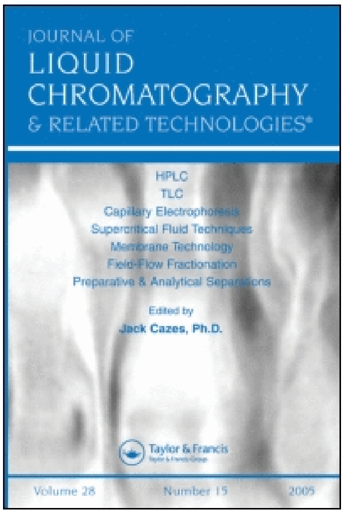

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LIQUID CHROMATOGRAPHY WITH MIXED MOBILE PHASES: INTERPRETATION OF THE MODEL CHROMATOGRAPHIC DATA BY MEANS OF THE SIMPLE LINEAR RELATIONSHIP

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ABSTRACT

A discussion is presented concerning the application of the simple linear relationships ln K_s vs. ln x and ln K_s vs. x , where K_s is the solute distribution coefficient and x is the mole fraction of the more efficient eluting solvent in the mobile phase, for analysing LC data calculated for different chromatographic models. It is shown that these linear relationships give a satisfactory representation of the LC data relating to some different models in a limited concentration region of the more efficient eluting solvent. Hence, it is difficult to select the LC model properly representing a given chromatographic system on the basis of the parameters obtained by fitting LC data to these linear relationships.

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INTRODUCTION

Two simple linear relationships are frequently used for interpreting the liquid chromatography (LC) data measured at different mobile phase compositions. They are (1-4):

$$\ln K_s = a_1 + b_1 \ln x \qquad (1)$$

$$\ln K_s = a_2 + b_2 x \qquad (2)$$

where K_s is the distribution coefficient of the s-th solute chromatographed in a binary eluent, x is the mole fraction of the more efficient eluting solvent in the mobile phase, a_i and b_i for $i = 1,2$ are parameters of the linear relationships 1 and 2. Analogous linear relationships to those given by equations 1 and 2 may be written in terms of the capacity ratio of the s-th solute and the volume fraction of the more efficient eluting solvent.

Equations 1 and 2 were discussed theoretically by several authors (5-11). Following Soczewiński's concept (5) of the solute adsorption during the LC process Jaroniec et al. (11) have proposed a general equation describing the dependence of the distribution coefficient upon mobile phase composition. When the elution strengths of the solvents forming an ideal binary mobile phase are considerably different (then at moderate and higher concentrations of the more efficient eluting solvent the stationary (surface) phase consists of molecules of this solvent and solute molecules, the concentration of which is infinitely low), the above mentioned equation becomes the so-called Snyder-Soczewiński equation 1, in which b_1 is equal to the ratio of molecular sizes of solute and solvent and $a_1 = \ln K_{s(1)}$, where $K_{s(1)}$ is the distribution coefficient of the s-th solute chromatographed in the more efficient eluting solvent (2,6). According to the papers (2,5,6,9,12) the Snyder-Soczewiński relationship relates to the LC model assuming the phase-exchange between solute and solvent molecules contained in the ideal stationary and mobile phases. In other words, equation 1 describes a pure displacement model, which gives a reasonable representation of many LC normal-phase systems (2,9,12).

However, equation 2 may be derived in terms of the LC model assuming classical partitioning of the solute between two, nearly ideal, stationary and mobile phases (9,12). On the other hand, equations 1 and 2 are frequently considered as empirical relationships and used for interpreting LC data in a limited concentration region (2,4,6,7). In this paper the utility of application of the simple linear relationships 1 and 2 for describing LC data calculated for different chromatographic models, is discussed. The present work shows that physicochemical interpretation of the linear parameters a_i and b_i obtained by fitting the chromatographic data to the linear relationships 1 and 2 is very difficult because these parameters can be discussed in terms of different models of the LC process.

THEORETICAL

Let us consider a chromatographic system with the s-th solute and a binary eluent. We designate the solute distribution coefficient by K_s and the mobile phase composition by x, where x is the mole fraction of the more efficient eluting solvent. The symbol K_{s1}

denotes the equilibrium constant describing the phase-exchange reaction between molecules of solute and 1-st solvent, which is assumed to be the more efficient eluting solvent. Thus, the adsorption energies of the solute and solvents "1" and "2" satisfy the following inequality:

$$\varepsilon_s > \varepsilon_1 > \varepsilon_2 \qquad (3)$$

The simple models of LC process are usually formulated by using the following assumptions (7):

1) solute and solvent molecules are spherical and have identical molecular sizes,
2) the surface phase is ideal,
3) the mobile phase may be considered as: an ideal solution (a), a regular solution (b), a solution containing pure associates of the more efficient eluting solvent (c) or a solution containing solvates consisting of one solute molecule and some molecules of the 1-st solvent,
4) the adsorbent surface may be considered as: energetically homogeneous (a) or energetically heterogeneous (b).

In this paper five models of LC process are considered: M1 (assumptions 1,2,3a,4a), M2 (assumptions 1,2,3b,4a), M3 (assumptions 1,2,3c,4a), M4 (assumptions 1,2,3d,4a) and M5 (assumptions 1,2,3a,4b). Table 1 contains the fundamental equations describing the dependence of K_s upon mobile phase composition for the models M1-M5.

