## Partition-Sorption Model for Describing Non-Specific Selectivity in Reversed-Phase Liquid Chromatography

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# PARTITION-SORPTION MODEL FOR DESCRIBING NON-SPECIFIC SELECTIVITY IN REVERSED-PHASE LIQUID CHROMATOGRAPHY

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## ABSTRACT

A combined partition-sorption mechanism is used to model the dependence of the non-specific selectivity on mobile phase composition. This dependence is described by an equation, which in addition to additivity terms, contains a term that takes into account the difference in the compositions of solvents in both mobile and stationary phases. It is shown that this term is proportional to the excess sorption isotherm which characterizes interactions of solvents with a chemically bonded phase. An illustrative example is presented using selectivity data for binary hydro-organic eluents on octadecyl bonded phases.

## INTRODUCTION

The incremental non-specific selectivity, $\alpha_{CO}$ for adjacent members in

a homologous series[1] is frequently used to study the hydrophobic

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interactions in reversed-phase liquid chromatography (RPLC)[1-3]. At a

constant mobile phase composition and in the cases where steric effects are

not significant the natural logarithm of $\alpha_C$ is constant over a range of

homolog pairs[1,2] and can be determined from the slope of a plot of $\ln k'_n$

vs. n. i.e.,

$$s = d \ln k'_n/dn = \ln \alpha_C = \ln (k'_{n+1}/k'_n) \tag{1}$$

where $k'_{n+1}$ and $k'_n$ are respectively the capacity factors for solutes with

n+1 and n carbon atoms.

Typically, when water-methanol is used as the mobile phase the

dependence of s on eluent composition is nearly linear over a wide range [1-

6]. However, non-linearity is observed for a majority of other mixed eluents,

e.g., water-acetonitrile, water-tetrahydrofuran and water-isopropanol[1,3-6] due

to differences in composition between the mobile phase and solvents that

are intercalated into the stationary (surface) phase[6].

In the current study the thermodynamic dependence of s on mobile

phase composition has been modeled via a combined partition-sorption

mechanism[7-9] which treats both the competitive interactions of solute and

solvent molecules with the chemically bonded phase as well as solute-

solvent and solvent-solvent interactions in the mobile and stationary phases.

## THEORY

In RPLC a solute's distribution between a binary eluent and a chemically bonded phase (CBP) is primarily controlled by differences in the interaction energies of the solute with the components of the mobile and stationary phases. From a thermodynamic viewpoint the distribution process is similar to classical partitioning of a compound between two immiscible liquids and can be expressed as the ratio of the solute's activity coefficients in the phases[7]. However, in contrast to classical partitioning the distribution process in RPLC with CBP is more complex because the composition of solvents that are incorporated into the stationary phase may not be either identical to or a simple linear function of the mobile phase's composition. Preferential sorption of one of the solvents into the stationary phase can be described in terms of a competitive sorption mechanism[7] and a partitioning mechanism can be used to model the distribution of a solute between both phases (i.e. a combined a partition-sorption (PS) model). For binary hydro-organic mobile phases the PS model leads to an expression for the capacity factor, $k'_n$, of a homolog with n carbon atoms in its alkyl chain[8,9]:

$$\ln k'_n = \phi'_o \ln k'_{n(o)} + \phi'_w \ln k'_{n(w)} + (\phi^\sigma_o - \phi'_o) [\ln \kappa_{n(o/w)} + \ln$$

$$(k'_{n(o)}/k'_{n(w)}] - \phi'_w \ln K_{ow} + \beta^\sigma_{ow} \phi^\sigma_o \phi^\sigma_w - \beta'_{ow} \phi'_o \phi'_w \qquad (2)$$

where $k'_{n(o)}$ and $k'_{n(w)}$ are the capacity factors for a solute in either the pure

organic solvent (o) or water (w). The volume fractions of organic solvent

and water in the mobile phase ($\ell$) are respectively, $\phi^\ell_o$ and $\phi^\ell_w$ and in the

stationary (surface) phase ($\sigma$) they are $\phi^\sigma_o$ and $\phi^\sigma_w$. The remaining four

terms in eqn. 2 describe contributions to $\ln k'_n$ associated with: (term 3) the

hypothetical partition coefficient, $\kappa_{n(o/w)}$, of the solute between the organic

and water phases, (term 4) the competitive sorption of solvents

characterized by the equilibrium constant $K_{ow}$ and (terms 5 & 6) the

organic-water interaction parameters, $\beta^\sigma_{ow}$ and $\beta^\ell_{ow}$, for the stationary and

mobile phases.

