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THEORETICAL DESCRIPTION OF ASSOCIATION EFFECTS IN LIQUID ADSORPTION CHROMATOGRAPHY WITH A MIXED MOBILE PHASE

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SUMMARY

A general treatment of liquid adsorption chromatography with a mixed mobile phase, starting with Snyder's displacement model and incorporating complexation reactions between solute and solvent molecules in the mobile phase, is discussed. This treatment leads to an equation defining the dependence of the capacity ratio on the mobile phase composition by means of the thermodynamic equilibrium constants describing this displacement process and complexation reactions in the mobile and stationary phases. This equation may be considerably simplified when only one type of complex forms in the solution.

INTRODUCTION

The first theoretical concepts of liquid–solid (adsorption) chromatography (LSC) with mixed mobile phases were proposed in the 1960s[1,2] and great developments have been made since then[3–8]. The most advanced and comprehensive description of LSC process was given by Snyder[1]. His formulation is one of the most popular treatments in the LSC theory and is still being developed by his group[5,8–15], Soczewiński[3,16,17], Jandera and Churáček[6,18], Jaroniec and co-workers[7,19–26] and others[27–32].

One of the fundamental assumptions in most models of LSC processes is the competitive character of solute adsorption, which underlies the so-called displacement model introduced by Snyder[1]. This assumption reflects the main features of the process of adsorption from multi-component liquid mixtures on solids, the studies of which give the theoretical foundations of LSC with multi-component mobile phases[33,34]. Most treatments start with the original Snyder displacement model[1] and incorporate additional details, treating effects such as surface heterogeneity of the adsorbent[22,25,26,35], non-specific interactions in the mobile and stationary phases[21,23,28,36,37], changeability of the stationary phase composition[23,25,26,38], localization of solute molecules over discrete adsorption sites[8,11], complexation reactions in the mobile and stationary phases, including solvent association and solvation when specific interactions between solute and solvent

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molecules (*e.g.*, hydrogen bonding) are possible[3,8,39–45], and other phenomena that were not treated in Snyder's book[1].

In this paper we discuss an LSC model that is an extension of the displacement model[1] incorporating complexation reactions between solute and solvent molecules in the mobile and stationary phases. The complexation equilibria play an important role in many chromatographic systems[3,8,42–45]. In previous papers[39–41] simple models of LSC process assuming one kind of complexes in the mobile phase, usually two-molecular complexes, were considered. Here, a general description of LSC process, involving a simultaneous formation of different multi-molecular complexes in the mobile and stationary phase, will be presented.

A GENERAL MODEL OF LIQUID ADSORPTION CHROMATOGRAPHY INVOLVING SPECIFIC INTERACTIONS BETWEEN SOLUTE AND SOLVENT MOLECULES IN THE MOBILE PHASE

Let us consider liquid adsorption chromatography with mixed mobile phase, in which specific interactions between solute and solvent molecules cause the formation of multi-molecular mixed and pure complexes in the mobile phase. With solid surfaces that interact strongly with adsorbate molecules, *e.g.*, a silica surface, the active centres (*e.g.*, silanol groups of the silica surface) can compete with solute–solvent complexes. Thus, stronger interactions of solute and solvent molecules with the active centres can preclude molecular complexes in the stationary phase. Taking into account the possibility of destruction of solute–solvent complexes in the surface phase by active centres of the solid surface, we can assume in this section that these complexes form only in the mobile phase. Further assumptions are as follows: (a) the surface solution is ideal; (b) adsorption has a competitive character and only unassociated molecules participate in the displacement process; (c) solute and solvent molecules have spherical shapes and different molecular sizes; (d) the total number of moles of all solvent molecules in the stationary phase is constant and independent of the presence of solute molecules because of their infinitely low concentration; (e) different multi-molecular complexes can form in the mobile phase; and (f) the adsorbent surface is energetically homogeneous.