The functions ln K_s vs. ln x and ln K_s vs. x may be expanded into a Taylor's series about the points ln x = 0 (then x = 1) and x = 1, respectively. Neglecting in these expansions the terms containing second and higher derivatives, we have:

TABLE 1

Equations describing the dependence of K_s upon mobile phase composition for LC models M1-M5

Model code	Equation	Ref.
M1	$K_s = [x/K_{s1} + (1-x)/K_{s2}]^{-1}$	13
M2	$K_s = [\phi_1 x + (1-x)\phi_2]^{-1}$ $\phi_1 = \exp[(\omega_{2s} - \omega_{1s} - \omega_{12})x + \omega_{12} - \omega_{2s}]/K_{s1}$ $\phi_2 = \exp[(\omega_{12} - \omega_{1s} + \omega_{2s})x - \omega_{2s}]/K_{s2}$	14
M3	$K_s = [x^*/K_{s1} + (1-x)/K_{s2}]^{-1}$ $x^* = [1 + 2Lx - (1+4Lx)^{1/2}]/(2L^2x)$; $0 < L < 1$	15,16
M4	$K_s = (1-Cx)[x/K_{s1} + (1-x)/K_{s2}]^{-1}$; $0 < C < 1$	15,16
M5	$K_s = [(x/K_{s1})^m + ((1-x)/K_{s2})^m]^{-1/m}$; $0 < m < 1$	17,18

Notation: K_{si} - phase-exchange constant for molecules of the s-th solute and i-th solvent; C - solvation equilibrium constant (16); L - association equilibrium constant (16); ω_{ij} and ω_{is} - interaction parameters between molecules i-j and i-s, respectively (14); m - parameter characterizing energetic heterogeneity of the adsorbent (17).

$$\ln K_s = \ln K_{s(1)} + (d \ln K_s/d \ln x)\big|_{x=1} \ln x \qquad (4)$$

and

$$\ln K_s = \ln K_{s(1)} + (d \ln K_s/dx)\big|_{x=1}(x - 1) \qquad (5)$$

Introducing a new parameter n defined by:

$$n = -(d \ln K_s/dx)\big|_{x=1} , \qquad (6)$$

we can rewrite equations 1 and 2 as follows:

$$\ln K_s = a_1 - n \ln x \tag{7}$$

and

$$\ln K_s = a_2 - n x \tag{8}$$

where

$$a_1 = \ln K_{s(1)} \; ; \; a_2 = \ln K_{s(1)} + n \; ; \; b_1 = b_2 = -n \tag{9}$$

Table 2 contains expressions defining the parameter n (i.e., slope of the linear relationships 7 and 8) for the models M1-M4. However, Table 3 contains expressions defining the parameter n_0, which appears in the following series:

$$\ln K_s = \ln K_{s(2)} - n_0 x \tag{10}$$

where

$$n_0 = -(d \ln K_s/dx)\big|_{x=0} \tag{11}$$

Equation 10 presents two first terms of the function $\ln K_s$ vs. x expanded about the point $x = 0$. If the dependence $\ln K_s$ vs. $\ln x$ shows a linear behavior about an arbitrary point $\ln x_0 \in (0,1)$, we can expand the function $\ln K_s$ about this point. Then, we may write:

$$\ln K_s = \ln K_s(x=x_0) + (d \ln K_s/d \ln x)\big|_{x=x_0}(\ln x - \ln x_0) \tag{12}$$

or

$$\ln K_s = a^* - n^* \ln x \tag{13}$$

where

$$a^* = \ln K_s(x=x_0) + n^* \ln x_0 \; ; \; n^* = -(d \ln K_s/d \ln x)\big|_{x=x_0} \tag{14}$$

The dependence $\ln K_s$ vs. $\ln x$ calculated according to the model M5 shows a linear segment inside the x-interval (0,1), which may be

TABLE 2

Expressions defining the slopes of the linear relationships 7 and 8 at $x \rightarrow 1$

Model code	Slope n	Comments
M1	$n_{id} = 1 - K_{21}$	$n_{id} < 1$
M2	$1 - K_{21}\exp(\omega_{12}) - \omega$ $\omega = \omega_{12} + \omega_{1s} - \omega_{2s}$	$\omega_{12}\uparrow, \omega_{1s}\uparrow \Rightarrow n\downarrow$ $\omega_{2s}\uparrow \Rightarrow n\uparrow$
M3	$[\beta - K_{21}]/\alpha$ $\alpha = [1+2L-(1+4L)^{1/2}]/(2L^2)$ $\beta = [(1+4L)^{1/2} - 2L(1+4L)^{-1/2} - 1]/(2L^2)$	$n < n_{id} < 1$ $n \in (\text{const}, n_{id})$ $L\uparrow \Rightarrow n\downarrow$
M4	$1 - K_{21} - C/(C-1)$	$n > n_{id}$; $C\uparrow \Rightarrow n\uparrow$ $n \in (n_{id}, \infty)$

Abbreviation $y\uparrow \Rightarrow n\downarrow$ ($y = \omega_{ij}, \omega_{is}, C, L$) denotes that n decreases when y increases.

TABLE 3

Expressions defining the slope of the linear relationship 10 at $x \rightarrow 0$

Model code	Slope n_0	Comments
M1	$n_{0,id} = K_{12} - 1$	$n_{0,id} \in (0, \infty)$
M2	$1 - K_{21}\exp(-\omega_{12})(1 - \omega_0)$ $\omega_0 = \omega_{12} - \omega_{1s} + \omega_{2s}$	
M4	$K_{12} - 1 + C$	$n > n_{0,id}$ $C\uparrow \Rightarrow n\uparrow$

approximated by the linear relationship 12. Similarly, the function ln K_s may be expanded with respect to the variable x about the point $x = x_0$ but the model studies showed that this expansion is not useful from practical viewpoint.

RESULTS AND DISCUSSION

This section presents the model studies refering to the LC models M1-M5 summarized in Table 1. First, we calculated the dependence of ln K_s upon mobile phase composition for the models M1-M5 according to the equations presented in Table 1. Next, these theoretical data were plotted in ln K_s - ln x and ln K_s - x coordinates. Analysing these plots we could find regions of the mobile phase composition, in which the dependences ln K_s vs. ln x and ln K_s vs. x are linear.

