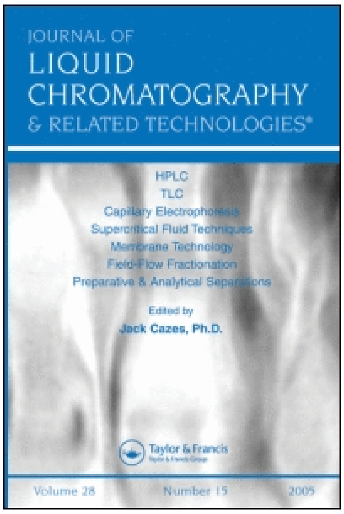

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A Model of Liquid Adsorption Chromatography Involving Solute-Solvent Interaction in the Mobile Phase, Energetic Heterogeneity of the Adsorbent, and Differences in Molecular Sizes of Solute and Solvents

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A MODEL OF LIQUID ADSORPTION CHROMATOGRAPHY INVOLVING SOLUTE-SOLVENT INTERACTION IN THE MOBILE PHASE, ENERGETIC HETEROGENEITY OF THE ADSORBENT, AND DIFFERENCES IN MOLECULAR SIZES OF SOLUTE AND SOLVENTS

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ABSTRACT

A simple model for liquid-solid chromatography (LSC) process with mixed mobile phases has been proposed. According to this model the LSC process is represented by suitable reversible phase-exchange reactions between molecules of solute and solvents and reversible solute-solvent reactions in the mobile phase. These reactions describe the competitive adsorption of solute molecules and formation of solute-solvent complexes in the mobile phase. Analytical equations for the capacity ratio, derived in terms of the model, involve solute-solvent interaction in the mobile phase, differences in molecular sizes of solute and solvents, energetic heterogeneity of the adsorbent and ideality of the

surface phase. Linear forms of these equations are very convenient for analysing the experimental chromatographic data.

INTRODUCTION

Theoretical and experimental studies of LSC with mixed mobile phases show that this process is determined by many factors. They are :

(a) competitive character of solute and solvent adsorption,

(b) non-specific solute-solvent and solvent-solvent interactions in the mobile and surface phases,

(c) specific solute-solvent and solvent-solvent interactions in the mobile and surface phases,

(d) dissociation of solutes in the mobile phase,

(e) differences in molecular sizes of solutes and solvents,

(f) energetic heterogeneity of the adsorbent and topography of adsorption sites onto surface,

(g) multilayer character of the surface phase and partition effects in LSC process, and

(h) orientation of solute and solvent molecules in the surface phase.

Quantitative estimation of the above effects was discussed by many authors (1-26). The most popular approach to LSC with binary mobile phases has been formulated by Snyder (1,2), which assumes the competitive character of solute and solvent adsorption. This approach involves also energetic heterogeneity of the solid surface (1) and solute-solvent localization effects (3). Recently, Snyder's treatment has been developed for LSC with multicomponent mobile phases (4-6). The LSC model of Snyder (1,2), described exactly in the review of Snyder and Poppe (7), has been considerably enriched by Soczewiński's studies (8, 9). On the other hand, Jaroniec et al.(10-17) described theoretically the LSC process by applying the general theory of adsorption from multicomponent liquid mixtures on solid surfaces and utilizing the fundamental studies of Snyder (1,2) and Soczewiński (8,9). The treatment of Jaroniec et al. involves energetic heterogeneity of the solid (10,12,15), non-ideality of both phases (10,11,13,14), differences in molecular sizes of solutes and solvents (13,14),and solute - solvent and solvent-solvent interactions (16,17). Recent studies of Jaroniec et al.(13,14,26) concern the correlation between adsorption and chromatographic parameters.

In this paper we shall present a general description of LSC process involving the formation of

solute-solvent complexes in the mobile phase, energetic heterogeneity of the solid surface, and differences in molecular sizes of solute and solvents.
In this description the most important factors determining the LSC process are considered.

