; subsequently, a quantity of work  $-\boldsymbol{\mu} \cdot \mathbf{F}_R - (1/2)\mathbf{F}_R \cdot \boldsymbol{\alpha} \cdot \mathbf{F}_R$  is liberated through the interaction of the dipole  $\boldsymbol{\mu}'$  with the field  $\mathbf{F}_R$ . The net amount of work for the process is, using (30) and (31),

$$W = -(1/2)f\boldsymbol{\mu} \cdot (\mathbf{1} - f\boldsymbol{\alpha})^{-1} \cdot \boldsymbol{\mu}. \quad (33)$$

There is additionally an entropy change due to polarization of the medium, which is  $\Delta S = f_S(\boldsymbol{\mu}')^2 d\epsilon/dT$  with  $f_S = 3/[4\pi\epsilon_0 a^3 (2\epsilon + 1)^2]$ . The quantity  $d\epsilon/dT$  is always negative, hence  $\Delta S < 0$ . This will, however, not be taken into consideration in view of the assumption of a regular solution for which  $s^E = 0$ . (Since neither  $f_S$  nor  $d\epsilon/dT$  are negligible, this implies that  $(\boldsymbol{\mu}')^2$  must tend to zero; nevertheless, the terms in  $\mu^2$  will be retained in what follows). Also the initial state  $E^\circ$  is redefined as pure separated liquids instead of the gas (i. e.  $E^\circ$  now contains the energies of vaporization of the two separated liquids). Neglecting the polarizability ( $\boldsymbol{\alpha} = 0$ ), we write for the change of energy

$$W_{A,B} = E_C + E_D - \frac{1}{2}\mu^2 f. \quad (34)$$

The quantum mechanical calculation of Liptay yields an expression for the dispersion energy  $E_D$  which may be summarized as

$$E_D = -Df', \quad (35)$$

where  $D$  is a proportionality constant (in turn a function of the molecular energy).  $f'$  is a quantity analogous to  $f$  in (32), obtained from this by replacing  $\epsilon$  with  $n^2$ , where  $n$  is the optical refractive index of the

solvent. Since for all but ferromagnetic materials the so-called Maxwell relation  $n^2 = \epsilon$  is applicable, we set  $f' = f$  and write (34) as

$$W_{A,B} = E_C - \left( \frac{1}{2}\mu^2 + D \right) f, \quad (36)$$

and factoring out the cavity radius  $a$  from this expression:

$$W_{A,B} = E_C - \frac{\mu^2 + 2D}{4\pi\epsilon_0 a^3} g \quad (37)$$

with

$$g = \frac{\epsilon - 1}{2\epsilon + 1}. \quad (38)$$

Without further information on the quantity  $E_C$ , this may be taken in the first instance as the product  $Pv$ , where  $P$  is the pressure and  $v$  the volume per molecule of the solute.

Finally, emphasis is made again on the underlying assumption of this treatment, namely that of extremely weak interactions between the solute and the solvent, much less than the thermal energy ( $\sim 2400 \text{ J mol}^{-1}$  at room temperature). As a consequence, the entropy of mixing will be the same as for a perfect solution ( $s^E = 0$ ), and there will be no nonidealities introduced by arrangements of the molecules in solution as is the case when electrostatic interactions (hydrogen bonding, etc.), known as orientation energy, are present. The entropy change due to polarization of the medium is neglected, as are the differences in volume between solvent and solute molecules.

#### 2.4. The Capacity Factor

In the chromatographic experiment [8] the solute (the pesticide) is equilibrated or partitioned between the stationary phase (double prime), assumed for simplicity to be a liquid, and the mobile phase (prime) consisting of a supercritical CO<sub>2</sub> solvent.

The capacity factor of species  $i$ ,  $k_i$ , is defined as:

$$k_i = \frac{t_{Ri} - t_M}{t_M}; \quad (39)$$

$t_{Ri}$  is the time spent by  $i$  in the column,  $t_M$  the time required by the unretained mobile phase to travel through the column; hence,  $t_{Ri} - t_M$  is the time spent by  $i$  in the stationary phase, and this way  $k_i$  is also the ratio of

the times spent by  $i$  in the stationary and the mobile phases, respectively. This ratio must correspond to the ratio of moles of  $i$  present in equilibrium in the stationary phase,  $n_i''$ , to those in the mobile phase,  $n_i'$ ,

$$k_i = \frac{n_i''}{n_i'}. \quad (40)$$

This is related to the ratio of mole fractions  $x_B''/x_B'$  for the solute B in the following way:

$$\begin{aligned} k_B &= \frac{x_B''(n_A'' + n_B'')}{x_B'(n_A' + n_B')} \approx \frac{x_B''n_A''}{x_B'n_A'} \\ &= \frac{x_B''\rho_A''V''}{x_B'\rho_A'V'} \approx \frac{x_B''V''}{x_B'V'}; \end{aligned} \quad (41)$$

since the amount of B dissolved in A is extremely low,  $n_A + n_B \approx n_A$  in each phase. Also the density of the solvent is assumed to be the same in both phases,  $\rho_A' = \rho_A''$ , since both phases are at the same temperature and pressure.  $V''$  and  $V'$  are the total volumes of the stationary and the mobile phases, resp.; they are constants for a particular column.

In the experiment below, the column consists of a long tube coated on the inside with a thin layer of thickness  $t$  and volume  $V''$  of the stationary (liquid) phase. The volume of the tube of radius  $r$  is  $V'$ , the volume of the mobile phase. Both phases extend through the whole length of the tube; hence the ratio of volumes is the ratio of areas, approximately  $2t/r$ .

### 3. Results and Discussion

The final expression for the prediction of the capacity factor of the chromatographic column as a function of temperature and pressure is obtained first of all by replacing (12) in (41)

$$\begin{aligned} \ln k_B &= \ln \frac{V''}{V'} + \int_{T_{\text{ref}}}^T \frac{\Delta_{\text{tr}}h_B^\circ}{RT^2} dT \\ &\quad - \int_{P_{\text{ref}}}^P \Delta_{\text{tr}}v_B^\circ dp + \ln \gamma_B' - \ln \gamma_B''. \end{aligned} \quad (42)$$

The first term  $\ln(V''/V')$  is a constant of the instrument with  $V''/V' \approx 2t/r$  (here  $V''/V' \approx 0.01$ ).

The second and third terms are simplified by assuming the enthalpy change of transfer of pure B,  $\Delta_{\text{tr}}h_B^\circ$ , and the volume change,  $\Delta_{\text{tr}}v_B^\circ$ , independent of temperature and pressure, resp.  $T_{\text{ref}}$  and  $P_{\text{ref}}$  can be set at the critical point of pure carbon dioxide,  $T_C$  and  $P_C$ .

$\Delta_{\text{tr}}h_B^\circ$  and  $\Delta_{\text{tr}}v_B^\circ$  are unknown parameters of the calculation, although the volume change is probably negligibly small and will, indeed, be set to zero below.

The last term  $-\ln \gamma_B''$  disappears with the assumption that the stationary phase is an ideal liquid solution (although it could as well be left as a constant, see below). The result is, omitting the prime on  $\gamma_B'$ , and integrating the ideal solution terms

$$\begin{aligned} \ln k_B &= \ln \frac{V''}{V'} - \frac{\Delta_{\text{tr}}h_B^\circ}{R} \left( \frac{1}{T} - \frac{1}{T_C} \right) \\ &\quad - \Delta_{\text{tr}}v_B^\circ (P - P_C) + \ln \gamma_B. \end{aligned} \quad (43)$$

To obtain  $\ln \gamma_B$  from (16), using (17) (regular solution) and (18), (29) is first written

$$H^M = G^E = \frac{n_A n_B}{n_A + n_B} N_{\text{Avo}} W_{A,B}, \quad (44)$$

where  $N_{\text{Avo}}$  is Avogadro's number. Then, performing the differentiation at  $T$  and  $P$  constant

$$\left( \frac{\partial G^E}{\partial n_B} \right)_{T,P} = N_{\text{Avo}} W_{A,B} (x_A)^2 = RT \ln \gamma_B. \quad (45)$$

Substituting this in (43), using (37) for  $W_{A,B}$  and taking into account the extreme dilution case  $x_A \approx 1$ , gives, with  $R = N_{\text{Avo}}k$ , where  $k$  is Boltzmann's constant and with  $N_{\text{Avo}}E_C = \bar{E}_C$ ,

$$\begin{aligned} \ln k_B &= \ln \frac{V''}{V'} - \frac{\Delta_{\text{tr}}h_B^\circ}{R} \left( \frac{1}{T} - \frac{1}{T_C} \right) \\ &\quad - \Delta_{\text{tr}}v_B^\circ (P - P_C) + \frac{\bar{E}_C}{RT} - \frac{\mu^2 + 2D}{4\pi\epsilon_0 a^3 k T} g. \end{aligned} \quad (46)$$