Now, the most interesting results of these model studies will be presented. First, we consider the model M1. Since the 1-st solvent is assumed to be more efficient eluting solvent the equilibrium constant K_{21} is smaller than unity and the parameter $n=n_{id}$ is also smaller than unity (see Table 2). Figure 1 presents the dependence of ln K_s vs. ln x calculated according to the model M1 (see Table 1) for different values of K_{21}, where the constant K_{21} is defined as follows: $K_{21} = K_{s(1)}/K_{s(2)}$ (2,6). It follows from Figure 1 that the curves ln K_s vs. ln x show a linear behavior at higher concentrations of x (ln x → 0). As $K_{21} \rightarrow 0$, the mobile phase composition range over which the function ln K_s is essentially linear increases. Moreover, the curves ln K_s vs. ln x refering to $K_{21} \rightarrow 0$ approach the Snyder-Soczewiński linear relationship:

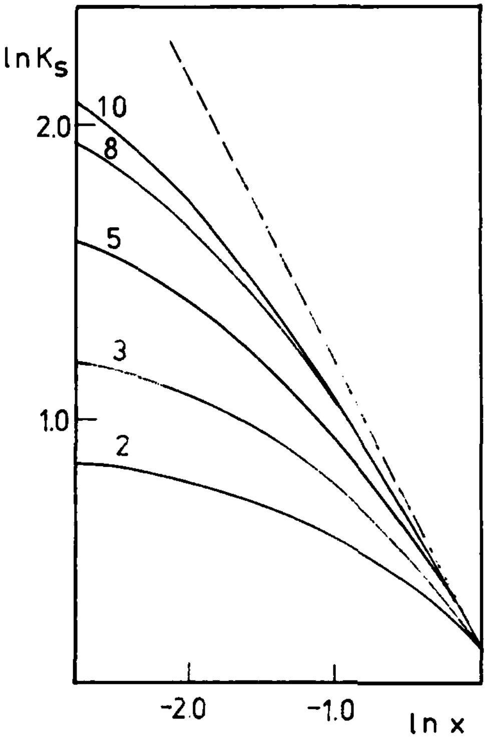

FIGURE 1. Theoretical curves ln K_s vs. ln x calculated according to the model M1 (see Table 1) for $K_{21} = K_{s(1)}/K_{s(2)}$, $K_{s(1)} = 1.25$ and $K_{s(2)} = 2, 3, 5, 8$ and 10 (numbers at the solid lines). The dashed line presents the Snyder-Soczewiński relationship (15).

$$\ln K_s = \ln K_{s(1)} - \ln x \qquad (15)$$

This relationship has the absolute slope equal to unity because we assumed identical molecular sizes of solute and solvents. Thus, for LSC systems with ideal phases and homogeneous adsorbents, characterized by the constant $K_{21} \approx 0$ (then the surface phase contains molecules of the 1-st solvent, whereas, concentration of molecules of solute and 2-nd solvent is infinitely low), the absolute slope of the linear regime of ln K_s vs. ln x is determined solely by the ratio of the molecular sizes of solute and solvents (in our case this ratio is equal to unity). However, if there exists a mixed composition of the surface phase ($0< K_{21}< 1$), then this slope depends additionally on the equilibrium constant K_{21}. Figure 1 shows that interpretation of LC data by means of the linear relationship 7 provides no information about chromatographic model. However, evaluating the equilibrium constant K_{21} from independent adsorption measurements (19) we have additional information about the surface phase composition, which makes interpretation of LC data easier.

The chromatographic data calculated according to the model M1 (see Figure 1) have been also presented in $\ln K_s$ - x coordinates (see Figure 2). It follows from Figure 2 that the curves $\ln K_s$ vs. x show a linear behavior about $x \rightarrow 0$ (equation 10) and $x \rightarrow 1$ (equation 8). For low values of K_{21} the slopes n and n_0 of the linear segments of the curves $\ln K_s$ vs. x at $x \rightarrow 0$ and $x \rightarrow 1$ are different. A comparison of the curves $\ln K_s$ vs. ln x (Figure 1) and $\ln K_s$ vs. x (Figure 2) plotted for low values of K_{21} (e.g., $K_{s(1)}=1.25$ and $K_{s(2)}=10$) shows that equation 7 approximates better LC data at $x \rightarrow 1$, whereas, equation 10 gives better approximation of these data at $x \rightarrow 0$. However, for the model M1 and $K_{21} \approx 1$ (similar adsorption of both solvents) the slopes n and n_0 of the curve $\ln K_s$ vs. x at $x \rightarrow 1$ and $x \rightarrow 0$ are similar; it means that these LC data may be approximated by the following expression:

$$\ln K_s = x \ln K_{s(1)} + (x-1) \ln K_{s(2)} \qquad (16)$$

Equation 16 may be obtained from equations 8 and 10 by approximating $\ln K_{21} \approx K_{21} - 1$.

The results presented in Figures 1 and 2 refer to the model M1, in which the mobile and surface phases are assumed to be ideal and

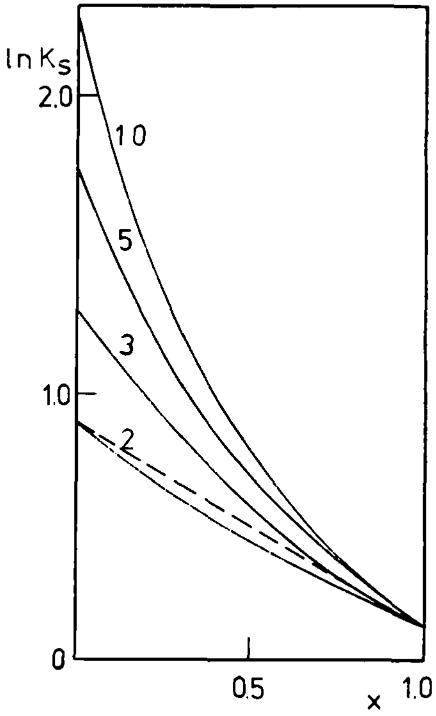

FIGURE 2. Theoretical curves ln K_s vs. x calculated according to the model M1 (see Table 1) for $K_{21} = K_{s(1)}/K_{s(2)}$; $K_{s(1)} = 1.25$ and $K_{s(2)} = 2$, 3, 5 and 10 (numbers at the solid lines). The dashed line presents the relationship 16 for $K_{21} = 2.0$.

