On Application of the Snyder-Soczewinski Equation for Describing of LSC Process with a Ternary Mobile Phase

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ON APPLICATION OF THE SNYDER-SOCZEWINSKI EQUATION FOR DESCRIBING OF LSC PROCESS WITH A TERNARY MOBILE PHASE

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ABSTRACT

A possibility of an application of the Snyder-Soczewinski relationship for describing of chromatographic systems with ternary mobile phases is analysed. The Snyder-Soczewinski type equation is derived for experimental data measured at constant ratio of mole fractions of less polar solvents. A physical meaning of the slope of the relationship is discussed.

INTRODUCTION

The Snyder-Soczewinski linear relationship is one of most popular equations used for describing of liquid adsorprtion chromatography with mixed mobile phase [1-5]. It has the following form

$$\log k'_{s} = \log k'_{s(1)} + m \log x_{1} \qquad (1)$$

where k'_{s}, $k'_{s(1)}$ are capacity ratios of the solute "s" in the mixed eluent and in the pure 1st solvent, respectively; x_{1} denotes the mole fraction of the 1st solvent in the mobile phase whereas m is a constant parameter. The 1st solvent is assumed to be most efficient eluting component of the mobile phase.

Eqn. (1) is usually used for describing chromatographic data measured in binary mobile phases. The method has been critically analysed by Borówko and Jaroniec [6]. It has been shown that the Snyder-Soczewinski relationship gives a satisfactory representation of experimental data in the limited concentration region (e.g. for $x_{1} \longrightarrow 1$). Moreover, the physicochemical interpretation of the constant m is a matter of some difficulty because it is a complex function of different parameters characterizing competitive solute and solvent adsorption, nonideality of the stationary and mobile phases, adsorbent heterogeneity, difference of molecular sizes of solute and solvent molecules and orientation of solute molecules relative to the adsorbent surface [6,7]. Despite the uncertainties associated with the interpretation of the physical meaning of the parameter m the Snyder-Soczewinski equation is of considerable practical importance.

Eqn. (1) has been sometimes used for describing of the chromatographic systems with ternary mobile phases [4,5]. This problem should be carefully discussed.

THEORETICAL ANALYSIS

Let us consider a chromatographic system with the sth solute, a ternary mobile phase and an energetically

homogeneous adsorbent. All molecules are spherical, and molecules of solvents have the same sizes. Elution strengths of the solvents satisfy the following inequalities: $\varepsilon_1 > \varepsilon_2 > \varepsilon_3$. Furthermore, we assume that the stationary and mobile phases are ideal. Then, the capacity ratio is given by [4]:

$$k'_s = q \, K_{s1} (y_1/x_1)^r \qquad (2)$$

where q is the parameter connected with chromatographic bed and independent of the nature of the solvent [1], K_{s1} denotes the constant characterizing adsorption in the binary solution (1,s), y_1 is the mole fraction of the 1st solvent in the stationary phase, whereas r is the ratio of the partial molar areas of the solute and solvent. The adsorption isotherm of the 1st solvent is given by well-known formula [4]:

$$y_1 = K_{13}x_1 \left[\sum_{i=1}^{3} K_{i3}x_i \right]^{-1} \qquad (3)$$

where K_{i3} is the adsorption constant for the binary solution (i,3); $K_{33} = 1$.

If the elution strength of the 1st solvent is considerably greater the elution strengths of the other solvents, then the mole fraction y_1 is practically equal to unity over the whole concentration region of x_1 except low concentration of the 1st solvent. Taking this fact into account in equations (2) and (3) we get the Snyder-Soczewinski relation (1), and

$$m = -r \qquad (4)$$

However, as follows from many studies adsorption of the other solvents considerably affects the

chromatographic process [4,5,8]. Let us assume that the ratio of mole fractions of components "3" and "2" in the mobile phase is constant

$$x_3/x_2 = w = \text{const} \tag{5}$$

In this case the mole fraction of the 1st solvent in the stationary phase may be expressed by the equation quite analogous to Everett's isotherm derived for a binary solutions [9]

$$y_1 = x_1/\left[x_1(1-K^*) + K^*\right] \tag{6}$$

where K^* is constant defined as

$$K^* = (K_{21} + wK_{31})/(w+1) \tag{7}$$

$$\text{for } K_{i1} = K_{i3}/K_{13} \quad (i = 2,3).$$

Combining eqns. (2), (3) and (6) we obtain

$$k'_s = k_{s(1)}\left[x_1(1-K^*) + K^*\right]^{-r} \tag{8}$$

for

$$k'_{s(1)} = qK_{s1} \tag{9}$$

If solute and solvents molecules have the same sizes ($r = 1$) eqn. (8) leads to the linear relationship $(1/k'_s)$ vs. x_1 discussed in the paper [10]. However, in the majority of practical applications of liquid adsorption chromatography molecules of the solute are bigger than molecules of the solvents. For such systems the equation of Snyder-Soczewinski type may be derived on a base of the general relationship (8).

