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STUDIES OF ADSORPTION AND PARTITION EFFECTS IN LIQUID CHROMATOGRAPHY WITH MIXED MOBILE PHASES

M. BORÓWKO and M. JARONIEC*

Institute of Chemistry, M. Curie-Skłodowska University, 20-031 Lublin (Poland)

SUMMARY

A general theory of liquid chromatography with mixed mobile phases formulated previously was utilized to study quantitatively the adsorption and partition effects in solute retention. The competitive adsorption of the solute and solvent was found to influence significantly the values of the distribution coefficient, whereas the solute-solvent interactions control mainly the shape of the dependence of this coefficient on the mobile phase composition.

The mechanism of solute retention in liquid chromatography with mixed mobile phases is mainly determined by the competitive adsorption of solute and solvent molecules (adsorption mechanism) and the differentiated interactions of solute molecules with solvent molecules in the stationary and mobile phases¹⁻⁴. If the adsorption effects are negligible then the source of the distribution of solute molecules between the surface-influenced stationary phase and the mobile phase is the differentiation in the solute-solvent interactions in both phases. The physical nature of this solute retention mechanism is analogous to classical partitioning and therefore it was called the "partition mechanism"². The adsorption mechanism of solute retention dominates in normal-phase liquid-solid chromatography, whereas the partition mechanism dominates in reversed-phase liquid chromatography. In previous papers^{2,3} a general theory of liquid chromatography was formulated for describing the adsorption and partition mechanisms of solute retention. Here, this theory is applied to study quantitatively the influence of these mechanisms on the dependence of the distribution coefficient on the mobile phase composition.

Let us consider retention of the s -th solute in a binary mixed solvent^{1,2}. For simplicity, let us assume that the molecules of both solvents have the same size. The equilibrium between the two solvents in the mobile phase and the surface-influenced stationary phase is described by the general expression¹⁻⁴

$$K_{12} = (x_1^\sigma \gamma_1^\sigma / x_1^l \gamma_1^l) (x_2^l \gamma_2^l / x_2^\sigma \gamma_2^\sigma) \quad (1)$$

with

$$x_1^\sigma + x_2^\sigma \approx 1 \text{ for } \rho = \sigma \text{ and } l \quad (2)$$

Here K_{12} is the equilibrium constant for the phase-exchange reaction between molecules of solvents 1 and 2, x_i^{ρ} ($i = 1, 2$) denotes the mole fraction of the i -th solvent in the ρ -th phase and γ_i^{ρ} is the activity coefficient of the i -th component in the ρ -th phase and $\rho = 1$ (bulk phase) or σ (stationary phase).

The retention of the s -th solute is characterized by the distribution coefficient¹:

$$k_s = \lim_{x_s^1 \rightarrow 0} (x_s^{\sigma}/x_s^1) \quad (3)$$

A general equation for the distribution coefficient is

$$k_s = K_{s1} (y_s^1/y_s^{\sigma}) (x_1^{\sigma}y_1^{\sigma}/x_1^1y_1^1) \quad (4)$$

where K_{s1} denotes the phase exchange between molecules of the s -th solute and first solvent, and γ_s^{ρ} is the activity coefficient of the s -th solute in the ρ -th phase. When competitive adsorption fully controls solute distribution we have:

$$k_s = K_{s1} (x_1^{\sigma}/x_1^1) \quad (5)$$

In this case all activity coefficients are equal to unity. For the pure partition model the distribution coefficient is defined as follows:

$$k_s = \gamma_s^1/\gamma_s^{\sigma} \quad (6)$$

Eqn. 6 is obtained from eqn. 4 for $K_{12} = K_{s1} = K_{s2} = 1$.

The model studies of adsorption and partition effects in liquid chromatography are discussed for a strictly regular solution. The stationary phase composition is calculated from the expression

$$x_1^{\sigma} = F/(1 + F) \quad (7)$$

where

$$F = K_{12}[x_1^1/(1 - x_1^1)] \exp \{ \chi_{12}^1[(1 - 2x_1^1) - q(1 - 2x_1^1)] \} \quad (8)$$

and

$$\chi_{12}^{\sigma} = q\chi_{12}^1 \quad (9)$$

Here q is a constant equal to the ratio of the numbers of neighbours in the same lattice layer to the total number of neighbours for each lattice site.