This is summarized in the following way ( $\Delta_{\text{tr}}v_B^\circ = 0$ ):

$$\ln k_B = c_0 + [c_1 + c_2 g(T, P)] \frac{1}{T}, \quad (47)$$

where the constants  $c_0$ ,  $c_1$  and  $c_2$  are

$$c_0 = \ln \frac{V''}{V'} + \frac{\Delta_{\text{tr}}h_B^\circ}{RT_C}, \quad (48)$$

$$c_1 = -\frac{\Delta_{\text{tr}}h_B^\circ - \bar{E}_C}{R}, \quad (49)$$

and

$$c_2 = -\frac{\mu^2 + 2D}{4\pi\epsilon_0 a^3 k}. \quad (50)$$

The constant  $c_0$  might also include other terms such as  $-\ln \gamma_B''$  for the stationary phase, neglected above, and the (presumably small)  $-\Delta_{tr} v_B^\circ (P - P_C)$  term, also neglected.

Experimental values of  $\varepsilon(T, P)$  for CO<sub>2</sub> were taken from Moriyoshi et al. [9], who also compiled the pressure-density-temperature ( $P, \rho, T$ ) relationship. The pressure range of these measurements is from 1 MPa to 30 MPa, well over the range of the chromatographic experiments from 15 MPa to 24 MPa. The temperature is limited to the range from 273.15 K to 353.15 K, while the chromatographic experiments did run effectively from 343.15 K to 393.15 K. It is claimed here that beyond this temperature, desorption is the governing mechanism of retention. This is explained as follows.

Plots of the function  $gM/\rho$  versus  $1/T$  at  $P = \text{const}$ , where  $M$  is the molecular weight of CO<sub>2</sub>, using the data of [9], gave excellent straight lines with correlation coefficients at  $P = 18$  MPa, 22 MPa and 26 MPa equal to  $r = 0.9996$ ,  $r = 0.9998$  and  $r = 0.9996$ , resp. in the range from  $T = 323.15$  K to 353.15 K. Even better straight lines were obtained for plots of  $\rho$  vs.  $T$  from the same source over the same  $T$  range. At  $P = 18$  MPa, this plot had a correlation coefficient  $r = 0.99992$  and from its slope a volume thermal expansion coefficient equal to  $0.0134 \text{ K}^{-1}$  was obtained. This is ten to fifteen times greater than that for an ordinary liquid. At 393.15 K, the (extrapolated) CO<sub>2</sub> density  $\rho = 251.3 \text{ kg m}^{-3}$  is only one third of its value at 323.15 K and has a level comparable to the density of an ideal gas at this  $T$  and  $P$ . This is the reason for the assumption that the CO<sub>2</sub> has lost its (liquidlike) solvent properties beyond  $T = 393.15$  K, and the behavior of the column is controlled by desorption at the high temperatures as required by Le Châtelier's principle for the exothermic adsorption reaction.

Capacity factors,  $k_B$ , of seven pesticides 2,4-D, 3,4-Dichloraniline, Diclofop, Diclofopmethyl, Lindan, Linuron and Methoxychlor, all of very similar structures were measured by Yang and Baumann [10] as a function of temperature and pressure. Figure 1 presents the logarithm of the measured capacity factors for the pesticides (except Diclofopmethyl, which was omitted for clarity) at the constant  $T = 393.15$  K as a function of  $g(P)$  defined by (38). Very good straight lines were obtained with correlation coefficients from  $r = 0.997$  for Lindan to  $r = 0.9998$  for 3,4-Dichloraniline, in agreement with equation (47). The slope  $c_2$  of this plot is determined according to (50) by the dipole moment

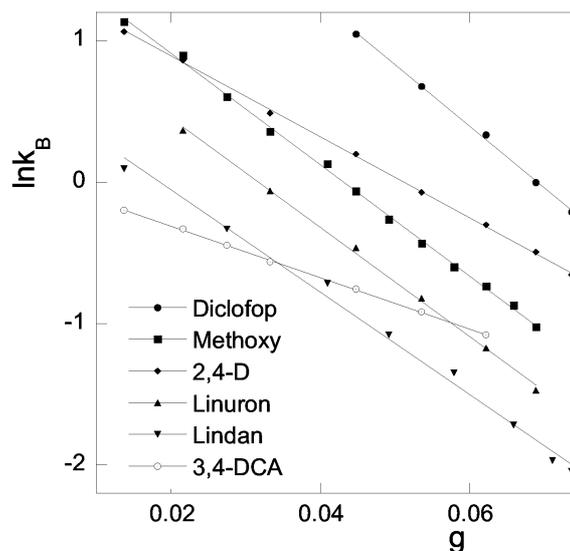


Fig. 1. Logarithm of the capacity factors,  $\ln k_B$ , of the six pesticides 2,4-D, 3,4-Dichloraniline (3,4-DCA), Diclofop, Lindan, Linuron and Methoxychlor (methoxy) at  $T = 393.15$  K as a function of  $g$ .