Note, when the condition (5) is satisfied the capacity ratio is a function of one variable x_1. Let us

consider a theoretical function $\log k'_s (\log x_1)$. It may be expanded into Taylor's serie about the point $\log x_1 = 0$ $(x_1 = 1)$. Neglecting in the expansion the terms containing second and higher derivatives we obtain

$$\log k'_s = \log k'_{s(1)} + \frac{d \log k'_s}{d \log x_1} \bigg|_{x_1=1} \log x_1 \qquad (10)$$

It appears that eqn. (10) is identical to the Snyder-Soczewinski relation (1) and

$$m = \frac{d \log k'_s}{d \log x_1} \bigg|_{x_1=1} \qquad (11)$$

For the assumed retention model we obtain

$$m = r(K^* - 1). \qquad (12)$$

The last expression is analogous to that obtained for a binary mixed solvent [6]. It follows from equations (12) and (7) that the slope of the Snyder-Soczewinski line depends upon properties of all solvents. It is easy to show that the parameter m increases when the ratio w decreases. If the 1st solvent plays a dominant role in the elution process the constant K^* tends to zero and the parameter m is given by eqn. (4). For binary mobile phases: (1,2) $(w = 0)$ and (1,3) $(w \rightarrow \infty)$ we have $K^* = K_{i1}$ $(i = 2,3)$.

As an illustration the results obtain for chromatographic experimental data measured by TLC technique [11.12] are shown in Figures 1 and 2.

Figure 1 shows plots $\log k'_s$ vs. $\log x_1$ for ternary solvent: acetone (1) - benzene (2) - carbon tetrachloride (3) and two binary mobile phases: acetone
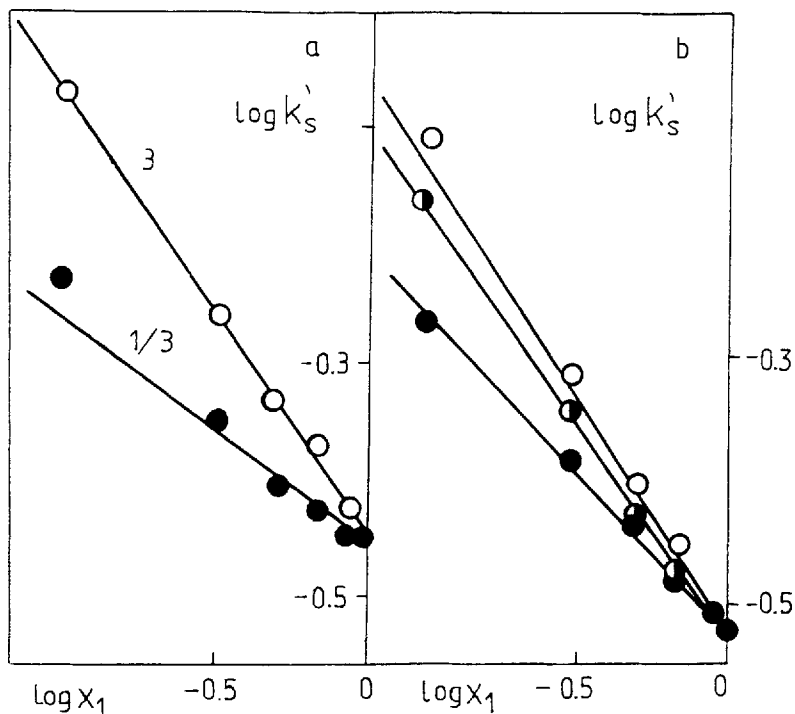
FIGURE 1. Comparison of experimental data with the Snyder-Soczewinski relationship (1) for mixed mobile phase: acetone (1) – benzene (2) – carbon tetrachloride (3). (a) s = o-nitrophenol and w = 1/3 (●), w = 3 (○); (b) s = nitrotoluene and w = 0 (●), w = 1 (◑), w ⟶ ∞ (○).