adsorbent is energetically homogeneous. In the case of the model M2 the mobile phase is assumed to be a regular solution, in which the molecular interactions are characterized by the parameters ω_{12}, ω_{1s} and ω_{2s}. For this model at $x \to 1$ the parameter n appearing in the linear equations 7 and 8 is a function of the equilibrium constant K_{21} and interaction parameters ω_{12}, ω_{1s} and ω_{2s} (see Table 2); its value increases as ω_{2s} increases and it decreases as ω_{12} and ω_{1s} increase. Moreover, n may be greater as well as smaller than unity; it depends upon relationship between values of K_{12} , ω_{12} , ω_{1s} and ω_{2s}. Figures

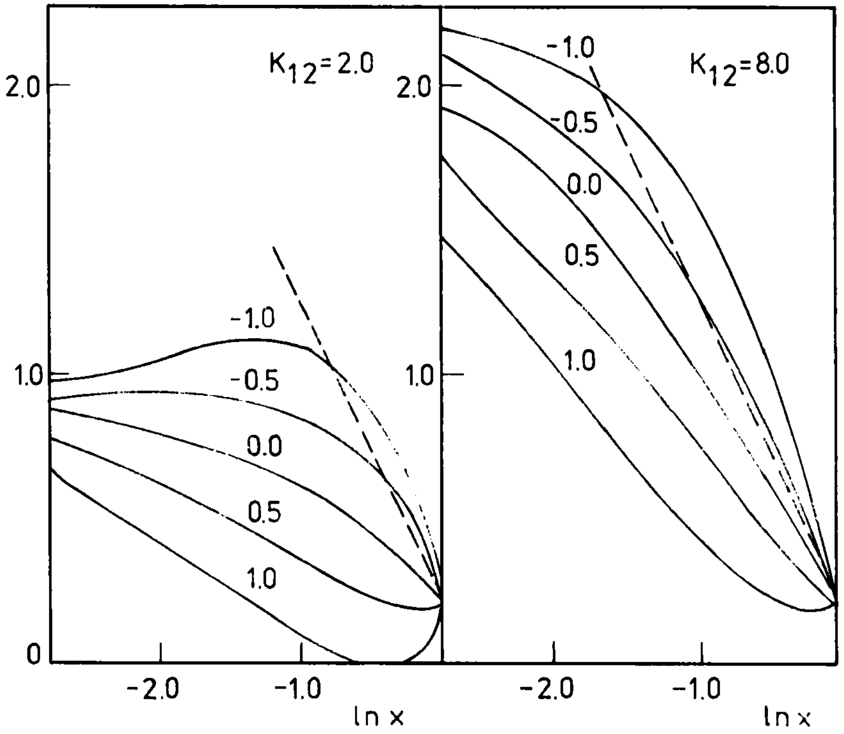

FIGURE 3. Theoretical curves ln K_s vs. ln x calculated according to the model M2 (see Table 1) for $K_{12} = 1/K_{21} = 2.0$ and 8.0 and different values of the parameter ω_{12} (numbers at the solid lines). The dashed line presents the Snyder-Soczewiński relationship 15.

3 and 4 present the curves ln K_s vs. ln x and ln K_s vs. x, respectively, calculated according to the model M2. It follows from these figures that for LC systems with mobile phases satisfying conditions of the regular solution the utility of equations 7 and 8 for approximating LC data is rather little. Although, for special values of the parameters ω_{12} , ω_{1s} , ω_{2s} and K_{21} the curves ln K_s vs. ln x show a linear behavior at x → 1 (for $\omega_{12} < 0$ and greater values of $K_{12} = 1/K_{21}$; see Figure 3 for $K_{12} = 8.0$) and at moderate values of x (for $\omega_{12} > 0$ and smaller values of K_{12}; see Figure 3 for $K_{12} = 2$).

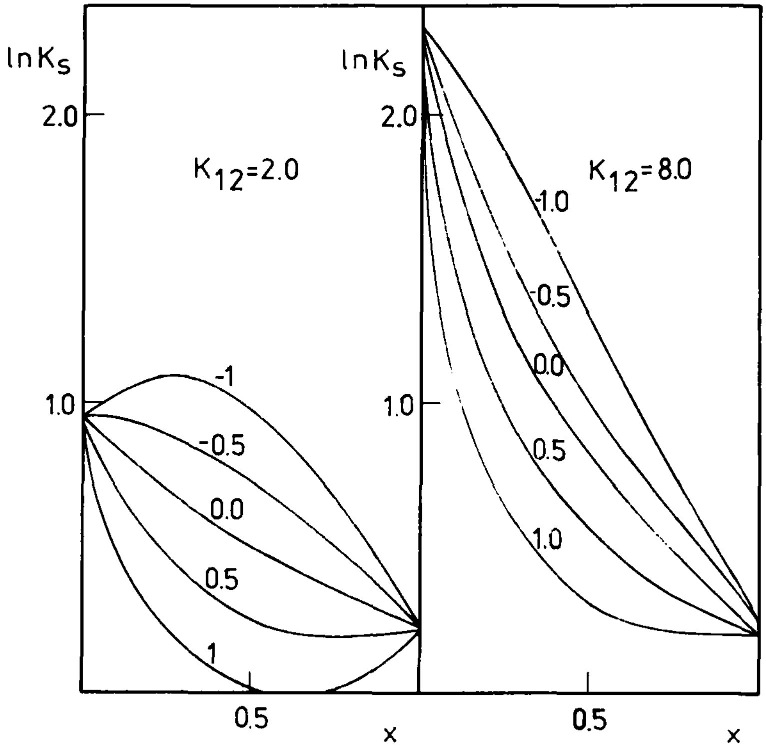

FIGURE 4. Theoretical curves ln K_s vs. x calculated according to the model M2 (see Table 1) for the same values of all parameters as in Figure 3.

Similarly, the curves ln K_s vs. x show a linear behavior for greater values of K_{12} and $\omega_{12} < 0$ (see Figure 4 for $K_{12} = 8$).