GENERAL CONSIDERATIONS

Let us consider the LSC process for the s-th substance (solute) chromatographed in n-component eluent. The components of the mixed eluent are numbered successively beginning from the most efficient eluting solvent to the weakest solvent. Thus, 1-st solvent is the more efficient one, however, n-th component is the weakest solvent. One of the main assumptions of the proposed model is that concerning the competitive character of solute adsorption. The adsorption process may be represented by the following reversible phase-exchange reactions (10) :

$$i_{(m)} + n_{(s)} \rightleftharpoons i_{(s)} + n_{(m)} \quad \text{for } i=1,2,\ldots,n-1 \quad (1)$$

$$s_{(m)} + r\, i_{(s)} \rightleftharpoons s_{(s)} + r\, i_{(m)} \quad \text{for } i=1,2,\ldots,n \quad (2)$$

where the subscripts (m) and (s) refer to the mobile and surface phases, respectively, "i" and "s" denote molecules of the i-th solvent and s-th solute, and r is the ratio of molecular sizes of the s-th solute and i-th solvent. The reactions 1 and 2 have been written by assuming the equality of molecular sizes of all solvents, i.e.,

$$w_1 = w_2 = \cdots = w_n = w \tag{3}$$

and inequality of molecular sizes of solute and solvents :

$$w_s \neq w \tag{4}$$

Thus, the parameter r is defined as follows :

$$r = w_s/w \tag{5}$$

The next assumptions are following :

(a) non-specific interactions between molecules of solute and solvents in the mobile phase are neglected,

(b) the surface phase is assumed to be monolayer and ideal,

(c) molecules of the s-th solute form complexes with molecules of 1-st solvent in the mobile phase,

(d) the total number of moles of all solvents in the surface phase is constant and independent upon the presence of solute molecules, because the solute concentration is infinitely low,

(e) molecules of solute and solvents have a spherical shape,

(f) the adsorbent surface may be energetically homogeneous and heterogeneous.

Since, the surface phase is ideal, the adsorption depends upon the global distribution of adsorption sites, however, it is independent upon topography of adsorption sites onto surface (27).

It means that our theoretical considerations, concerning heterogeneous adsorbents, are valid for solids showing random and patchwise distribution of adsorption sites onto surface.

Now, we shall return to the assumption (c). According to this assumption, molecules of the s-th solute form associates with molecules of the most efficient eluting solvent in the mobile phase. However, the silanol groups of the silica surface can compete with complexes in the surface phase. Thus, stronger interactions of molecules of the s-th solute and 1-st solvent with the silica silanols can preclude solute-solvent interactions in the surface phase. Taking into account the possibility of destruction of the solute-solvent complexes in the surface phase by the silica silanols, we assume that these complexes form only in the mobile phase. Moreover, let us assume that one molecule of the solute can bound q molecules of 1-st solvent according to the following reaction :

$$s_{(m)} + q\ 1_{(m)} \rightleftharpoons 1_q s_{(m)} \qquad (6)$$

where $1_q s_{(m)}$ denotes the (q+1)-molecular complex in the mobile phase.

In the next section equations for the capacity ratio will be discussed by using the assumptions (a) - (f). However, in the Appendix we shall discuss the possibility of extension of these equations by applying the additional assumption that molecules of 1-st solvent form p-molecular complexes.

EQUATIONS FOR THE CAPACITY RATIO

Homogeneous surfaces

According to Snyder (1) the capacity ratio for the s-th solute, k'_s , chromatographed in the mixed mobile phase is proportional to the distribution coefficient k_s :

$$k'_s = \beta\ k_s \qquad (7)$$

where

$$k_s = y^o_s / x^o_s \qquad (8)$$

and y^o_s and x^o_s are the total mole fractions of the s-th solute in the surface and mobile phases, respectively, however, β is characteristic for a given adsorbent and independent upon the eluent nature in a good approximation.

The thermodynamic equilibrium constant relating to the reaction between molecules of the s-th solute and 1-st solvent on a homogeneous surface is :

$$K_{1s} = (y_s/x_s)\cdot(x_1/y_1)^r \tag{9}$$

However, the equilibrium constant for the reaction 6 is expressed as follows :

$$L_q = x_q/(x_s\, x_1{}^q) \tag{10}$$

In the above x_s and y_s are the mole fractions of single molecules of the s-th solute in the mobile and surface phases,respectively, x_q is the mole fraction of the complex $1_q s$ in the mobile phase defined as the ratio of the number of complexes $1_q s$ to the total number of molecules in the mobile phase.