Since the concentration of the solute can be assumed to be infinitely

low, the sum of the volume fractions of both solvents in each phase is

equal to unity, i.e.,

$$\phi^\ell_o + \phi^\ell_w = \phi^\sigma_o + \phi^\sigma_w = 1 \tag{3}$$

Thus, equation 2 can be transformed into a slightly different form:

$$\ln k'_n = \phi^\sigma_o \ln k'_{n(o)} + \phi^\sigma_w \ln k'_{n(w)} + (\phi^\sigma_o - \phi^\ell_o) \ln \kappa_{n(o/w)}$$
$$- \phi^\ell_w \ln K_{ow} + \beta^\sigma_{ow} \phi^\sigma_o \phi^\sigma_w - \beta^\ell_{ow} \phi^\ell_o \phi^\ell_w \tag{4}$$

Since the constant $K_{ow}$ is independent of the solute and the

interaction parameters $\beta^\ell_{ow}$ and $\beta^\sigma_{ow}$ are only slightly dependent on the

solute, eqns. 2 and 4 can be rewritten in terms of the logarithm of the non-specific selectivity, s (cf., eqn. 1):

$$s = \phi'_o s_o + \phi'_w s_w + (\phi^\sigma_o - \phi'_o) (s^\bullet_{(o/w)} + s_o - s_w) \tag{5}$$

and

$$s = \phi^\sigma_o s_o + \phi^\sigma_w s_w + (\phi^\sigma_o - \phi'_o) s^\bullet_{(o/w)} \tag{6}$$

In the above expressions the quantities $s_o$, $s_w$ and $s^\bullet_{(o/w)}$ are defined as follows:

$$s_o = \ln \alpha_{C(o)} = \ln (k'_{n+1(o)}/k'_{n(o)}) \tag{7}$$

$$s_w = \ln \alpha_{C(w)} = \ln (k'_{n+1(w)}/k'_{n(w)}) \tag{8}$$

$$s^\bullet_{(o/w)} = \ln (\kappa_{n+1(o/w)}/\kappa_{n(o/w)}) \tag{9}$$

At lower concentrations of the organic[6] for some RPLC systems the quantity s is satisfactorily represented by the first two terms in eqn. 6. In more general cases, the full form of eqn. 5 is necessary to describe the dependence of s on mobile phase composition. The first two terms of eqn. 5 represent the additivity of s with respect to the composition of the mobile phase and the third term is used to account for deviations of s due to differences in composition of the organic solvent between the mobile and stationary phases, $\phi^\sigma_o - \phi'_o$.

In certain cases the values $s_o$ and $s_w$ can be obtained from chromatographic retention measurements carried out using the individual solvents.[1,4,10]. In other cases these values must be evaluated by extrapolation of the $s(\phi'_w)$ - dependence to $\phi'_w = 0$ and $\phi'_w = 1$.[1,4,6] If the values for $s_o$ and $s_w$ are known, eqn. 5 contains only $s^\bullet_{(o/w)}$ and $\phi^\sigma_o$, as unknown quantities and the surface composition $\phi^\sigma_o$ can be evaluated independently by measuring the excess sorption isotherm for the organic-water liquid mixture in contact with the chemically bonded phase.[11] Evaluation of $\phi^\sigma_o$ by this latter procedure is not easy for RPLC systems because the thickness of the stationary phase can change with mobile phase composition. Alternatively $\phi^\sigma_o$, and $s^\bullet_{(o/w)}$ can be determined chromatographically from $s(\phi'_w)$ - data.