For $K_{12} \neq 1$ the general eqn. 4 gives the following expression for the distribution coefficient, k_s

$$k_s = K_{s1} (x_1^{\sigma}/x_1^1) \exp [\alpha(x_1^1 - qx_1^{\sigma}) + \beta] \quad (10)$$

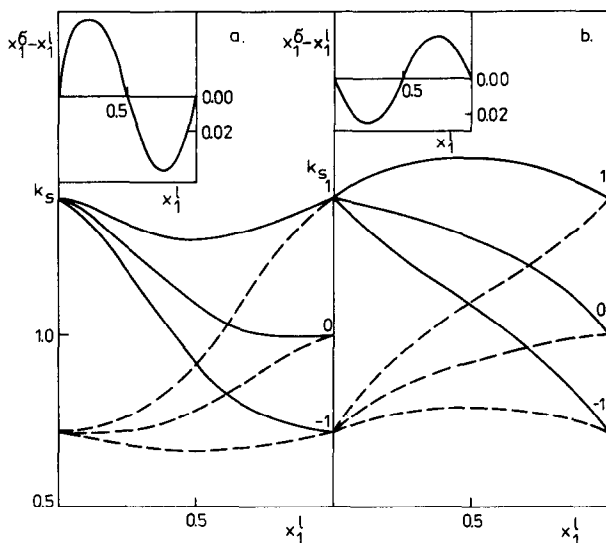


Fig.1. Partition model. Theoretical curves of k_s vs. x_1^l and the excess adsorption isotherms $n_1^e = x_1^s - x_1^l$ plotted for $\chi_{12}^1 = 1$ (a), $\chi_{12}^1 = -1$ (b) and different values of the parameters $\chi_{1s}^1 = -1, 0, 1$ and $\chi_{2s}^1 = -1$ (---) and 1 (—); $q = \frac{2}{3}$.

where

$$\alpha = \chi_{12}^1 + \chi_{1s}^1 - \chi_{2s}^1 \quad (11)$$

$$\beta = (1 - q) (\chi_{2s}^1 - \chi_{12}^1) \quad (12)$$

and χ_{is}^1 ($i = 1, 2$) is the interaction parameter that characterizes the solution (i, s).

For the pure partition model, eqn. 6 leads to:

$$k_s = \exp\{(\chi_{1s}^1 - \chi_{12}^1) (x_1^l - qx_1^s) - \chi_{12}^1 [x_1^l (1 - x_1^l) - qx_1^s (1 - x_1^s)] + \chi_{2s}^1 (1 - q)\} \quad (13)$$

Now we will discuss the influence of the mobile phase composition on the distribution coefficient for particular retention models. First, the pure displacement model will be analysed. In this case the interaction parameter, χ_{12}^1 , is equal to zero. Then the function $k_s = k_s(x_1^l)$ has the analytical form

$$k_s = K_{s1} / [K_{21} + (1 - K_{21}) x_1^l] \quad (14)$$

where $K_{21} = 1/K_{12}$. It follows from previous papers^{1,4} that for $K_{12} > 1$ the function $k_s(x_1^l)$ decreases. For $K_{12} = K_{s1} = K_{s2} = 1$ the distribution of a solute between two phases occurs according to the partition mechanism. Fig. 1 shows the function $k_s(x_1^l)$ calculated according to eqn. 13. From this figure we can conclude that: (i) the function $k_s(x_1^l)$ may be strictly decreasing for $\chi_{2s}^1 > \chi_{1s}^1$ or increasing for $\chi_{2s}^1 < \chi_{1s}^1$; (ii) this

