CHROM. 11,451

LIQUID ADSORPTION CHROMATOGRAPHY WITH A TWO-COMPONENT MOBILE PHASE

I. EFFECTS OF NON-IDEALITY OF THE MOBILE PHASE

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(First received May 12th, 1978; revised manuscript received September 6th, 1978)

SUMMARY

Analytical expressions for the distribution coefficient of a chromatographed compound, taking into account the non-ideality of a two-component mobile phase, have been derived in terms of Snyder's theory of liquid adsorption chromatography and the theory of liquid adsorption formulated by Everett and Myers. Model calculations have been made by assuming regularity of the mixed mobile phase.

INTRODUCTION

The optimization of chromatographic separations is one of the most important problems in chromatography. In the case of liquid adsorption chromatography (LC) this problem involves the prediction of the optimal mobile-phase gradient for a given chromatographed mixture[1]. Most methods of determining the optimal mobile-phase gradient are based on the dependence of the capacity ratio on the composition of the mobile phase[1–6].

The most advanced studies, concerning the prediction of the capacity ratio in LC with a mixed mobile phase, have been made by Snyder[7,8], Soczewiński[9,10], Ościk[11,12], Jandera and Churáček[13,14], and Scott and Kucera[15]. Snyder's approach[7,8], one of the most popular treatments in LC theory, involves one- and two-component mobile phase. In this formulation, chromatographic systems with two-component mobile phases have been discussed by assuming homogeneity of the adsorbent surface and ideality of the mobile phase. The papers of Jandera and Churáček[13,14] develop Snyder's idea[7,8]; however, the approaches of Soczewiński[9,10] and Scott and Kucera[15] lead to analytical expressions for the capacity ratio which are analogous to those obtained on the basis of Snyder's treatment. Recently, Poppe and co-workers[16] have extended Snyder's equations for LC with an ideal mobile phase to LC with a non-ideal phase. Another approach to LC with a multicomponent ideal or regular mobile

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phase has been proposed by Ościk[11]. This treatment was examined by using experimental thin-layer chromatographic (TLC) data[12]. A comparison of Ościk's treatment with Snyder's approach has recently been made by Jaroniec et al.[17].

In this paper the influence of nonideality of the mobile phase on the distribution coefficient is discussed in terms of Snyder's treatment and the theory of liquid adsorption of Everett and Myers. Model calculations of the distribution coefficient have been performed for two-component mobile phases, because these phases are usually employed in experiments.

GENERAL CONSIDERATIONS

Let us consider the distribution of a given compound S between the solvent A (mobile phase) and the stationary phase. The distribution coefficient $K'_{(A)S}$ is defined by

$$K'_{(A)S} = y_S/x_S \qquad (1)$$

where x_S and y_S are the mole fractions of the sample S in the mobile and stationary phases, respectively. The distribution coefficient in eqn. 1 is equal to the distribution coefficient $K_{(A)S}$ divided by the volume of adsorbed solvent per gram of adsorbent, V_a, i.e.

$$K'_{(A)S} = K_{(A)S}/V_a$$

where

$$K_{(A)S} = c_S^{\sigma}/c_S \text{ and } V_a = V/\eta_A W$$

Here, c_S and c_S^{σ} are the concentrations of the sample S in the mobile (in mole/ml) and adsorbed phase (in mole/g), respectively, V is the total volume of unadsorbed phase (in ml) in an adsorption system and W is the total weight of adsorbent (in g) in the adsorption system. At very low sample concentrations

$$x_S = \frac{n_S}{n_A + n_S} \approx \frac{n_S}{n_A}; \quad y_S = \frac{n_S^{\sigma}}{n_A^{\sigma} + n_S^{\sigma}} \approx \frac{n_S^{\sigma}}{n_A^{\sigma}} \qquad (2)$$

and the distribution coefficient $K'_{(A)S}$ is equal to

$$K'_{(A)S} = k'_{(A)S} \cdot \frac{n_A}{n_A^{\sigma}} = k'_{(A)S} \eta_A \qquad (3)$$