The total mole fractions of the s-th solute and all solvents in the mobile and surface phases may be expressed as follows :

$$y_s^o = y_s \tag{11a}$$

$$y_i^o = y_i \quad \text{for } i=1,2,\dots,n \tag{11b}$$

$$x_s^o = x_s + x_q = x_s + L_q x_s x_1{}^q \tag{12a}$$

$$x_1^o = x_1 + q x_q = x_1 + qL_q x_s x_1{}^q \approx x_1 \tag{12b}$$

$$x_i^o = x_i \quad \text{for } i=2,3,\dots,n \tag{12c}$$

Equations 7,8,9,11 and 12 give :

$$k'_s = \beta K_{1s} (y_1/x_1)^r/(1 + L_q x_1{}^q) \qquad (13)$$

or

$$\lg k'_s = \lg(\beta K_{1s}) + r \lg(y_1/x_1) - \lg(1+L_q x_1{}^q) \qquad (14)$$

For the special values of r , q and L_q equations 13 and 14 give the majority of the well-known relationships. For $L_q = 0$ (absence of solute-solvent interaction) equation 14 gives the expression derived by Jaroniec et al.(13) ; it is :

$$\lg k'_s = \lg(\beta K_{1s}) + r \lg (y_1/x_1) \qquad (15)$$

If 1-st solvent is considerably strongly adsorbed than other solvents, the mole fraction y_1 is close to unity for the whole concentration region except the low concentrations of x_1. Then, equation 15 becomes the most popular expression, called as Snyder - Soczewiński relationship (7) :

$$\lg k'_s = \lg(\beta K_{1s}) - r \lg x_1 \qquad (16)$$

For $r=1$, $y_1=1$ and $q=1$ equation (13) reduces to the expression obtained by Soczewiński (8), Jaroniec and Piotrowska (16) :

$$k'_s = \beta K_{1s}/[x_1(1 + L_1 x_1)] \qquad (17)$$

However, for r=1 (identical molecular sizes of solute and solvents) and $L_q=0$ equation 13 gives :

$$k'_s = \beta K_{1s}(y_1/x_1) \tag{18}$$

Expressing the mole fraction y_1 by (15) :

$$y_1 = K_{1n}x_1/(x_n + \sum_{j=1}^{n-1} K_{jn}x_j) \tag{19}$$

and taking into account the following equalities :

$$K_{jn} = k'_{ns}/k'_{js} \tag{20a}$$

$$k'_{1s} = \beta\ K_{1s} \text{ for } L_q = 0 \tag{20b}$$

we have :

$$1/k'_s = \sum_{j=1}^{n} (x_j/k'_{js}) \tag{21}$$

Equation 21 has been derived by Jaroniec et al.(15) and it is equivalent with Snyder's fundamental assumption (1) :

$$k'_s = \sum_{j=1}^{n} y_j\ k'_{js} \tag{22}$$

where k'_{js} is the capacity ratio of the s-th solute chromatographed in the j-th pure solvent.

Equation 13 may be transformed to the following linear form :

$$y_1{}^r/(k'_s x_1{}^r) = (\beta K_{1s})^{-1} + (L_q/\beta K_{1s})\ x_1{}^q \tag{23}$$

Two special cases of equation 23 are interesting for analysis of the chromatographic data. They are obtained from equation 23 for $r = 1$:

$$y_1/(k'_s\, x_1) = (\beta K_{1s})^{-1} + (L_q/\beta K_{1s})\, x_1^{\,q} \tag{24}$$

and for $q = 1$:

$$y_1^{\,r}/(k'_s x_1^{\,r}) = (\beta K_{1s})^{-1} + (L_1/\beta K_{1s})\, x_1 \tag{25}$$

The mole fraction y_1 appearing in equations 24 and 25 may be evaluated by using the analytical equation 19 or by applying the following relationship (10,13):

$$y_1 = n_1^e/n^s + x_1 \tag{26}$$

where n_1^e is the adsorption excess of 1-st solvent, which may be measured experimentally, and n^s is the total number of moles in the surface phase. Assuming $y_1 = 1$ (this assumption is frequently used in LSC) equations 24 and 25 reduce to the very simple relations :

$$1/(k'_s x_1) = (\beta K_{1s})^{-1} + (L_q/\beta K_{1s})\, x_1^{\,q} \tag{27}$$

$$1/(k'_s x_1^{\,r}) = (\beta K_{1s})^{-1} + (L_1/\beta K_{1s})\, x_1 \tag{28}$$

Equations 27 and 28 are especially convenient for interpretation of the chromatographic data, because they define k'_s in a simple way.

