

CHROM. 11,033

## DEPENDENCE OF THE CAPACITY RATIO ON THE COMPOSITION OF THE BINARY MOBILE PHASE IN LIQUID-SOLID ADSORPTION CHROMATOGRAPHY

J. NARKIEWICZ, M. JARONIEC, M. BORÓWKO and A. PATRYKIEJEW

*Department of Theoretical Chemistry, Institute of Chemistry, M. Curie-Skłodowska University, Nowotki 12, 20031 Lublin (Poland)*

(First received November 29th, 1977; revised manuscript received February 15th, 1978)

---

### SUMMARY

The dependence of the capacity ratio on the composition of the binary mobile phase is discussed in terms of Snyder's treatment. The relationships obtained for the capacity ratio have been tested on experimental data. The derivation of the relationship for the capacity ratio discussed by Jandera and Churacek has been examined.

---

### INTRODUCTION

Increasing interest in gradient elution chromatography as a rapid method of analysis has made desirable the elucidation of the theoretical basis of the process of liquid-solid adsorption chromatography. The basic problems involved are optimization of the time of analysis and the resolution. One of the main parameters that determines the process of elution is the capacity ratio. Although in isocratic elution at an infinitely low concentration of the sample the capacity ratio remains constant for a given chromatographic system, in gradient elution it is necessary to know the relationship between the capacity ratio,  $k_{AB}$ , and the composition of the mobile phase A-B.

It follows from many papers<sup>1-8</sup> that three types of relationships describing the dependence between the capacity ratio and the concentration of the component that is the more efficient eluent in a binary mobile phase can be distinguished:

$$\log k'_{AB} = a + b \log x_B \quad (1a)$$

$$\log k'_{AB} = a + b x_B \quad (1b)$$

$$1/k'_{AB} = a + b x_B \quad (1c)$$

where  $x_B$  is the molar fraction (or concentration) of the more efficient eluent B in the binary mobile phase A-B and  $a$  and  $b$  are constants. Numerous studies<sup>5,7,9</sup> have

shown that these three relationships can be used to characterize a chromatographic system.

#### DISCUSSION OF THE JANDERA-CHURACEK DERIVATION OF THE RELATIONSHIP BETWEEN $\log k'_{AB}$ AND $\log x_B$

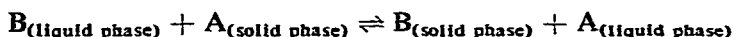
Jandera and Churacek<sup>7</sup> derived eqns. 1a and 1b; the former was obtained on the basis of Snyder's theory of liquid-solid adsorption chromatography<sup>10</sup>. Their derivation of eqn. 1a requires further comment. According to their derivation, the constants  $a$  and  $b$  are expressed by  $a = \log k'_B$  and  $b = -n = -\omega_S/\omega_B$ , where  $k'_B$  is the capacity ratio for a sample compound S in pure solvent B and  $\omega_S$  and  $\omega_B$  are the molecular areas occupied by molecules of sample S and solvent B, respectively.

Let us discuss the constants  $a$  and  $b$  according to Snyder's treatment<sup>10</sup>. Snyder obtained the following expression:

$$\varepsilon_{AB} = \varepsilon_A + (\alpha\omega)^{-1} \log [x_B 10^{-\alpha\omega(\varepsilon_A - \varepsilon_B)} + 1 - x_B] \quad (2)$$

for the strength  $\varepsilon_{AB}$  of a binary solvent A-B, assuming the following:

(a) an expression for equilibrium constant,  $K$ , defining the following reaction:



$$K = 10^{\alpha\omega(\varepsilon_B - \varepsilon_A)} = \frac{y_B (1 - x_B)}{(1 - y_B) x_B} \quad (3)$$

(b) a relationship between the capacity ratios  $k'_{AB}$  and  $k'_B$ :

$$\log (k'_{AB}/k'_A) = \alpha \omega (\varepsilon_A - \varepsilon_{AB}) \quad (4a)$$

$$\log (k'_B/k'_A) = \alpha \omega (\varepsilon_A - \varepsilon_B) \quad (4b)$$

(c) additivity of the capacity ratios  $k'_A$  and  $k'_B$ :

$$k'_{AB} = y_B k'_B + (1 - y_B) k'_A \quad (5)$$

(d) equality of the molecular areas occupied by molecules of adsorbed samples, solvents A and B:

$$\omega_A = \omega_B = \omega_S = \omega \quad (6)$$

In the above equations,  $k'_A$  denotes the capacity ratio for a sample compound in pure solvent A;  $\alpha$  is the surface activity function;  $\varepsilon_A$  and  $\varepsilon_B$  denote the strengths of the solvents A and B, respectively; and  $y_B$  is the molar fraction of solvent B in the surface phase. Jandera and Churacek, again introducing eqn. 2 into eqn. 4a but this time omitting Snyder's assumption about the equality of the molecular areas of