Figures 5 and 6 refer to the model M3, which assumes association of molecules of the 1-st solvent in the mobile phase. It follows from Figure 5 that the dependence ln K_s vs. ln x is linear in a wide region of x neighbouring with the point x=1 for higher values of K_{12} and L. The parameter n is always smaller than n_{id} and it decreases as L increases (see Table 2). In the case of the dependence ln K_s vs. x (equation 8) the greater regions of the mobile phase composition in

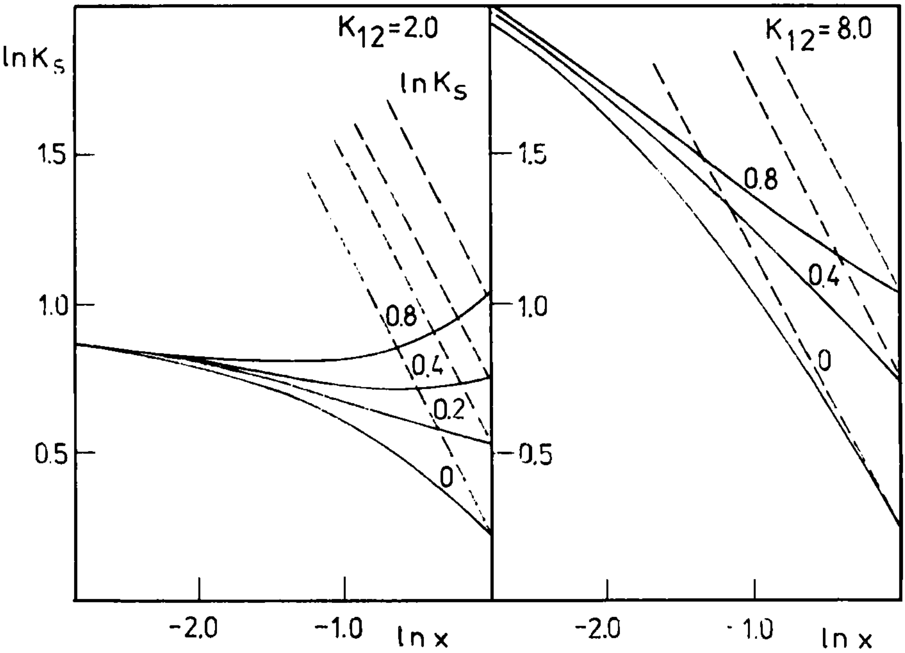

FIGURE 5. Theoretical curves ln K_s vs. ln x calculated according to the model M3 for K_{12} = 2.0 and 8.0 and different values of the association constant L (numbers at the solid lines). The dashed lines present the Snyder-Soczewiński linear relationship 15.

which it is essentially linear are observed for small values of K_{12} (see Figure 6).

In the case of the model M4 assuming solute-solvent association (solvation) in the mobile phase the parameter n is always greater then n_{id}. The dependence ln K_s vs. ln x (see Figure 7) shows a linear behavior at x → 1 for higher values of K_{12} and smaller values of C but the x-region of its linearity is smaller in comparison to that observed in Figure 5 for K_{12} = 8.0 . An interesting result is presented in Figure 8 for lower value of K_{12} (K_{12} = 2.0); the dependence ln K_s vs. x shows a linear behavior at x → 0 and x → 1 and the x-region of

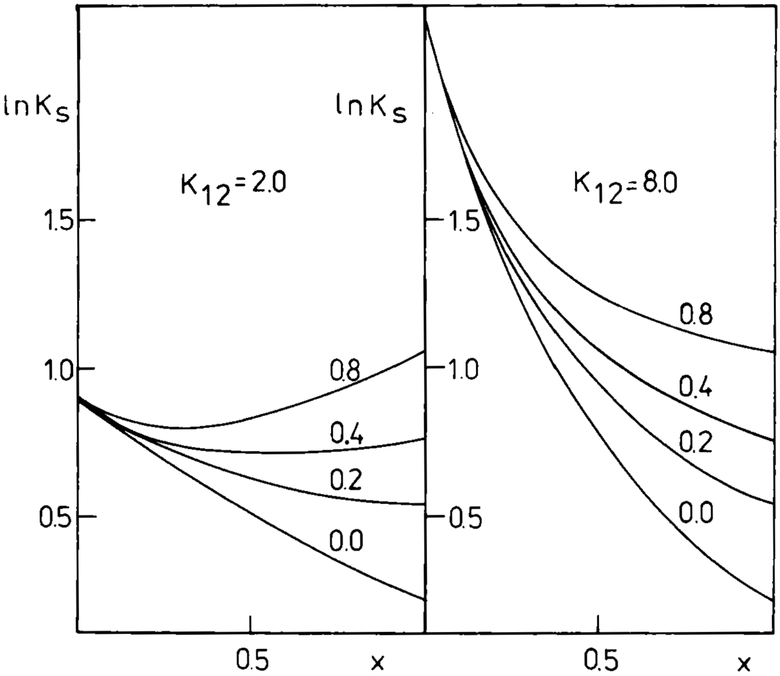

FIGURE 6. Theoretical curves ln K_s vs. x calculated according to the model M3 (see Table 1) for the same values of all parameters as in Figure 5.

its linearity increases as C increases. The parameters n and n_0 are greater always than n_{id} and $n_{0,id}$, respectively, and they increase as C increases. Moreover, for smaller values of K_{12} , e.g., K_{12} = 2.0 (both solvents show similar adsorption), the parameters n and n_0 are similar and the linear relationships 8 and 10 coincide; it means that for comparable adsorption of both solvents and stronger solute-solvent specific interactions the linear equation 2 gives a satisfactory representation of LC data in the whole mobile phase composition.