Heterogeneous surfaces

Let us consider a heterogeneous surface showing L types of adsorption sites. The equilibrium constant 9 for the l-th type of adsorption sites is defined as follows :

$$K_{1s,l} = (y_{s,l}/x_s)\cdot(x_1/y_{1,l})^r \tag{29}$$

Since, the equilibrium constant L_q refers to the mobile phase only, it may be assumed to be independent upon the distribution of adsorption sites onto surface. Thus, combining equations 7,8,11,12 and 29 we have :

$$k'_{s,l} = \beta K_{1s,l}(y_{1,l}/x_1)^r/(1 + L_q x_1{}^q) \tag{30}$$

where

$$k'_{s,l} = y^o_{s,l}/x^o_s = y_{s,l}/x^o_s \tag{31}$$

Following Snyder (1) and Jaroniec et al.(10,12), the capacity ratio of the s-th solute on the entire heterogeneous surface is defined as follows :

$$k'_s = \sum_{l=1}^{L} f_l\, k'_{s,l} =$$

$$[\,\beta\, x_1{}^{-r}(1+L_q x_1{}^q)^{-1}]\cdot \sum_{l=1}^{L} f_l\, K_{1s,l}(y_{1,l})^r \tag{32}$$

where

$$\sum_{l=1}^{L} f_l = 1 \tag{33}$$

and f_l is the ratio of the number of adsorption sites of the l-th type to the total number of adsorption sites.Using the approximation proposed by Jaroniec et al.(10,12) for the sum appearing in equation 32 we have:

$$k'_s = \beta K_{1s}\, y_1{}^{r/m} / [\, x_1{}^{r}(1 + L_q x_1{}^{q})] \qquad (34)$$

where m is the heterogeneity parameter,which changes from zero to unity, and K_{1s} is an averaged equilibrium constant referring to the entire surface.

Equation 34 for m=1 reduces to equation 13, which has been derived for homogeneous surfaces. However, for $L_q = 0$ it becomes the following relationship :

$$\lg k'_s = \lg(\beta K_{1s}) + (r/m)\lg(y_1/x_1{}^{m}) \qquad (35)$$

Equation 35 has been derived by Jaroniec et al.(14). The mole fraction y_1 may be calculated according to the relationship 26 or by using the following analytical equation (28) :

$$y_1 = (K_{1n}x_1)^{m} / [\, x_n + \sum_{j=1}^{n-1}(K_{jn}x_j)^{m}\,] \qquad (36)$$

Assuming in equation 34 r=1 and $L_q=0$ and applying the expression 36 for y_1 ,in which K_{jn} are equal to k'_{ns}/k'_{js} ,we have :

$$(1/k'_s)^{m} = \sum_{j=1}^{n}(x_j/k'_{js})^{m} \qquad (37)$$

Equation 37 has been derived by Jaroniec et al.(12) and it is equivalent to the following relationship :

$$k'_s = \sum_{j=1}^{n} k'_{js}\, y_j^{1/m} \tag{38}$$

However, assuming in equations 13 and 34 that $y_1 = 1$, we obtain the following expression :

$$k'_s = \beta K_{1s}/[\, x_1^r(1 + L_q x_1^q)\,] \tag{39}$$

Thus, assumption that the surface phase contains mainly molecules of 1-st solvent, i.e., $y_1=1$, eleminates influence of the energetic heterogeneity on the LSC process. The heterogeneity effects play an important role in LSC with the mixed eluents containing similar solvents ; then $y_1 \neq 1$ in a wide concentration range.

MODEL CALCULATIONS FOR LSC WITH BINARY ELUENTS

The model calculations have been performed for binary eluent "1+2" by using the following equations:

$$k'_s = \left[\left(\frac{x_1}{k'_{1s}(1+L_q)}\right)^m + \left(\frac{1-x_1}{k'_{2s}}\right)^m\right]^{-1/m} \cdot \frac{1}{(1+L_q x_1^q)} \tag{40}$$

and

$$k'_s = [\, k'_{1s}(1+L_q)\,]/[\, x_1^r(1+L_q x_1^q)\,] \tag{41}$$

where

$$k'_{1s} = \beta K_{1s}/(1 + L_q) \qquad (42)$$

Equation 40 has been obtained from equations 36 and 34 with $r=1$,however, equation 41 relates to the relationship 39.