$\mu$  of the molecule, the dispersion interaction  $D$  and the cavity radius  $a$ . Assuming a constant molar volume for all the molecules equal to  $10^{-4} \text{ m}^3 \text{ mol}^{-1}$  as a measure of the cavity radius  $a$ , the quantity  $\sqrt{(\mu^2 + 2D)}$  ranges from  $43 \times 10^{-30} \text{ Cm}$  for 3,4-Dichloraniline, possibly the smallest molecule of the pesticides, to  $67 \times 10^{-30} \text{ Cm}$  for Dichlofopmethyl, the largest molecule. This range would be altered somewhat by the value of  $a$ . Since the measured dipole moments of these pesticides are  $\sim 20 \times 10^{-30} \text{ Cm}$  [11], this suggests that dispersion interactions dominate over dipole forces in these systems, consistent with the assumption that the excess entropy of mixing for these solutions is zero.

Results analogous to Fig. 1, using the same theory and similar molecules were reported in [12] for the logarithm of solubility against  $g$  of supercritical CO<sub>2</sub>. However, since the sample is injected into the chromatography column in vaporized form at high temperature, the results presented here have greater precision than the solubility measurements, where true equilibrium is difficult to determine and errors of fifty per cent or more in the equilibrium solubility are common [13].

In Fig. 2, the same data as in Fig. 1 are plotted as  $k_B$  versus the pressure for selected molecules (for clarity). The regression lines of Fig. 1 are drawn over the data to show the relevance of the theory developed here for the interaction of the solvent with the solute. Straight lines were reported originally by Liptay [5] for the

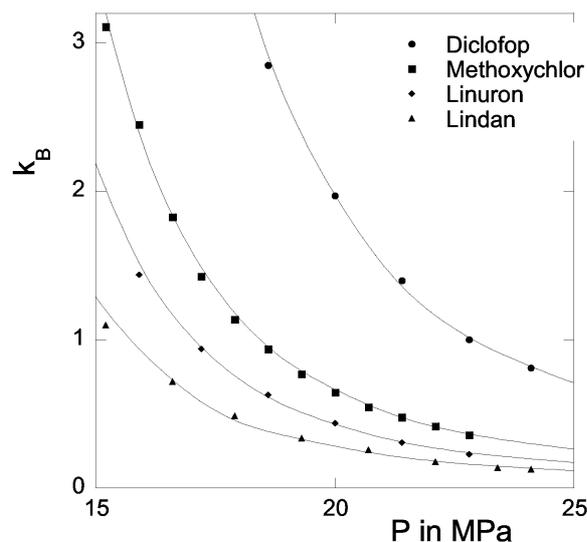


Fig. 2. Capacity factors of selected pesticides against pressure at  $T = 393.15$  K. Regression lines from Figure 1.

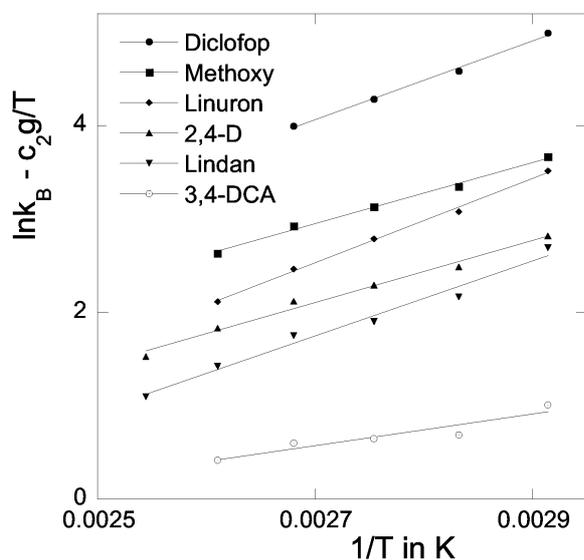


Fig. 3.  $\ln k_B - c_2g/T$  against the inverse of temperature,  $1/T$ , for six pesticides at  $P = 18.6$  MPa.

wavenumber of the absorption maximum of the solute as a function of  $g$ , which was varied by choosing the solvent (solvatochromic effect) and in the analysis of the solubility data in [13].