Equation describing the dependence of the distribution coefficient upon mobile phase composition according to the model M5 (see Table 1)

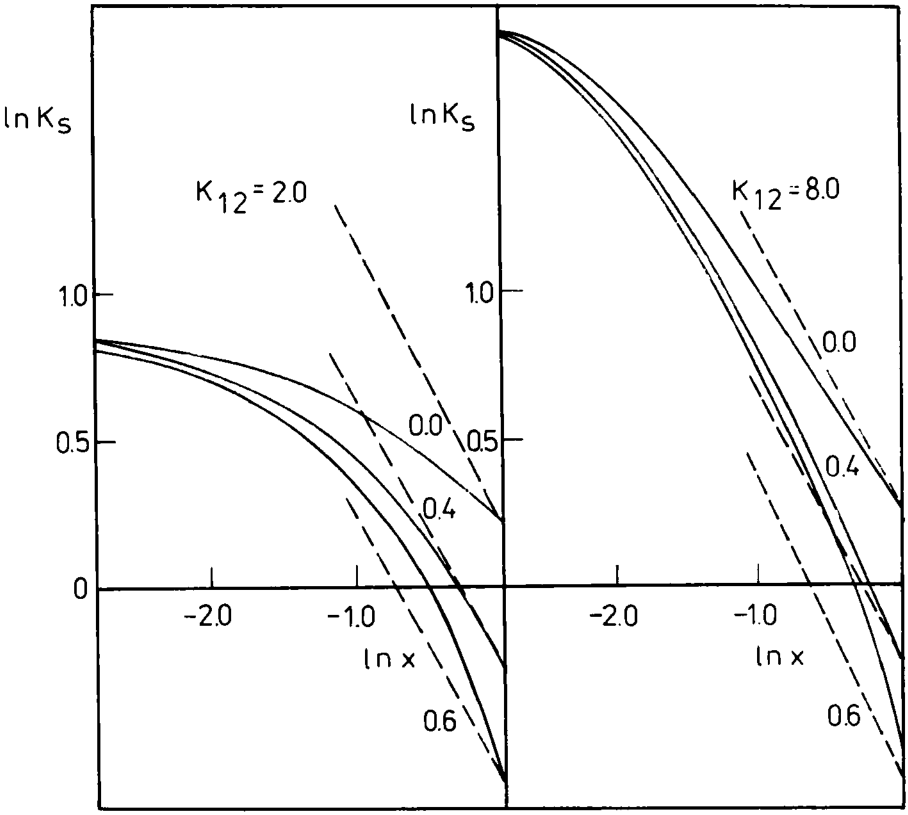

FIGURE 7. Theoretical curves ln K_s vs. ln x calculated according to the model M4 (see Table 1) for K_{12} = 2.0 and 8.0, and different values of the solvation constant C (numbers at the solid lines). The dashed lines present the Snyder-Soczewiński linear relationship 15.

has been derived by using an approximation (17,18). This equation cannot be expanded into a Taylor's series about the points $x = 0$ and $x = 1$. However, it may be expanded according to the formula 12 about the point $x_0 \in (0,1)$. According to equation 14 we have:

$$n^* = \frac{(x_0/K_{s(1)})^m - x_0(1-x_0)^{m-1}/(K_{s(2)})^m}{(x_0/K_{s(1)})^m + [(1-x_0)/K_{s(2)}]^m} < 1 \qquad (17)$$

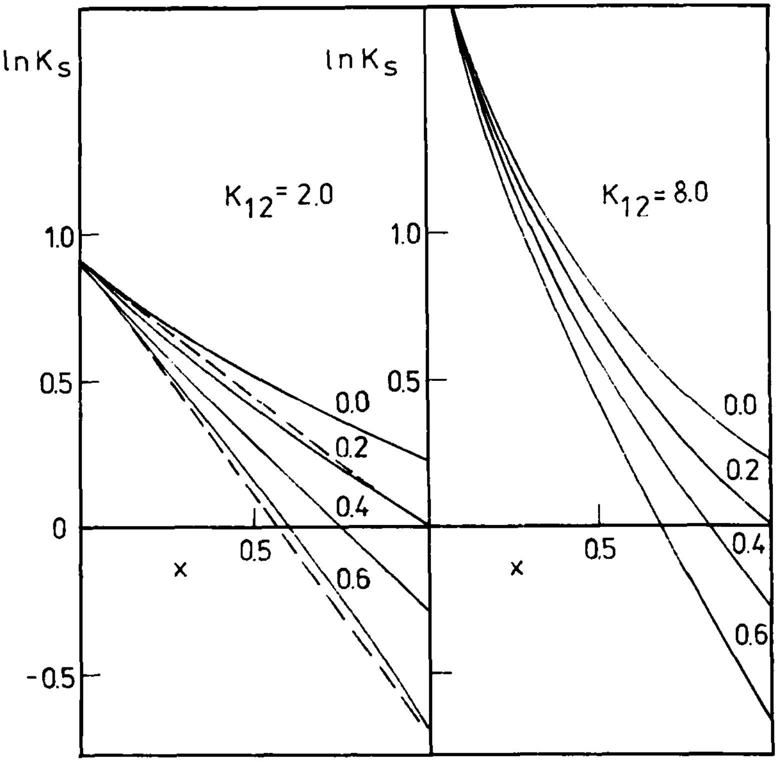

FIGURE 8. Theoretical curves ln K_s vs. x calculated according to the model M4 (see Table 1) for the same values of all parameters as in Figure 7. The dashed lines present the linear relationship 16.

It means that n* is smaller than unity. Figures 9 and 10 present the curves ln K_s vs. ln x and ln K_s vs. x calculated according to the model M5 (see Table 1). Presentation of LC data relating to the model M5 in ln K_s - ln x coordinates shows that there exists a wide region of the mobile phase composition (small and moderate values of x) in which the dependence ln K_s vs. ln x is essentially linear. In contrast to this, the dependence ln K_s vs. x is not linear in this region and is not suitable for presenting LC data calculated according to M5.