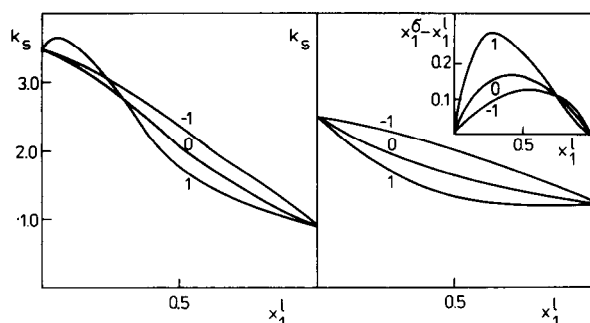


Fig. 2. Mixed model. Theoretical curves of k_s vs. x_1^I and the excess adsorption isotherm for $K_{12} = 2$, $K_{s1} = 1.25$, $\chi_{1s}^I = -1$, $\chi_{2s}^I = 1$ (left), $\chi_{1s}^I = \chi_{2s}^I = 0$ (right) and different values of the parameter $\chi_{12}^I = -1, 0, 1$; $q = \frac{2}{3}$.

function may have one extremum, a maximum for $\chi_{12}^I < 0$ or a minimum for $\chi_{12}^I > 0$; (iii) solute-solvent and solvent-solvent interactions affect the solute retention in quite different ways, an increase in χ_{1s}^I and χ_{2s}^I causing an increase in the distribution coefficient, whereas the opposite effect is observed when χ_{12}^I increases. The excess adsorption isotherms ($x_1^I - x_1^I$) associated with the curves $k_s(x_1^I)$ are also presented in Fig. 1.

In the case of mixed solute retention for particular values of the parameters χ_{1s}^I and χ_{2s}^I , the curves $k_s(x_1^I)$ corresponding to different values of the parameter χ_{12}^I may interact. For $x_1^I \rightarrow 0$ an increase in χ_{12}^I causes an increase in the distribution coefficient; the opposite effect is observed for high concentrations of the first solvent (Fig. 2). When the adsorption constants are sufficiently high a maximum in such a curve can occur even for mixed solvents characterized by a positive deviation from Raoult's law.

Fig. 3 presents a comparison of the curves k_s vs. x_1^I and the excess adsorption isotherms calculated for different models of solute retention. Curve 1 is for the mixed model. In this case the solute retention is caused by the difference in adsorption potentials of the solute and solvents, and the difference in the solute-solvent

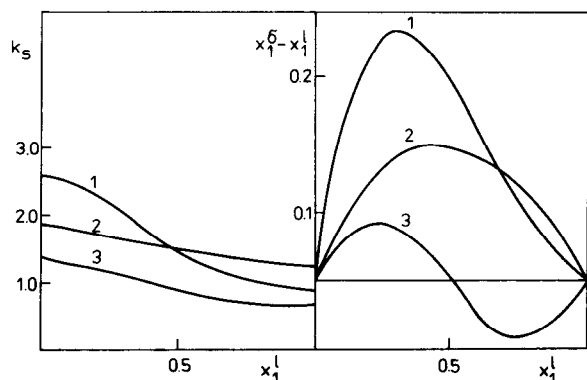


Fig. 3. Comparison of solute retention models: mixed model with $K_{s1} = 1.25$, $K_{12} = 1.5$, $\chi_{1s}^I = 1$, $\chi_{2s}^I = -1$, $\chi_{12}^I = 1$ (curve 1); displacement model with $K_{s1} = 1.25$, $K_{12} = 1.5$, $\chi_{12}^I = \chi_{1s}^I = \chi_{2s}^I = 0$ (curve 2) and partition model with $K_{s1} = K_{s2} = K_{12} = 1$, $\chi_{1s}^I = 1$, $\chi_{2s}^I = -1$ and $\chi_{12}^I = 1$ (curve 3); $q = \frac{2}{3}$.

interactions in both phases. For the system investigated the equilibrium constants are $K_{s1} = 1.25$, $K_{12} = 1.5$. Curve 2 represents the pure displacement (adsorption) model; it was calculated for $\chi_{12}^1 = \chi_{1s}^1 = \chi_{2s}^1 = 0$ and the remaining parameters were the same as for curve 1. Curve 3 corresponds to the pure partition model. From Fig. 3, the interactions with the adsorbent surface (adsorption effects) have a predominant influence on the value of the distribution coefficient, however the partition effects control the course of the dependence of the distribution coefficient on the mobile phase composition.

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