According to Snyder[1], the capacity ratio of the sth solute chromatographed in a mixed eluent k'_s is proportional to the distribution coefficient k_s:

$$k'_s = \beta k_s \tag{1}$$

where k_s is the ratio of the total molar fractions of the sth solute in the stationary and mobile phases, *i.e.*,

$$k_s = y^\circ_s / x^\circ_s \tag{2}$$

As the surface phase is assumed to be ideal, the total molar fraction of the sth solute in the surface phase, y°_s, is equal to the molar fraction of unassociated solute molecules in this phase, y_s; thus

$$k'_s = \beta y_s / x^\circ_s \tag{3}$$

The fundamental stage of the chromatographic process is the displacement of solvent molecules from the stationary phase by solute molecules contained in the mobile phase. This process may be represented by the following quasi-chemical reversible reaction:

$$s_{(m)} + r1_{(s)} \rightleftarrows s_{(s)} + r1_{(m)} \tag{4}$$

with the equilibrium constant expressed as follows

$$K_{s1} = (y_s/x_s)\,(x_1/y_1)^r \tag{5}$$

where subscripts (m) and (s) refer to the mobile and stationary phases, respectively; x_1 and y_1 are molar fractions of unassociated molecules of the 1st solvent in the mobile and stationary phases, respectively; and r is the ratio of the surface area occupied by one solute molecule to that occupied by one solvent molecule (surface areas occupied by molecules of all solvents are assumed to be identical).

According to our model, the molecules of the sth solute and 1st solvent can form $(q+1)$-molecular solvates composed from q solvent molecules and one solute molecule. This process occurring in the mobile phase may be represented as follows:

$$s_{(m)} + q1_{(m)} \rightleftarrows 1_q s_{(m)} \text{ for } q = 1,2,3,\ldots, Q \tag{6}$$

where

$$C_q = z_q/(x_s x_1^q) \tag{7}$$

and z_q is the molar fraction of $(q+1)$-molecular solvates in the mobile phase calculated to a good approximation as the ratio of the number of $(q+1)$-molecular solvates to the total number of molecules contained in the mobile phase[43]. Similarly, molecules of the 1st solvent can form p-molecular pure associates in the mobile phase. The equilibrium constant describing the formation of these associates is

$$L_p = z'_p/(x_1)^p \text{ for } p = 2,3,4,\ldots,P \tag{8}$$

where z'_p is the molar fraction of p-molecular associates of the 1st solvent in the mobile phase. This molar fraction is expressed by the ratio of the number of p-molecular associates to the total number of all molecules contained in the mobile phase. The total molar fractions of the sth solute and 1st solvent in the mobile phase containing all types of associates are expressed as follows:

$$x_s^\circ = x_s + \sum_{q=1}^{Q} z_q = x_s\left(1 + \sum_{q=1}^{Q} C_q x_1^q\right) \tag{9}$$

$$x_1^\circ = x_1 + \sum_{q=1}^{Q} q z_q + \sum_{p=2}^{P} p z'_p \approx x_1 + \sum_{p=2}^{P} p L_p x_1^p \tag{10}$$

Substituting eqn. 9 into eqn. 3 and combining it with eqn. 5, we obtain

$$k'_s = \beta K_{s1} (y_1/x_1)^r \left(1 + \sum_{q=1}^{Q} C_q x_1^q\right)^{-1} \tag{11}$$

Eqn. 11 contains the molar fractions y_1 and x_1 referring to unassociated molecules of the 1st solvent in the stationary and mobile phases, respectively. As, according to our earlier assumption, the stationary phase contains unassociated molecules only, the molar fraction y_1 is equal to the total molar fraction y_1°. However, in the case of the mobile phase the molar fraction x_1 may be evaluated by solving the following equation:

$$x_1^\circ = x_1 + \sum_{p=2}^{P} pL_p x_1^p \tag{12}$$

In eqn. 12 the summation with respect to p should be performed until a finite integer number P. This limitation of the sum appearing in eqn. 12 indicates that the mobile phase contains two-, three- and so on to P-molecular associates. For a mobile phase containing one type of solvates and one type of associates of the 1st solvent, eqns. 11 and 12 assume considerably simpler forms:

$$k'_s = \beta K_{s1} (y_1/x_1)^r (1 + C_q x_1^q)^{-1} \tag{13}$$

$$x_1^\circ = x_1 + pL_p x_1^p \tag{14}$$

Eqns. 13 and 14 were discussed in previous papers[40,41] for $q = 1$ and $p = 2$.