where $k'_{(A)S}$ is the capacity ratio

$$k'_{(A)S} = \frac{n_S^{\sigma}}{n_S} \qquad (4)$$

n_S and n_A are the numbers of moles of the sample S and solvent A in the mobile phase, respectively, n_S^{σ} and n_A^{σ} are the numbers of moles of S and A in the adsorbed phase

and η_A is a parameter, to a first approximation, assumed to be characteristic of a given adsorbent and independent of the nature of the solvent[7]. The thermodynamic equilibrium constant

$$K_{SA}^{th} = \frac{y_S x_A}{y_A x_S} \tag{5}$$

at very low sample concentrations, i.e.,

$$K_{SA}^{th} = y_S/x_S$$

is equal to the distribution coefficient $K'_{(A)S}$. Thus,

$$K'_{(A)S} = K_{SA}^{th} \tag{6}$$

Let us now consider a two-component mobile phase A–B. According to Snyder's approach[7], the combined distribution coefficient $K'_{(AB)S}$ is given by:

$$K'_{(AB)S} = (1 - y_B)K'_{(A)S} + y_B K'_{(B)S} \tag{7}$$

For an ideal mobile phase, the mole fraction y_B may be calculated from the Langmuir-type equation:

$$y_B = \frac{K_{BA}^{th} x_B}{x_A + K_{BA}^{th} x_B} \tag{8}$$

Using the relationship[18] between the thermodynamic equilibrium constants K_{BA}^{th}, K_{SA}^{th} and K_{SB}^{th}, i.e.,

$$K_{BA}^{th} = K_{SA}^{th}/K_{SB}^{th} \tag{9}$$

we have

$$y_B = \frac{x_B/K_{SB}^{th}}{(x_A/K_{SA}^{th}) + (x_B/K_{SB}^{th})} = \frac{x_B/K'_{(B)}}{(x_A/K'_{(A)S}) + (x_B/K'_{(B)S})} \tag{10}$$

Substitution of eqn. 10 into eqn. 7 gives

$$\frac{1}{K'_{(AB)S}} = \frac{1}{K'_{(A)S}} + \left(\frac{1}{K'_{(B)S}} - \frac{1}{K'_{(A)S}}\right)x_B \tag{11}$$

Eqn. 11 has been discussed previously[19], and may also be obtained directly from the definition of the distribution coefficient $K'_{(AB)S} = y_S/x_S$. For this purpose we consider the adsorption of the sample S from a three-component ideal liquid mixture A–B–S. Following Minka and Myers[18], we have

$$y_S = \frac{x_S}{(x_A/K'_{(A)S}) + (x_B/K'_{(B)S}) + x_S} \approx \frac{x_S}{(x_A/K'_{(A)S}) + (x_B/K'_{(B)S})} \tag{12}$$

Using eqn. 12 and the definition of the distribution coefficient $K'_{(AB)S}$, we obtain eqn. 11.

NON-IDEAL TWO-COMPONENT MOBILE PHASE

In the case of a non-ideal mobile phase the thermodynamic equilibrium constant K_{BA}^{th} is expressed as

$$K_{BA}^{th} = \frac{a_B^\sigma a_A}{a_A^\sigma a_B} = \frac{y_B x_A}{y_A x_B} \cdot \frac{\gamma_B^\sigma \gamma_A}{\gamma_A^\sigma \gamma_B} \tag{13}$$

where a_i and γ_i are the activity and activity coefficient of the i-th solvent in the mobile phase, respectively, and the superscript σ refers to the adsorbed phase. Following Sircar and Myers[20], we assume an ideal adsorbed phase and a non-ideal mobile phase. Then,

$$K_{BA}^{th} = \frac{y_B x_A}{y_A x_B} \cdot \frac{\gamma_A}{\gamma_B} \tag{14}$$

where the activity coefficients γ_A and γ_B refer to the two-component liquid mixture A–B. The mole fraction y_B, calculated from eqn. 14, may be substituted into eqn. 7. Now, we assume that the mobile phase is regular and the influence of the sample S on the activities γ_A and γ_B can be neglected. Then, according to the theory of regular solutions[21],

$$\gamma_i = \exp[q(1 - x_i)^2] \quad \text{for} \quad i = A, B; \quad q < 2 \tag{15}$$