Figure 1 shows the theoretical dependences k'_s vs. x_1 calculated according to equation 40 for different parameters m , q and L_q .All curves k'_s vs. x_1 ,presented in Figure 1, have been calculated by assuming equality of molecular sizes of solute and solvents ($r=1$).Figure 1a shows the k'_s-dependences drawn for $k'_{1s}=1$, $k'_{2s}=3$ (small difference in the elution strengths of both solvents), $L_q=0$ (neglect of the solute-solvent interactions in the mobile phase) and different values of m . The parameter m causes a reduction of the capacity ratio,when m tends to zero. Moreover, the k'_s-curves show a minimum for smaller values of m . The exact discussion concerning the influence of m on the k'_s-curves has been presented in (29).

Figure 1b shows the influence of q on the k'_s -curves. These curves,calculated for $k'_{1s}=1$, $k'_{2s}=3$, $m=1$, $L_q=1$ and $q=1,2,4$ (the solid lines),have been compared with the curve predicted by equation 21 (the dashed line); they lie above the dashed line,which is predicted by the simplest model of LSC process.

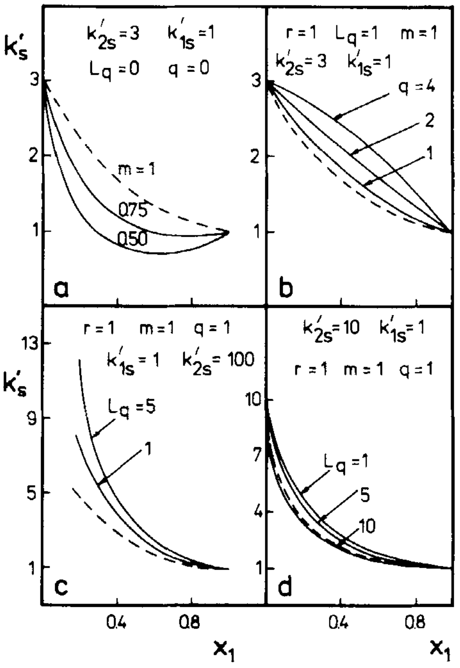

FIGURE 1 - The theoretical dependences k'_s vs. x_1 calculated according to equation 40 for different values of m , q and L_q.The dashed lines have been calculated by using equation 21 for binary eluents.

Figures 1c and 1d show the k'_s-curves calculated according to equation 40 for m=1 (energetic homogeneity of the adsorbent), q=1 (one molecule of 1-st solvent bounds one molecule of the solute) and different values of L_q . The k'_s-curves,calculated for $k'_{2s} \gg k'_{1s}$, lie above the dashed line (c.f.,Figure 1c).The distances between the solid lines and the dashed line increase gradually with increasing of L_q .The more complex behaviour of the k'_s-curves is observed for similar values of k'_{1s} and k'_{2s} (c.f.,Figure 1d).

Figure 2 shows the k'_s-curves calculated according equation 41 for $k'_{1s}=1$ and different values of r , q and L_q .These curves are compared with the Snyder - Soczewiński dependence 16 for r=1 (the dashed lines). Figure 1a presents the typical k'_s-dependences predicted by Snyder-Soczewiński relationship 16 for r = 0.5, 1 and 2 .

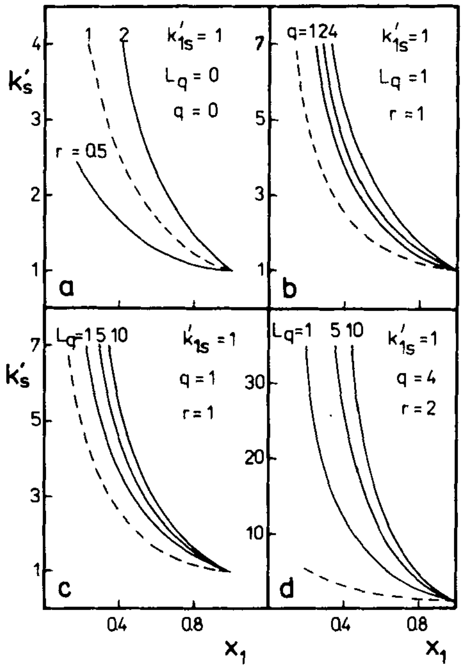

FIGURE 2 - The theoretical curves k'_s vs. x_1 calculated according to equation 41 for $k'_{1s}=1$ and different values of r , q and L_q .The dashed lines have been calculated by using Snyder-Soczewiński equation 16 .