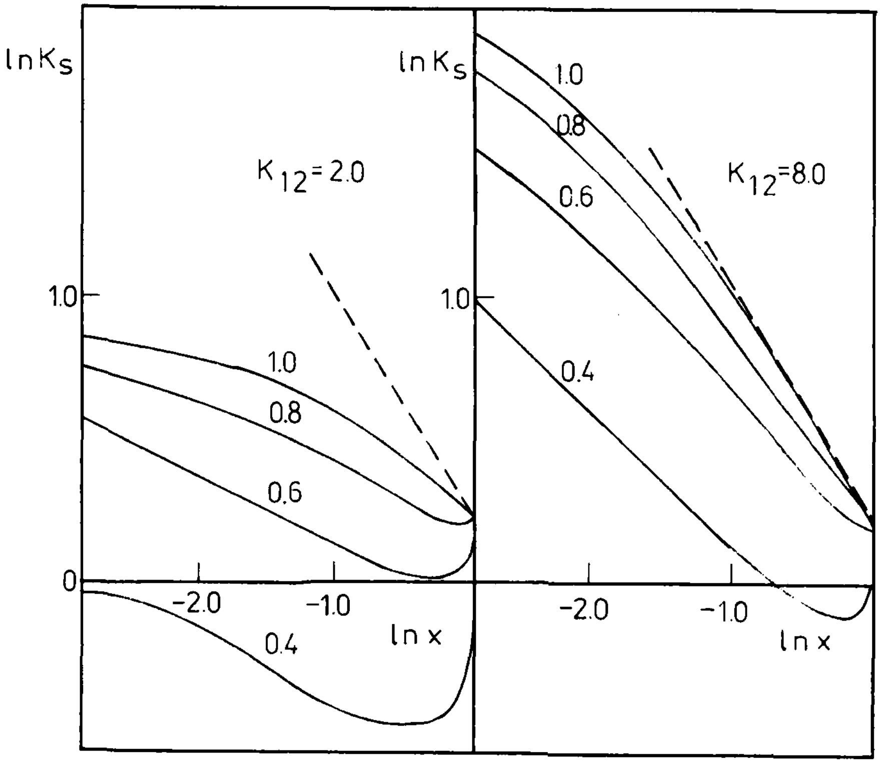

FIGURE 9. Theoretical curves ln K_s vs. ln x calculated according to the model M5 (see Table 1) for K_{12} = 2.0 and 8.0 and different values of the heterogeneity parameter m (numbers at the solid lines). The dashed lines present the Snyder-Soczewiński relationship 15.

The model studies presented in Figures 1-10 were performed by assuming equality of the molecular sizes of solute and solvent molecules. Then, the ratio of molecular sizes of solute and solvent molecules r is equal to unity. Under this assumption the Snyder-Soczewiński relationship 15 has a unit slope. For r ≠ 1 this relationship is given by:

$$\ln K_s = \ln K_{s(1)} - r \ln x \qquad (18)$$

Equation 18 describes LC model, in which molecules of the more efficient eluting solvent (1-st solvent) are strongly adsorbed on the solid

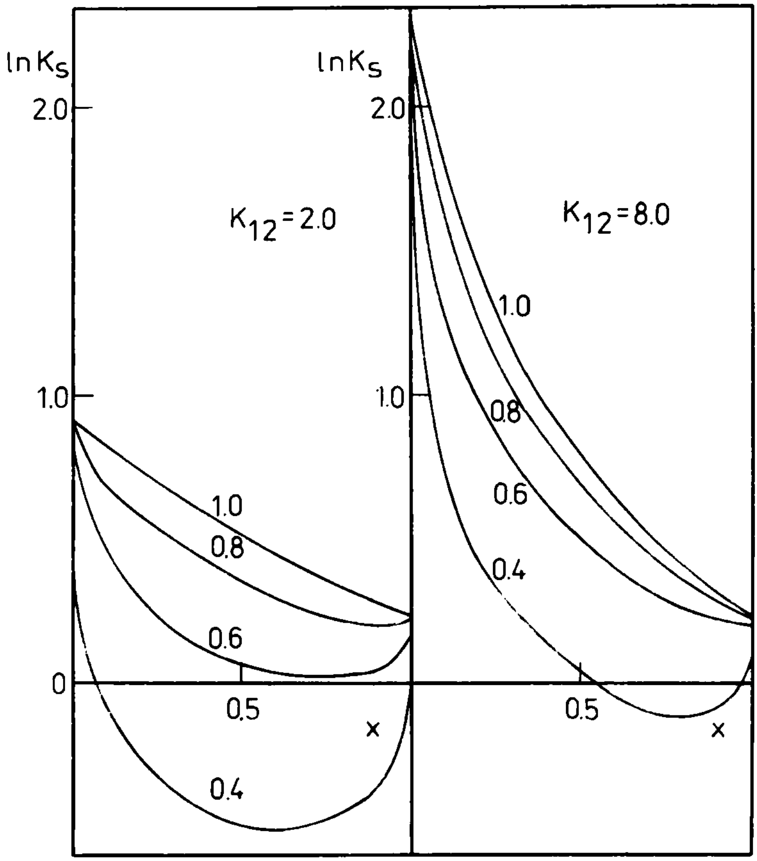

FIGURE 10. Theoretical curves ln K_s vs. x calculated according to the model M5 for the same parameters as in Figure 9.

surface and in consequence, the surface solution does not contain molecules of the 2-nd solvent ($K_{12} >> 1$). An analogous relationship to equation 7, involving difference in molecular sizes of solute and solvent molecules ($r \neq 1$), may be written as follows:

$$\ln K_s = a_1 - \eta \ln x \quad ; \quad \eta = n\, r \tag{19}$$

where n is defined by equation 6. However, for $r \neq 1$ the constant $K_{12} = (K_{s2}/K_{s1})^{1/r}$ (2).