and

$$\frac{\gamma_A}{\gamma_B} = \exp[-q(1 - 2x_B)] \tag{16}$$

where q is defined as

$$q = \frac{Nz}{RT}[u_{AB} - 0.5(u_{AA} + u_{BB})] \tag{17}$$

Here N is Avogadro's number, z is the number of nearest neighbours to a given lattice site, u_{ij} $(i, j = A, B)$ is the interaction energy between a pair of molecules i, j on adjacent lattice sites, R is the gas constant and T is the absolute temperature. In the case of an ideal liquid mixture A–B, the interaction energies u_{AA} and u_{BB} are identical, $i.e.$,

$$u_{AA} = u_{AB} = u_{BB}$$

and then parameter q is equal to zero. Eqns. 14 and 16 give

$$y_B = \frac{\alpha x_B}{x_A + \alpha x_B} \tag{18}$$

The constant α is defined as

$$\alpha = K_{BA}^{th}\frac{\gamma_B}{\gamma_A} = \frac{K_{SA}^{th}\gamma_B}{K_{SB}^{th}\gamma_A} = \frac{K_{SA}^{th}}{K_{SB}^{th}}\exp[q(1-2x_B)] \tag{19}$$

For an ideal adsorbed phase and a non-ideal mobile phase S–A, the thermodynamic constant K_{SA}^{th} is

$$K_{SA}^{th} = \frac{y_S x_A}{y_A x_S} \cdot \frac{\gamma_A}{\gamma_{S(A)}} \tag{20}$$

where $\gamma_{S(A)}$ is the activity coefficient of sample S in the solvent A. For infinitely low concentrations of sample S, applying relationships $x_A \approx y_A \approx 1$ and $\gamma_A \approx 1$ (see eqn. 15), we obtain

$$K_{SA}^{th} = \frac{y_S}{x_S \gamma_{S(A)}} = \frac{K'_{(A)S}}{\gamma_{S(A)}} \tag{21}$$

Similarly, for K_{SB}^{th} we have

$$K_{SB}^{th} = K'_{(B)S}/\gamma_{S(B)} \tag{22}$$

Substitution of eqns. 21 and 22 in eqn. 19 gives

$$\alpha = \varkappa\frac{K'_{(A)S}}{K'_{(B)S}}\exp[q(1-2x_B)] \tag{23}$$

where

$$\varkappa = \gamma_{S(B)}/\gamma_{S(A)} \tag{24}$$

However, combination of eqns. 7 and 18 gives:

$$K'_{(AB)S} = \frac{x_B\left(\varkappa K'_{(A)S}\, e^{q(1-2x_B)} - K'_{(A)S}\right) + K'_{(A)S}}{x_B\left(\varkappa\frac{K'_{(A)S}}{K'_{(B)S}}\, e^{q(1-2x_B)} - 1\right) + 1} \tag{25}$$

Eqn. 25 defines the dependence of $K'_{(AB)S}$ on the mole fraction, x_B. This equation has been obtained by assuming ideality of the adsorbed phase, regularity of the mobile phase, homogeneity of the adsorbent surface and applying Snyder's definition of $K'_{(AB)S}$ in eqn. 7.

In Figs. 1–4 the theoretical dependences of $K'_{(AB)S}$ vs. x_B, calculated according to eqn. 25 for $\varkappa = 1$, are presented. Figs. 1 and 2 show the functions $K'_{(AB)S}(x_B)$ for $K'_{(B)S} = 3$, 1.5 and 0.5 and assuming $K'_{(A)S} = 5$, $q = 0$ (ideal mobile phase) (Fig. 1) and $q = -2$ (Fig. 2). Figs. 3 and 4 present the functions $K'_{(AB)S}$ for different values of q the parameter which characterizes the interactions in the mobile phase A–B.