The other parts of Figure 2 show the k'_s-curves calculated for r=1 and different values of q (Figure 2b) and L_q (Figures 2c and 2d). These curves lie above the k'_s-curve plotted according to Snyder-Soczewiński relationship 16 .The k'_s-values, calculated for a given value of x_1 ,increase with increasing of the number of 1-st solvent molecules forming complexes with one molecule of the solute (the parameter q) and solute-solvent interaction energy (it is connected with the parameter L_q).

In Figure 3 the k'_s-curves presented in Figures 2b and 2c have been plotted in the logarithmic scale. In this scale Snyder-Soczewiński relationship 16 is linear. The dependences lg k'_s vs. lg x_1 ,plotted for q=1,2,4 (Figure 3a) ,may be approximated by the straight lines, which show deviations at higher concentrations of x_1 .Similarly, the dependences lg k'_s vs. lg x_1 ,plotted for q=1 and different values of L_q ,are linear in a wide concentration region (Figure 3b). Although, these dependences have been plotted for r=1, their slopes are not equal to that predicted by Snyder-Soczewiński equation 16 .

It follows from Figure 3 that the analysis of the chromatographic data by means of Snyder-Soczewiński relationship 16 creates a difficulty in physicochemical interpretation of its slope, because a good

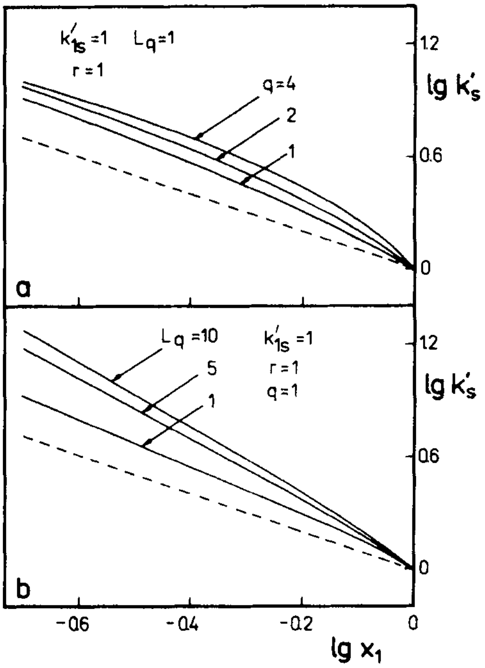

FIGURE 3 - The k'_s-curves ,calculated according to equation 41 for different values of q and L_q,plotted in the logarithmic scale.The dashed lines have been calculated by using Snyder-Soczewiński equation 16 .

linearity of the dependence of lg k'_s vs. lg x_1 is observed for different models of the LSC process.According to Snyder-Soczewiński linear plot 16 the ordinate is equal to k'_{1s} .However, the ordinates of the linear segments of the lg k'_s-plots (the solids lines in Figure 3)are not equal to k'_{1s} .This fact may be very helpfull during interpretation of Snyder-Soczewiński model of the LSC process.

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APPENDIX

The LSC model, representing by the reactions 1 , 2 and 6 , may be extended by assuming that molecules of 1-st solvent form p-molecular complexes in the mobile phase. The equilibrium constant M_p , describing the formation of the complexes in the mobile phase, may be defined in an analogous way to equation 10 :

$$M_p = x_p / x_1{}^p \tag{A.1}$$

where x_p is the mole fraction of p-molecular complexes formed by molecules of 1-st solvent in the mobile phase. Taking into account equations A.1 and 12b , the total mole fraction x_1^o may be defined as follows:

$$x_1^o = x_1 + qx_q + px_p \approx x_1 + px_p = x_1 + pM_p x_1{}^p \tag{A.2}$$

The solution of equation A.2 with respect to x_1 is a function of x_1^o , i.e.,

$$x_1 = X(x_1^o; p, M_p) \tag{A.3}$$

For two-molecular complexes (p=2), the solution of equation A.2 is the following :

$$x_1 = X(x_1^o; 2, M_2) = [(1+8M_2 x_1^o)^{1/2} - 1]/(4M_2) \tag{A.4}$$

Analytical solutions of equation A.2 are also possible for three- and four-molecular complexes, i.e., p=3 and 4 .