Equation (47) suggests that plotting the quantity  $\ln k_B - c_2g/T$  against the inverse of the temperature,  $1/T$ , at constant pressure should give straight lines with a slope  $c_1$  which is determined according to (49) by the molecular quantities  $\Delta_{tr}h_B^\circ$  and  $\bar{E}_C$ . This is in-

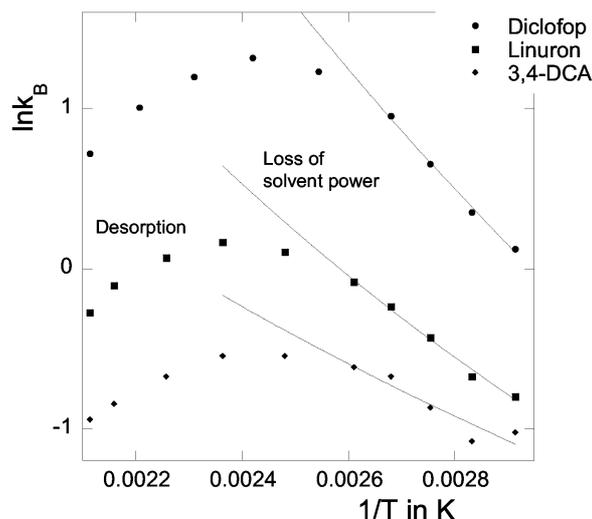


Fig. 4.  $\ln k_B$  against  $1/T$  for selected pesticides at  $P = 18.6$  MPa. Lines are calculated according to (47) which takes into account the loss of solvent power due to the very large volume thermal expansion of the supercritical CO<sub>2</sub> but does not include the phenomenon of desorption at high temperature.

deed confirmed in Fig. 3 for all the pesticides at  $P = 18.6$  MPa (Diclofopmethyl data are omitted again for clarity). Except for the 3,4-Dichloraniline data, which have a regression coefficient  $r = 0.94$ , all other data have regression coefficients better than  $r = 0.99$ . However, quite abruptly at 393.15 K the data begin to deviate strongly from the straight lines. This is attributed to the phenomenon of desorption, as mentioned above, which may be controlled by equilibrium according to Le Châtelier's principle as well as by the kinetics of the (endothermic) desorption reaction with a high energy of activation.

From the slopes of the data in Fig. 3 according to (49) typical values of the quantity  $\Delta_{tr}h_B^\circ - \bar{E}_C$  are obtained in the range from  $-27$  kJ mol<sup>-1</sup> to  $-35$  kJ mol<sup>-1</sup> (except for the 3,4-Dichloraniline with a low value of  $-14$  kJ mol<sup>-1</sup>). With  $P = 18.6$  MPa and assuming again a typical molar volume of  $v = 10^{-4}$  m<sup>3</sup> mol<sup>-1</sup>, the energy needed to create a cavity in the solvent equal to the size of the solute is estimated to be  $\bar{E}_C = Pv = 1.86$  kJ mol<sup>-1</sup>. If this is neglected, the slopes in this plot give transition enthalpies within the range of 0 to 40 kJ mol<sup>-1</sup>, which is usual for the heat evolved in physical adsorption. The values from the slopes are, however, not consistent with those from the intercept (by about a factor of three) suggesting that additional constants are required in (48).

Finally, representative experimental  $\ln k_B$  data at  $P = 18.6$  MPa are plotted against  $1/T$  in Fig. 4. Also plotted on this graph are the predicted lines from (47) with the constants  $c_0$ ,  $c_1$  and  $c_2$  for each molecule obtained from the pressure and temperature runs as explained above. As  $T$  increases, these lines reflect the loss of solvent power due to the huge thermal expansion of the supercritical fluid. Beyond  $T = 393.15$  K, where the solvent has lost its liquidlike density, the retention should increase without bound. The desorption phenomenon, which is expected both on equilibrium and kinetic grounds, reverses the trend, and the capacity factor now decreases rapidly.

This work represents an attempt to a systematic study of the solute solvent interactions in both phases of the chromatographic column, following the seminal contributions of Liptay and his associates. Future efforts should concentrate on an accurate description of the interactions in both phases with a wider range of molecules and experimental conditions.

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