The function $K'_{(AB)S}(x_B)$ decreases for all values of $x_B \in (0, 1)$, if $K'_{(AS)} > K'_{(B)S}$. For $q \neq 0$ this function has an inflection point, which is clearly observed if $K'_{(A)S}$ and $K'_{(B)S}$ are little different (see Fig. 4). Thus, for a regular mobile phase, i.e., $q \neq 0$, the dependence of the distribution coefficient $K'_{(AB)S}$ on x_B is different from that obtained for an ideal mobile phase, i.e., $q = 0$ (see Figs. 3 and 4). For low concentrations of x_B, $K'_{(AB)S}$ (for $q < 0$) $> K'_{(AB)S}$ (for $q = 0$); however, after the inflection point (at high values of x_B) this inequality is reversed. Our conclusions, resulting from model calculations, are in a good agreement with the theoretical and experimental studies of Poppe and co-workers[16,22], which generalize Snyder's theory to non-ideal mobile phase. However, our treatment seems to be more general, because we assume Snyder's eqn. 7 and the theories of Everett[21] and Minka and Myers[18] to describe the adsorption from liquid mixtures.
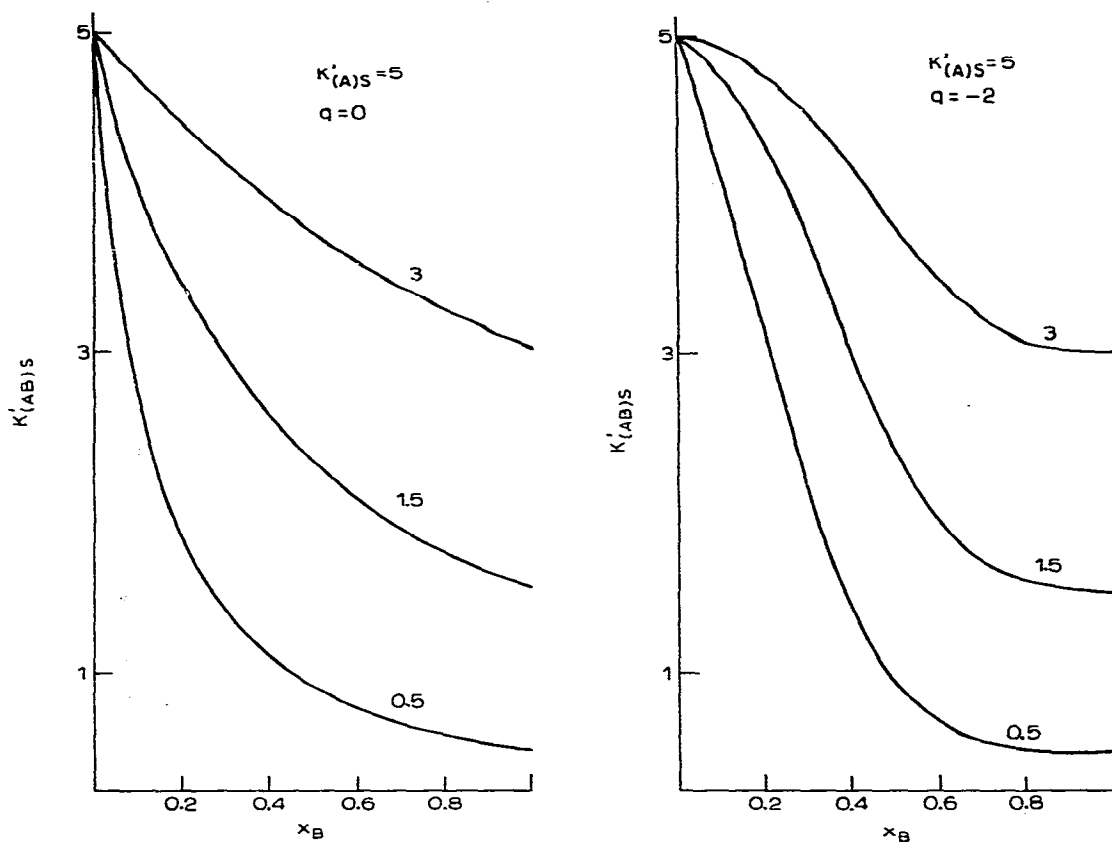

Fig. 1. Theoretical dependences of $K'_{(AB)S}$ vs. x_B calculated according to eqn. 25 for $K'_{(A)S} = 5$, $\varkappa = 1$, $q = 0$ and different values of $K'_{(B)S}$ (numbers on the curves).