TABLE 4

Values of the parameter $\eta = r n$ for solutes chromatographed in the systems 1a, 1b, 1c, 2a, 2b and 2c (20,21)

Solute	Values of η for systems:					
	1a	1b	1c	2a	2b	2c
Naphthalene	0.54	0.13	0.13	-	0.24	0.21
2-Methylnaphthalene	0.54	0.13	0.14	-	0.25	-
2,3-Dichlorophenol	1.30	0.42	0.60	0.71	-	0.40
2,4-Dichlorophenol	1.22	0.42	0.60	0.77	-	0.44
2,5-Dichlorophenol	1.28	0.51	0.48	0.73	-	0.40
2,6-Dichlorophenol	1.14	0.30	0.36	0.70	-	0.33
o-Nitrophenol	1.24	0.16	0.30	-	-	0.16
9-Methylantracene	0.81	0.15	-	0.44	-	-
N-Phenyl-1-naphylamine	1.42	0.28	-	1.05	-	-
2-Nitro-p-toluidyne	-	0.54	0.74	-	0.60	-
5-Nitro-o-toluidyne	-	0.84	1.10	-	0.70	-
o-Nitroaniline	-	0.46	0.72	1.33	0.50	0.57
m-Nitroaniline	-	0.64	1.00	-	0.66	0.74
p-Nitroaniline	-	0.78	1.20	-	0.75	1.15
Anthracene	0.72	-	-	0.30	-	-
Pyrene	0.74	-	-	0.54	-	-
Phenanthrene	0.74	-	-	0.50	-	-
Chrysene	0.86	-	-	0.70	-	-
Fluorenone	1.10	-	0.26	-	-	0.20

Systems: 1a - benzene(1)-cyclohexane(2)- silica gel; 1b - acetone(1)-benzene(2)-silica gel; 1c - ethyl acetate(1)-benzene(2)-silica gel; 2a - benzene-cyclohexane-aluminium oxide; 2b acetone-benzene-aluminium oxide; 2c - ethyl acetate-benzene-aluminium oxide.

Generally, the parameter η is determined by the ratio of molecular sizes of solute and solvent molecules r and n, where n is a complex function of different parameters and its definition depends on the LC model (see Table 2). In Table 4 the values of η are summarized for different solutes chromatographed in three different mobile phases and two adsorbents (20,21). These values were evaluated according to an equation correlating the adsorption and chromatographic data; it is (20):

$$\ln K_s = a_1 + \eta \ln [n_1^e/(n^s x) + 1] \qquad (20)$$

where n_1^e is the adsorption excess of the 1-st solvent measured in the eluent-adsorbent system and n^s is the total number of moles in the surface phase (20). It is easy to see in Table 4 that for majority solutes the values of η are smaller than unity whereas for these systems the values of r are greater than unity; it means that the simple model leading to the linear relationship 18 cannot be applied for interpreting the data in question. For the systems presented in Table 4 the contribution of n to the value of η is significant. Since the values of n are considerably smaller than unity and in consequence, the η-values become smaller than unity although the r-values exceed unity.

CONCLUSIONS

It follows from the discussion presented in the previous section that LC data relating to different chromatographic models can be approximated in a limited region of the mobile phase composition by the linear relationships 1 and 2. Therefore, a physicochemical interpretation of the parameters a_i and b_i is very difficult because they are complex functions of different parameters characterizing competitive solute and solvent adsorption, nonideality of the surface and mobile phases, adsorbent heterogeneity and difference of molecular sizes of solute and solvent molecules. Thus, the linear parameters a_i and b_i evaluated from LC data provide a scant information about LC model and additional data (e.g., adsorption measurements) are required to suggest a solute retention mechanism.

Analysis of the linear segments appearing in the curves $\ln K_s$ vs. ln x and $\ln K_s$ vs. x leads to several conclusions, which may be useful for interpretation of LC data. They are:

1) The parameter n may be smaller than unity as : surface phase contains molecules of both solvents (model M1), a special relation exists between interaction parameters (model M2), association of molecules of the 1-st solvent occurs in the mobile phase (M3) and adsorbent surface is heterogeneous (model M5).

2) The parameter n may be greater than unity as solute-solvent interactions are strong (models M2 and M4).

3) For higher values of K_{12} (strong adsorption of 1-st solvent) the curves ln K_s vs. ln x are essentially linear in a wide region of the mobile phase composition (at x → 1), however, for smaller values of K_{12} (comparable adsorption of both solvents) an analogous linearity is observed in the case of the dependence of ln K_s vs. x.

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REFERENCES

1. Soczewiński, E., Anal. Chem., 41, 1969, 179.
2. Jaroniec, M., Martire, D.E. and Borówko, M., Advances Colloid Interface Sci., in press.
3. Jaroniec, M., Dawidowicz, A. and Jaroniec, J.A., J. Liquid Chromatogr., 8, 1985, 441.
4. Soczewiński, E. and Jusiak, J., Chromatographia, 14, 1981, 23.
5. Soczewiński, E., J. Chromatogr., 130, 1977, 23.
6. Jaroniec, M. and Ościk, J., Journal HRC & CC, 5, 1982, 3.
7. Jaroniec, M. and Jaroniec, J.A., J. Liquid Chromatogr., 7, 1984, 393.
8. Jandera, P. and Churacek, J., Advances in Chromatogr., 19, 1980, 125.

9. Snyder, L.R. and Poppe, H., J. Chromatogr., 184, 1980, 363.

10. Martire, D.E. and Jaroniec, M., J. Liquid Chromatogr., in press.

11. Jaroniec, M., Różylo, J.K. and Ościk-Mendyk B., J. Chromatogr., 179, 1979, 237.

12. Jaroniec, M. and Martire, D.E., J. Chromatogr., submitted for publication.

13. Jaroniec, M., Narkiewicz, J. and Borówko, M., Chromatographia, 11, 1978, 581.

14. Borówko, M., J. Colloid Interface Sci., 102, 1984, 519.

15. Borówko, M. and Jaroniec, M., J. Chem. Soc. Faraday I, 79, 1983,363.

16. Jaroniec, M. and Jaroniec, J.A., J. Chromatogr., 295, 1984, 377.

17. Borówko, M. and Jaroniec, M., Chromatographia, 12, 1979, 672.

18. Jaroniec, M., Różylo, J.K. and Golkiewicz, W., J. Chromatogr., 178, 1979, 27.

19. Jaroniec, M. and Ościk-Mendyk, B., J. Chem. Soc. Faraday I, 77, 1981, 1277.

20. Ościk-Mendyk, B., Różylo, J.K. and Jaroniec, M., Journal HRC & CC, 4, 1981, 74.

21. Ościk-Mendyk, B., Jaroniec, M. and Różylo, J.K., Chem. Anal., 29, 1984, 29.