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Note

Simple model of liquid–solid chromatography involving solute–solvent and solvent–solvent interactions
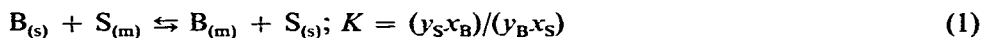
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In previous papers[1,2], the solute–solvent and solvent–solvent interactions in the mobile and surface phases have been discussed in terms of Snyder's theory of liquid–solid chromatography (LSC)[3]. These interactions may also be described in terms of the formation of associates between molecules of solute and solvent in the mobile and surface phases[4]. This approach is more suitable for the investigation of specific molecular interactions.

Recently, Jaroniec and Piotrowska[4] considered theoretically the solvent–solvent and solute–solvent association in LSC with a binary mobile phase by assuming energetic homogeneity of the adsorbent surface and the same molecular size for all components. They discussed three models involving the formation of double associates BS, BB or AB, where A and B denote the solvents or single molecules of the solvents and S denotes the solute or a single molecule of the solute. From the theoretical discussion[4] and experimental studies it is seen that the mixed associates BS and BB play an important rôle in the chromatographic process.

In this note, we discuss the simple model involving the simultaneous formation of double associates BB and BS in the mobile phase. However, in the surface phase the silanol groups of the silica surface can compete with BS and BB associates in the adsorbed phase. Thus, stronger interactions of S and B molecules with the silica silanols can preclude BB and BS interactions in the surface phase. Taking into account the possibility of destruction of the associates BS and BB in the surface phase by the silica silanols, we assume that these associates form only in the mobile phase. The above model may be represented by the following quasichemical reactions

$$B_{(s)} + S_{(m)} \leftrightarrows B_{(m)} + S_{(s)}; \quad K = (y_S x_B)/(y_B x_S) \tag{1}$$

$$B_{(m)} + B_{(m)} \leftrightarrows BB_{(m)}; \quad L = x_{BB}/(x_B)^2 \tag{2}$$

$$B_{(m)} + S_{(m)} \leftrightarrows BS_{(m)}; \quad M = x_{BS}/(x_B x_S) \tag{3}$$

where the subscripts (m) and (s) refer to the mobile and surface phases, respectively, K, L and M are the equilibrium constants of reactions 1–3 and x_i and y_i (i = B, S, BB, BS) are the mole fractions of the ith individual in the mobile and surface phases,

respectively. The total mole fractions of B and S in the mobile and surface phases may be expressed as:

$$x_B^0 = x_B + x_{BS} + 2x_{BB} \approx x_B + 2Lx_B^2 \tag{4}$$

$$x_S^0 = x_S + x_{BS} = x_S + Mx_Bx_S \tag{5}$$

$$y_B^0 = y_B \quad \text{and} \quad y_S^0 = y_s \tag{6}$$

The distribution coefficient, $k_{(AB)S}$, for solute S and mobile phase A–B is defined as:

$$k_{(AB)S} = y_S^0/x_S^0 \tag{7}$$

Combining eqns. 1, 5, 6 and 7 we have:

$$k_{(AB)S} = Ky_B/[x_B(1 + Mx_B)] \tag{8}$$

Solution of eqn. 4 with respect to x_B gives:

$$x_B = [(1 + 8Lx_B^0)^{1/2} - 1]/(4L) = X_B/(4L) \tag{9}$$

Finally, eqns. 8 and 9 lead to the general expression:

$$k_{(AB)S} = 16L^2Ky_B/[X_B(4L + MX_B)] \tag{10}$$

Eqn. 10 may be simplified by applying the following assumptions: (a) when the difference between the elution strengths of both solvents is large and at high values of x_B^0, the mole fraction y_B may be approximated by unity, and (b) for small values of L the variable X_B may be approximated by

$$X_B = 4Lx_B^0 (1 - 2Lx_B^0) \tag{11}$$

Taking into account eqn. 10, the assumptions (a) and (b) and neglecting terms involving third and higher powers of x_B^0, we have:

$$1/(k_{(AB)S}x_B^0) = 1/K + [(M - 2L)/K] x_B^0 \tag{12}$$

The constant K is always greater than zero, therefore, the sign of the slope of eqn. 12 is dependent upon the sign of $(M - 2L)$ only. If the magnitude of the equilibrium constant M, corresponding to the solute–solvent association, is greater than that of the constant $2L$, corresponding to association of solvent B, then the slope is positive. However, if $2L > M$ a negative slope is observed.

Eqn. 10 and especially its simplified form, eqn. 12, may be useful in the determination of the effects of solute–solvent and solvent–solvent interactions in LSC with mixed mobile phases.

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