Fig. 2. Theoretical dependences of $K'_{(AB)S}$ vs. x_B calculated according to eqn. 25 for $K'_{(A)S} = 5$, $\varkappa = 1$, $q = -2$ and different values of $K'_{(B)S}$ (numbers on the curves).

Now, we consider the possibility of calculating $K'_{(AB)S}$ from the definition (see eqn. 1):
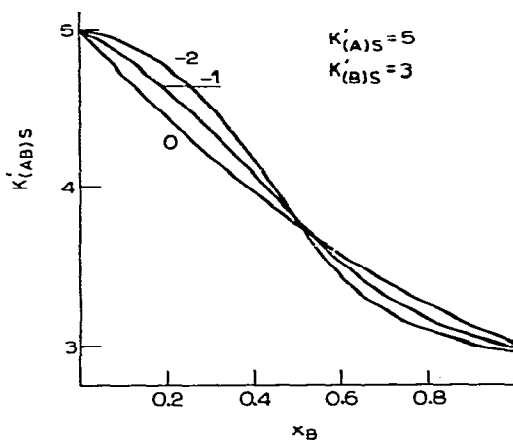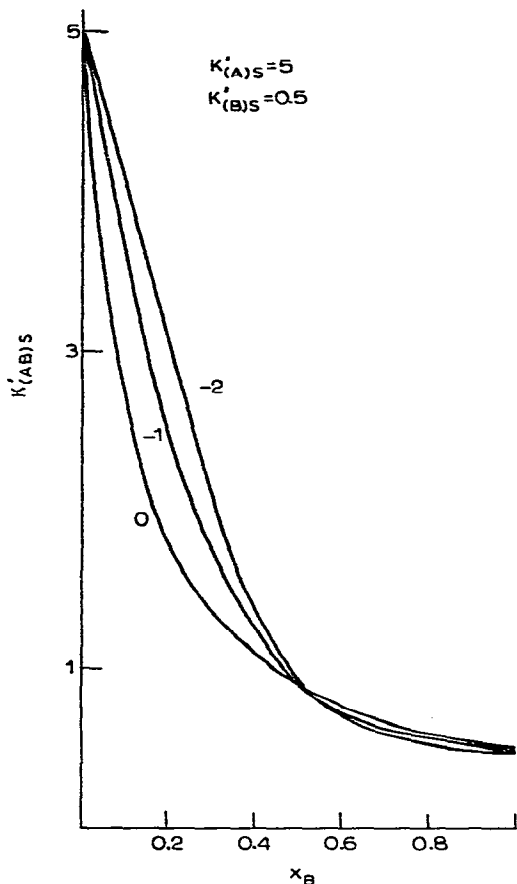
$$K'_{(AB)S} = y_S/x_S \qquad (26)$$

Fig. 3. Theoretical dependence of $K'_{(AB)S}$ vs. x_B calculated according to eqn. 25 for $K'_{(A)S} = 5$, $K'_{(B)S} = 0.5$, $\varkappa = 1$ and different values of q (numbers on the curves).

Fig. 4. Theoretical dependences of $K'_{(AB)S}$ vs. x_B calculated according to eqn. 25 for $K'_{(A)S} = 5$, $K'_{(B)S} = 3$, $\varkappa = 1$ and different values of q (numbers on the curves).

In the case of adsorption from a non-ideal three-component liquid mixture, eqn. 12 may be rewritten as

$$y_S = \frac{x_S \gamma_{S(AB)}}{(a_A/K_{SA}^{th}) + (a_B/K_{SB}^{th}) + x_S \gamma_{S(AB)}} \tag{27}$$

At very low sample concentrations, from eqns. 26 and 27 we have

$$K'_{(AB)S} = \frac{\gamma_{S(AB)}/\gamma_{S(A)}}{(a_A/K'_{(A)S}) + (\varkappa a_B/K'_{(B)S})} \tag{28}$$

where $\gamma_{S(AB)} \neq 1$ is a function of x_A and x_B. The method of calculation of $\gamma_{S(AB)}$ is described in ref. 18. Assuming that $K'_{(A)S} \gg K'_{(B)S}$ we have

$$K'_{(AB)S} = K_{SB}^{th} \gamma_{S(AB)}/a_B \tag{29}$$

This equation is very similar to that derived by Poppe and co-workers[16].