– benzene and acetone – carbon tetrachloride. The agreement of the experimental points and the linear relationship (1) is satisfactory in the whole studied region of x_1. An analysis of the results confirms our theoretical conclusions. When the concentration of carbon tetrachloride in the mobile phase increases (Fig. 1a) the slope m decreases. Moreover. the line plotted for ternary eluent lie between those plotted for the suitable binary solvents (Fig. 1b).

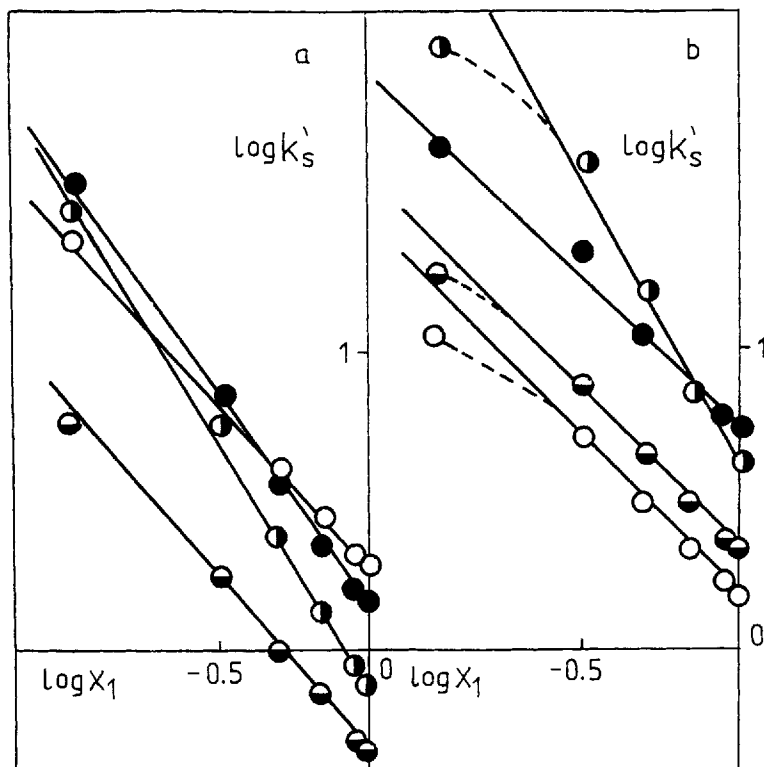FIGURE 2. Comparison of experimental data with the
Snyder-Soczewinski relationship (1) for:
(a) ethyl acetate (1) - cyclohexane (2) - heptane (3),
w = 1 and s: isoquinoline (○), 2,3-dichlorophenol
(◑), p-nitroaniline (◐), dinitrobenzene (●),
(b) chloroform (1) - cyclohexane (2) - heptane (3),
w = 1, and s: 2,4,6-trichlorophenol (○), 2,3-dichloro-
phenol (◑), 3,4-dichlorophenol (●), p-nitroaniline
(◐).

   In Figure 2 the results obtained for two ternary
mobile phases: ethyl acetate (1) - cyclohexane (2) -
heptane (3) and chloroform (1) - cyclohexane (2) -
heptane (3) are presented. Both less polar components
of the mobile phase have been always mixed in the 1:1
mole fraction ratios. Ethyl acetate is stronger
adsorbed than chloroform. For both ternary solvents the
Snyder-Soczewinski equation gives a good approximation
of the experimental data for $x_1 > 0.5$. However, for the
mobile phase containing less polar solvent (e.g. carbon
tetrachloride) considerable deviations from linear plot
are observed when $x_1 < 0.5$. In this case the equation
discussed in the paper [10] seems to be more useful.

CONCLUSIONS

   The Snyder-Soczewinski relationship may be used
for interpreting chromatographic data measured in
ternary mixed solvents when:

1) almost whole adsorbent surface is covered by the 1st
solvent ($y_1 \approx 1$) or

2) the ratio of mole fractions ot both less polar
solvents in the mobile phase is constant.

   For strong adsorption of the 1st solvent functions
$\log k_s'$ vs. $\log x_1$ are essentially linear in a wide
region of the mobile phase composition. When
competitive asorption of the other solvents plays
a considerable role the Snyder-Soczewinski equation can
approximate experimental data for $x_1 \rightarrow 1$.
   In a general case the slope (m) in the linear
dependence (1) is a complex function of various

parameters. When stationary and mobile phases are ideal the coefficient m depends upon: (1) difference in molecular sizes of the solute and solvents, (2) constants characterizing adsorption of all solvents, (3) the ratio of mole fractions of less polar solvent.

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