In some instances the equilibrium constants C_q and L_p may be approximated by the following expressions:

$$C_q = (C_1)^q \text{ for } q \geqslant 1 \tag{15}$$

$$L_p = (L_2)^{p-1} \text{ for } p \geqslant 2 \tag{16}$$

where C_1 is the constant describing annexation of one solvent molecule to the solute molecule; however, L_2 is expressed by means of the interaction energy between two solvent molecules. If we assume that the energies connected with each annexation of one solvent molecule to a given complex are identical, then the constants C_q and L_p can be expressed by eqns. 15 and 16. This means that complexes are formed gradually and the annexation process of each subsequent solvent molecule is independent of the number of solvent molecules being involved in the complex.

Taking into account eqns. 15 and 16 in eqns. 9 and 10, we obtain

$$x_s^\circ = x_s \left[1 + \sum_{q=1}^{Q} (C_1 x_1)^q\right] \tag{17}$$

$$x_1^\circ = x_1\left[1 + \sum_{p=2}^{P} p(L_2x_1)^{p-1}\right] = x_1\left[\sum_{p=1}^{P-1}(p + 1)(L_2x_1)^p\right] \quad (18)$$

When $C_1x_1 < 1$ and $L_2x_1 < 1$ for each value of x_1 and Q and P are assumed to be high numbers, then eqns. 17 and 18 may be approximated as follows:

$$x_s^\circ = x_s/(1 - C_1x_1) \text{ for } C_1x_1 < 1 \quad (19)$$

$$x_1^\circ = x_1/(1 - L_2x_1)^2 \text{ for } L_2x_1 < 1 \quad (20)$$

Solving eqn. 20 with respect to x_1, we obtain

$$x_1 = (1 + 2L_2x_1^\circ - \sqrt{1 + 4L_2x_1^\circ})/(2L_2^2x_1^\circ) \quad (21)$$

Eqns. 3, 5 and 19 give the following expression:

$$k_s' = \beta K_{s1}(y_1/x_1)^r(1 - C_1x_1) \quad (22)$$

which is analogous to eqn. 11. The molar fraction x_1 appearing in eqn. 22 is expressed by eqn. 21 and substituting it to eqn. 22 we obtain

$$k_s' = \beta K_{s1}y_1^r\left[(1 + 2L_2x_1^\circ - \sqrt{1 + 4L_2x_1^\circ})/(2L_2^2x_1^\circ)\right]^{-r} \cdot$$

$$\left[(2L_2^2x_1^\circ - C_1 - 2C_1L_2x_1^\circ + C_1\sqrt{1 + 4L_2x_1^\circ})/(2L_2^2x_1^\circ)\right] \quad (23)$$

Eqn. 23 involves the formation of multi-molecular complexes in the mobile phase, containing different numbers of solvent molecules.

SIMPLER MODELS OF LIQUID ABSORPTION CHROMATOGRAPHY WITH A MIXED MOBILE PHASE

The capacity ratio k_s' for a solute chromatographed in the mobile phase containing solute and solvent complexes is a function of the molar fraction of the 1st solvent in the stationary phase y_1. As the solute concentration in the mobile phase is infinitely low, the molar fraction y_1 is dependent on the molar fractions of all solvents in the mobile phase. It may be evaluated from the excess adsorption data measured for the 1st solvent[7,23,45] or by using isotherm equations[7,38,43]. In a chromatographic model without solvent association, the molar fraction y_1 may be expressed by the simple Everett equation[38]; however, for the system showing solvent association the expression defining y_1 should take this effect into account[43].