If the organic solvent is preferentially sorbed by the chemically bonded phase (i.e., the equilibrium constant $K_{ow} > 1$), then when it is at high concentration in the mobile phase (i.e., low concentration of water) the stationary phase will contain only a negligible amount of water and the volume fraction $\phi^\sigma_o$ can be approximated by unity, i.e.,

$$\phi^\sigma_o \approx 1 \text{ for } \phi'_o \longrightarrow 1 \tag{10}$$

Introducing eqn. 10 into eqn. 5 gives:

$$s = \phi'_o s_o + \phi'_w s_w + \phi'_w (s^\bullet_{(o/w)} + s_o - s_w) \tag{11}$$

which can be simplified to:

$$s = s_o + \phi'_w \, s^\bullet_{(o/w)} \text{ for } \phi'_w \longrightarrow 0 \tag{12}$$

For RPLC systems where assumption 10 above holds, equation 12 predicts that the low-concentration part of the $s(\phi'_w)$ - dependence should be linear with an intercept $s_o$ and a slope $s^\bullet_{(o/w)}$. Alternatively $s^\bullet_{(o/w)}$ can be evaluated from the excess selectivity function, which at low values of $\phi'_w$ is proportional to $\phi'_w$:

$$s - \phi'_o \, s_o - \phi'_w \, s_w = (s^\bullet_{(o/w)} + s_o - s_w)\phi'_w \tag{13}$$

In doing this the values of s in the individual pure solvents (i.e., $s_o$ and $s_w$) must be known and then $s^\bullet_{(o/w)}$ can be evaluated from the slope of the excess selectivity function in a region of the curve obtained for low values of $\phi'_w$.

The excess selectivity function provides information about the excess sorption isotherm. For RPLC systems the excess sorption isotherm of organic solvent can be evaluated by dividing the excess selectivity function by $s^\bullet_{(o/w)} + s_o - s_w$, i.e.,

$$\phi^\sigma_o - \phi'_o = (s - \phi'_o s_o - \phi'_w s_w)/(s^\bullet_{(o/w)} + s_o - s_w) \tag{14}$$

Equation 14 provides a simple means of estimating the sorption excess, $\phi^{\sigma}{}_{o}$ - $\phi^{t}{}_{o}$, of organic solvent in a chemically bonded phase. In doing this, it should be noted that best results are obtained if chromatographic measurement are made over a wide range of mobile phase compositions and a large number of experimental points are obtained at the high-concentration region of the organic solvent; the data in this region are used to evaluate $s^{*}{}_{(o/w)}$.

## EXPERIMENTAL

In the current paper the methylene selectivity data published by Colin et al.[1] were used to evaluate the excess sorption isotherms according to eqn. 14 for three RPLC systems. These data tabulated as $s = \ln \alpha_{C}$ vs. $\phi^{t}{}_{w}$ were used because they cover a wide range of mobile phase concentrations. The values of s for each hydro-organic mobile phase were calculated from the arithmetic average of the results for five different series of homologs and two packing materials. The homologs were n-alkanes, n-alkylbenzenes, n-chloroalkanes, n-methylesters and n-alcohols. These solutes were chromatographed at a temperature of $298 \pm 0.2K$ using binary combination of water and methanol, acetonitrile and tetrahydrofuran as the mobile phase. The packing materials were Lichrosorb RP 18 (Merck) and Hypersil ODS (Shandon). Other experimental are given in the original paper.[1]
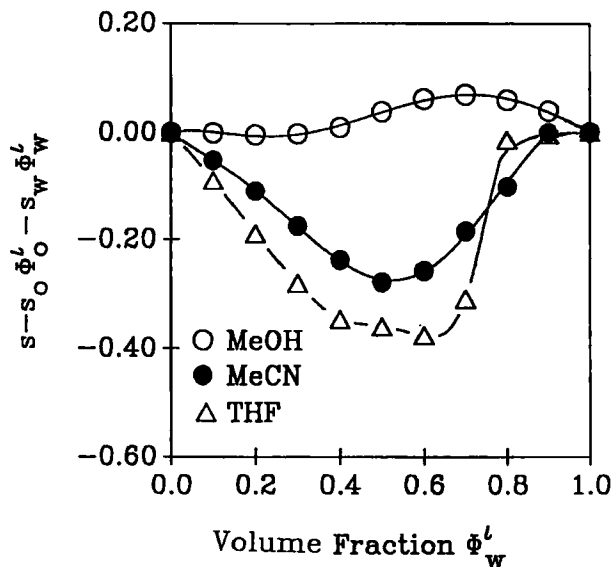
Fig. 1 Excess selectivity function $s\text{-}s_o\phi^l_o - s_w\phi^l_w$ plotted against $\phi^l_w$ for binary hydro-organic mobile phases with methanol (MeOH), acetonitrile (MeCN) and tetrahydrofuran (THF).