TABLE I

THE PARAMETERS K_{AB}^{th} AND q CALCULATED ACCORDING TO EQN. 31

Sample S	Mobile phase A–B	K_{BA}^{th}	q
3-Aminopyridine	Chloroform–benzene	2.94	−0.22
2-Amino-6-methylpyridine	Chloroform–benzene	3.57	−0.24
2-Aminopyridine	Butyl acetate–benzene	4.35	0.13
3-Aminopyridine	Butyl acetate–benzene	4.00	0.15
6-Methylquinoline	Benzene–cyclohexane	5.55	0.23
2,6-Dimethylquinoline	Benzene–cyclohexane	5.88	0.18
6-Methylquinoline	Chloroform–carbon tetrachloride	3.13	−0.037
Isoquinoline	Chloroform–carbon tetrachloride	3.57	−0.022

APPLICATION

For the purpose of illustration, the experimental TLC data of Ościk and Chojnacka[23] have been used to examine eqn. 25. First, these data have been recalculated by means of the relationship

$$R_M = \log k' \tag{30}$$

and then they have been approximated by using the following linear form of eqn. 25

$$G(x_B) = 2qx_B + d \tag{31}$$

where

$$G(x_B) = \ln\frac{K'_{(AB)S} - K'_{(B)S}}{K'_{(A)S} - K'_{(AB)S}} + \ln\frac{x_B}{1 - x_B}$$
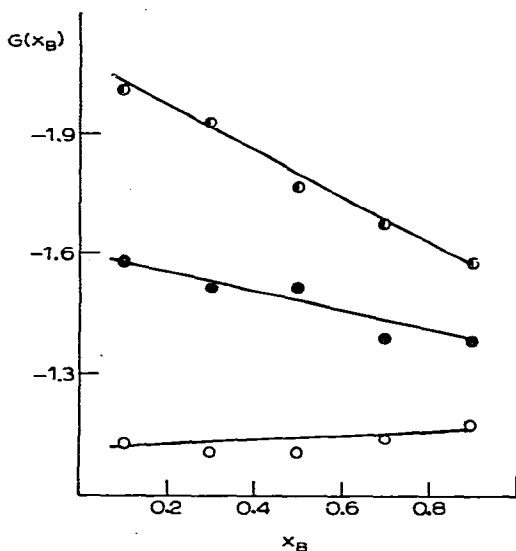

Fig. 5. Linear dependences of $G(x_B)$ plotted according to eqn. 31 for the adsorption systems: (●) 2-aminopyridine (S)–butyl acetate (B)–benzene (A); (◑) 2,6-dimethylquinoline (S)–benzene (B)–cyclohexane (A); (○) 6-methylquinoline (S)–chloroform (B)–carbon tetrachloride (A).

and
$$d = -\ln K_{BA}^{th} - q$$

The parameters K_{BA}^{th} and q are summarized in Table I.

Fig. 5 shows the experimental dependences $G(x_B)$ for some adsorption systems. It follows from Table I that K_{BA}^{th} and q, calculated for different chromatographed samples and the same mobile phase A–B, are practically independent of the sample; thus they may be used to compare the different mobile phase used in LC.

CONCLUSIONS

The distribution coefficient $K'_{(AB)S}$ for a non-ideal two-component mobile phase may be evaluated according to eqn. 28 or eqns. 7 and 14. In the case of a regular mobile phase the distribution coefficient is given by eqn. 25, which may be easily linearized (see eqn. 31). This linear form is very convenient for approximating the experimental data. The model calculations of $K'_{(AB)S}$ for a regular two-component mobile phase show that the influence of the interaction parameter q on the shape of the dependence $K'_{(AB)S}$ vs. x_B may be significant, if Snyder's definition for $K'_{(AB)S}$, eqn. 7, is used.

ACKNOWLEDGMENTS

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