In most chromatographic systems the difference between the elution strengths of solvents is great. The stationary phase contains mainly molecules of the most efficient eluting solvent, *e.g.*, solvent 1. This means that for moderate and higher

concentrations of the 1st solvent in the mobile phase y_1 is equal to unity to a good approximation. For many chromatographic systems this condition is fulfilled for all values of x_1 greater than 0.15[3,7,23,34]. Putting $y_1 = 1$ in eqns. 11, 13, 22 and 23, we obtain simpler expressions defining the capacity ratio for moderate and higher values of x_1. These expressions become considerably simpler when only one type of complex is formed in the mobile phase. First, we shall consider the model involving only solvation effects in the mobile phase. Then,

$$L_p = 0 \text{ for } p = 2,3,4,\ldots \text{ and } x_1^0 = x_1 \tag{24}$$

For this model equation, k_s' may be written as follows:

$$k_s' = \beta K_{s1} (x_1^\circ)^{-r} \left[1 + \sum_{q=1}^{Q} C_q (x_1^\circ)^q \right]^{-1} \tag{25}$$

Eqn. 25 for $r = 1$ (molecular sizes of solute and solvent molecules are identical) may be transformed into a polynomial, which is very convenient for evaluating the constants C_q from chromatographic data:

$$(k_s' x_1^\circ)^{-1} = (\beta K_{s1})^{-1} \left[1 + \sum_{q=1}^{Q} C_q (x_1^\circ)^q \right] \tag{26}$$

Eqn. 26 for $Q = 1$ gives the following relationship:

$$(k_s' x_1^\circ)^{-1} = (\beta K_{s1})^{-1} (1 + C_1 x_1^\circ) \tag{27}$$

which has been verified experimentally by using high-performance liquid chromatographic (HPLC) data[42,44]. However, eqn. 22 for $y_1 = 1$ and $r = 1$ takes the following linear form:

$$k_s' x_1^\circ = \beta K_{s1} (1 - C_1 x_1^\circ) \tag{28}$$

Eqns. 27 and 28 involve solvation effects in the mobile phase; the first refers to the model assuming the formation of two-molecular solvates (one solute molecule and one solvent molecule) in the mobile phase, whereas eqn. 28 refers to the mobile phase containing solvates with different numbers of solvent molecules.

Now we shall consider a simplified model involving only association of the 1st solvent in the mobile phase. For $y_1 = 1$ and $r = 1$, eqn. 23 gives

$$k_s' = 2\beta K_{s1} L_2^2 x_1^\circ / (1 + 2L_2 x_1^\circ - \sqrt{1 + 4L_2 x_1^\circ}) \tag{29}$$

The square root appearing in eqn. 29 may be approximated as follows:

$$\sqrt{1 + 4L_2 x_1^\circ} = 1 + 2L_2 x_1^\circ - 2L_2^2 (x_1^\circ)^2 + 4L_2^3 (x_1^\circ)^3 \text{ for } 4L_2 x_1^\circ < 1 \tag{30}$$

Eqns. 29 and 30 give

$$k'_s = \beta K_{s1}(x_1^\circ)^{-1}(1 - 2L_2x_1^\circ)^{-1} \quad (31)$$

Eqn. 31 may be transformed to the following linear form:

$$(k'_s x_1^\circ)^{-1} = (\beta K_{s1})^{-1}(1 - 2L_2x_1^\circ) \quad (32)$$

An analogous relationship to eqn. 32 was obtained earlier[39] and verified experimentally by using HPLC[42] and thin-layer chromatographic[45] data. Thus, the type of linear dependence in eqn. 32 is identical with that in solvation (eqn. 27). However, the slopes of the linear eqns. 32 and 27 have opposite signs; in eqn. 27 the slope is positive, whereas in eqn. 32 it is negative. This result is very important for the interpretation of chromatographic data. In solvation in the mobile phase another linear relationship has been derived, *viz.*, eqn. 28, which has negative slope in the coordinates $k'x_1^\circ$ *vs.* x_1°.

DISCUSSION OF SPECIFIC INTERACTIONS BETWEEN SOLUTE AND SOLVENT MOLECULES IN THE MOBILE AND STATIONARY PHASES

In the previous sections we discussed equations for the capacity ratio of a solute chromatographed in a binary eluent, which involve solute–solvent and solvent–solvent complexation effects in the mobile phase. In this section we shall extend these equations, taking into account analogous complexation effects in the stationary phase also.

Of course, the complexation effects in the stationary phase are generally weaker than those in the mobile phase but they may be significant in the chromatographic systems in which the solute–adsorbent interactions are comparable to the solute–solvent and solvent–solvent interactions, *e.g.*, see Fig. 20 in ref. 8.