## RESULTS AND DISCUSSION

Shown in Fig. 1 are plots of the excess selectivity function $s\text{-}s_o\phi^l_o - s_w\phi^l_w$ vs the volume fraction $\phi^l_w$ for three different binary hydro-organic mobile phases, i.e., water-methanol, water-acetonitrile and water-tetrahydrofuran. These data were calculated from the methylene selectivity data reported by Colin et al.[1]. For the water-methanol mobile phase the excess selectivity function oscillates slightly about zero and thus to a good approximation it is additive with respect to $s_o$ and $s_w$, and the third term in

eqn. 5 can be neglected. These results are in agreement with previous studies[6] where the composition of both the mobile phase and stationary phase were found to be similar when binary combination of water-methanol are used as the eluent (i.e., $\phi^{\sigma}_0 - \phi^t_0 \sim 0$).

Although the excess selectivity functions for water-acetonitrile and water-tetrahydrofuran were negative over the whole range of binary concentrations, the data were fitted well at low-concentrations by eqn. 13 which was used to calculate values of $s^*_{(o/w)}$. For acetonitrile-water $s^*_{(o/w)}$ = 0.47, whereas for tetrahydrofuran-water $s^*_{(o/w)}$ = 0.68. Since in both systems $s^*_{(o/w)} > 0$, the hypothetical partition coefficients of the methylene group are greater than unity, i.e., the methylene group favors organic phase. This effect is stronger for tetrahydrofuran (i.e., larger value of $s^*_{(o/w)}$) than acetonitrile.

The excess selectivity can be used to evaluate the excess sorption isotherm, $\phi^{\sigma}_0 - \phi^t_0$, via eqn. 14. The value of $s_w$ reported by Colin et al.[1] was 1.36 and the values of $s_0$ were respectively 0.25 and 0.0 for acetonitrile and tetrahydrofuran. By substituting these values along with the values of $s^*_{(o/w)}$ into eqn. 14 the excess selectivity functions shown in Fig. 1 can be converted into the excess sorption isotherms (cf., Fig. 2). The excess sorption isotherms of acetonitrile and tetrahydrofuran are positive over the whole concentration region due to preferential sorption of the organic solvent by the alkyl bonded phases. These results are in good agreement with the other studies.[6,11]
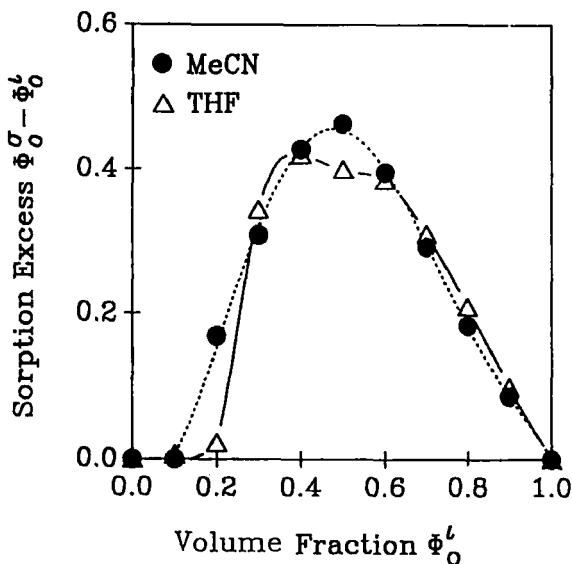
Fig. 2 Excess sorption isotherms of acetonitrile (MeCN) and tetra-
hydrofuran (THF) from water on an octadecyl bonded phase.

The current example has been used to demonstrate that excess

selectivity data provide information about the difference in the

compositions of solvents in both phases. Conversion according to eqn. 14

of the excess selectivity function, $s-s_o \phi^l_o -s_w \phi^l_w$, to the sorption excess,

$\phi^\sigma_o - \phi^l_o$, requires accurate selectivity data, which permit evaluation of the

realistic values of $s_o$, $s_w$ and $s^*_{(o,w)}$. The knowledge of an accurate

proportionality factor between the selectivity and sorption excesses (cf.,

eqn. 14) is especially important for comparing the sorption excesses of

different organic solvents.

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