Combining equations 34 and A.3 , we have :

$$k'_s = \beta K_{1s}\, y_1^{\,r/m} \,[\, X(x_1^o;p,M_p)]^{-r} \cdot$$
$$[\, 1 + L_q\, X^q(x_1^o;p,M_p)\,]^{-1} \qquad (A.5)$$

For $M_p=0$ (then $p=1$) equations A.2 and A.3 give :

$$x_1 = X(x_1^o;1,0) = x_1^o \quad , \qquad (A.6)$$

however, equation A.5 becomes equation 34.

For $y_1 = 1$ we obtain the relationship analogous to equation 39 :

$$k'_s = k'_{1s}\,(1+L_qA^q)\cdot[A/X(x_1^o;p,M_p)\,]^{r} \cdot$$
$$[\, 1 + L_qX^q(x_1^o;p,M_p)\,]^{-1} \qquad (A.7)$$

where

$$A = X(1;p,M_p) \qquad (A.8)$$

$$k'_{1s} = \beta K_{1s}\, A^{-r}(1+L_qA^q) \qquad (A.9)$$

Assuming in equation A.7 that $r=1$, $q=1$ and $p=2$, we have :

$$k'_s = 16\beta K_{1s}M_2^{\,2}\,[\,(1+8M_2x_1^o)^{1/2}-1\,]^{-1}\cdot$$
$$[\, 4M_2 + L_1(1+8M_2x_1^o)^{1/2} - L_1\,]^{-1} \qquad (A.10)$$

For small values of M_2 equation A.10 gives (16,17) :

$$k'_s = \beta K_{1s}\,(x_1^o)^{-1}[\, 1 + (L_1-2M_2)x_1^o\,]^{-1} \qquad (A.11)$$

Now, we consider equation A.5 for $r=1$ and $y_1 < 1$. It means that the surface phase contains molecules of all solvents. Such situation is observed for solvents having similar adsorption energies. In the case of association of 1-st solvent in the bulk phase, the mole fraction y_1 is given by the expression analogous to equation 36 :

$$y_1 = [\, K_{1n}X(x_1^o;p,M_p)]^m / \left[x_n{}^m + [\, K_{1n}X(x_1^o;p,M_p)]^m + \sum_{j=2}^{n-1}(K_{jn}x_j)^m \right] \qquad (A.12)$$

Combining equations A.12 with A.5 for $r=1$, we have :

$$k'_s = \beta K_{1s}K_{1n} \left[x_n{}^m + [\, K_{1n}X(x_1^o;p,M_p)]^m + \sum_{j=2}^{n-1}(K_{jn}x_j)^m \right]^{-\frac{1}{m}} \cdot$$

$$[\, 1 + L_q\, X^q(x_1^o;p,M_p)]^{-1} \qquad (A.13)$$

For boundary-concentrations, i.e., $x_1^o=1$ and $x_2=x_3=\ldots=x_n=0$, we have :

$$k'_{1s} = \beta K_{1s}\, [\, A(1+L_qA^q)]^{-1} \qquad (A.14)$$

The equilibrium constants K_{jn}, K_{js} and K_{ns} fulfil the following condition :

$$K_{jn} = K_{ns}/K_{js} \qquad (A.15)$$

where

$$k'_{js} = \beta\, K_{js} \quad \text{for } j=2,3,\ldots,n \qquad (A.16)$$

Since, 1-st solvent forms p-molecular complexes in the bulk phase, the relationship between k'_{1s} and K_{1s} is more complex than that defining k'_{js} by means of K_{js} for $j > 1$ (see equations A.14 and A.16).

Taking into account the relationships A.14 and A.16 in equation A.13 ,we have :

$$k'_s = \left\{ \left[\frac{X(x_1^o;p,M_p)}{k'_{1s}A(1+L_qA^q)} \right]^m + \sum_{j=2}^{n} (x_j/k'_{js})^m \right\}^{-1/m} \cdot$$

$$[\, 1 + L_q\, X^q(x_1^o;p,M_p)]^{-1} \qquad (A.17)$$

For $n=2$, $M_p=0$ equation A.17 becomes equation 40.

Applying a similar procedure to that described above we can derive the further equations for the capacity ratio by assuming that the mobile phase contains one- , two- and p-molecular complexes of 1-st solvent and they can bound one molecule of the solute.These equations contain many parameters. Therefore,they are little interesting for analysis of the chromatographic data.