The complexation phenomena in the stationary phase may be represented by quasi-chemical reactions analogous to those representing the specific interactions in the mobile phase[39]. Thus, expressions analogous to eqns. 7 and 8 may be written for the stationary phase:

$$C_q^s = w_q/(y_s y_1^q) \text{ for } q = 1,2,...,Q \quad (33)$$

$$L_p^s = w'_p/(y_1)^p \text{ for } p = 2,3,...,P \quad (34)$$

where C_q^s and L_p^s are equilibrium association constants analogous to the constants C_q and L_p but referring to the stationary phase, w_q and w'_p are molar fractions of $(q + 1)$-molecular solvates and p-molecular associates of the 1st solvent in the stationary phase. The total molar fractions of the sth solute and the 1st solvent in the stationary phase containing all types of associates are expressed by equations analogous to eqns. 9 and 10:

$$y_s^\circ = y_s\left(1 + \sum_{q=1}^{Q} C_q^s y_1^q\right) \quad (35)$$

$$y_1^\circ \approx y_1 + \sum_{p=2}^{P} pL_p^s y_1^p \tag{36}$$

Substituting eqns. 9 and 35 into eqn. 3 and combining it with eqn. 5, we obtain the general equation for the capacity ratio involving complexation effects in the mobile and stationary phases:

$$k_s' = \beta K_{s1} \left(\frac{y_1}{x_1}\right)^r \left[\frac{1 + \sum_{q=1}^{Q} C_q^s y_1^q}{1 + \sum_{q=1}^{Q} C_q x_1^q}\right] \tag{37}$$

where the molar fractions x_1 and y_1 refer to unassociated molecules of the 1st solvent in the mobile and stationary phases, respectively, and may be evaluated by means of eqns. 12 and 36.

Assumption of analogous relationships for the constants C_q^s and L_p^s to those given by eqns. 15 and 16, and application of these relationships in eqns. 35 and 36, makes summation with respect q and p possible; then, we have

$$y_s^\circ = y_s/(1 - C_1^s y_1) \text{ for } C_1^s y_1 < 1 \tag{38}$$

$$y_1^\circ = y_1/(1 - L_2^s y_1)^2 \text{ for } L_2^s y_1 < 1 \tag{39}$$

Eqns. 38 and 39 lead to the following expression for the capacity ratio:

$$k_s' = \beta K_{s1} \left(\frac{y_1}{x_1}\right)^r \left[\frac{1 - C_1 x_1}{1 - C_1^s y_1}\right] \tag{40}$$

where

$$y_1 = (1 + 2L_2^s y_1^\circ - \sqrt{1 + 4L_2^s y_1^\circ})/[2(L_2^s)^2 y_1^\circ] \tag{41}$$

and x_1 is defined by eqn. 21. Of course, eqn. 40 is considerably simpler than eqn. 37. With high enough concentrations of the more efficient eluting solvent in the mobile phase, ensuring complete coverage of the surface by this solvent, we have $y_1^\circ = 1$. Putting this value in eqns. 40 and 41, we obtain:

$$k_s' = A(x_1)^{-r}(1 - C_1 x_1) \tag{42}$$

where x_1 is defined by eqn. 21 and

$$A = \beta K_{s1} \cdot \frac{[0.5(L_2^s)^{-2}(1 + 2L_2^s - \sqrt{1 + 4L_2^s})]^r}{1 - 0.5C_1^s(L_2^s)^{-2}(1 + 2L_2^s - \sqrt{1 + 4L_2^s})} \tag{43}$$

It follows from eqns. 42 and 43 that in the case in question the complexation effect in the stationary phase is constant; eqn. 42 is analogous to the expression defining the capacity ratio for an ideal stationary phase but only constant A is dependent on the equilibrium constants K_{s1}, C_1^s and L_2^s.

For $r = 1$ and $x_1 = x_1^\circ$ (no association of the 1st solvent), eqn. 42 gives

$$k'_s x_1^\circ = A(1 - C_1 x_1^\circ) \tag{44}$$

which is similar to eqn. 28. Eqns. 28 and 44 involve the solvation effects in the mobile phase and eqn. 44 contains additionally a constant contribution deriving from the solvation in the stationary phase.

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