the sample compound S and the more efficient eluent B, as well as neglecting the term  $1 - x_B$  in eqn. 2, obtained eqn. 1a. A direct consequence of neglecting the term  $1 - x_B$  is an irregular behaviour of eqn. 1a in the region of infinitely low concentrations of  $x_B$ . In real systems, it would be expected that  $k'_{AB}$  will tend towards  $k'_A$  at  $x_B \rightarrow 0$ , whereas eqn. 1a gives  $k'_{AB} \rightarrow \infty$  within this limit. Eqn. 1a also suggests that  $k'_{AB}$  for any sample component chromatographed does not depend on the properties of the less efficient eluent A in the binary solvent mixture A-B. Hence, it can be concluded that for a less efficient eluent in the binary mobile phase,  $k'_{AB}$  will be constant at a given concentration of the more efficient eluent B. However, numerous experimental data show that  $k'_{AB}$  at a given concentration  $x_B$  is dependent on the properties of all components of the mobile phase. The treatment of Jandera and Churacek resulted in a value of  $n \neq 1$ , which is due to the incorrect application of eqn. 6. Although the values of  $n$  in eqn. 1a may be different from unity, which is often confirmed experimentally, the correct application of Snyder's assumption leads to the value  $n = 1$ .

#### DERIVATION OF THE DEPENDENCE OF THE CAPACITY RATIO IN TERMS OF SNYDER'S THEORY

In the light of the above discussion, it seems appropriate to derive a relationship between the capacity ratio,  $k'_{AB}$ , and the composition of the binary mobile phase in which the parameters depend on the properties of both the solvents of the mobile phase and the sample being chromatographed. Moreover, this relationship should be correct for the whole range of concentrations  $x_B$ . Such a relationship can be obtained by using Snyder's assumptions (a)-(d) above. Combining eqn. 4b with eqn. 3, we obtain

$$k'_A/k'_B = \frac{y_B(1-x_B)}{(1-y_B)x_B} \quad (7)$$

Then, elimination of the variable  $y_B$  from eqns. 5 and 7 leads to

$$\frac{1}{k'_{AB}} = \frac{1}{k'_A} + \left( \frac{1}{k'_B} - \frac{1}{k'_A} \right) x_B \quad (8)$$

This equation is related to the empirical relationship in eqn. 1c. Of course, eqn. 8, assuming  $1 - x_B \ll Kx_B$ , gives

$$\log k'_{AB} = \log k'_B - \log x_B \quad (9)$$

which corresponds to the special case of the empirical relationship in eqn. 1a, *i.e.*,

$$\log k'_{AB} = a - \log x_B \quad (10)$$

with  $-b = n = 1$ . It can easily be seen that eqn. 8 predicts correctly the values of  $k'_{AB}$  at the limiting concentrations of  $x_B$  ( $x_B = 0$  and  $x_B = 1$ ) and is a direct consequence of Snyder's theory<sup>10</sup>, *i.e.*, this equation is obtained from Snyder's theory

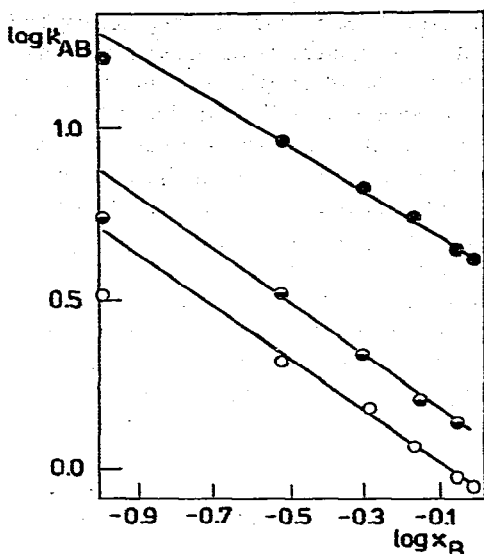


Fig. 1. Linear dependences plotted according to eqn. 1a. (●) A = C<sub>6</sub>H<sub>6</sub>, B = C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, S = 2-amino-3-methylpyridine, stationary phase = alumina; (○) A = CCl<sub>4</sub>, B = CHCl<sub>3</sub>, S = 2,6-dimethylquinoline, stationary phase = alumina; (◐) A = CCl<sub>4</sub>, B = CHCl<sub>3</sub>, S = quinoline, stationary phase = silica gel.

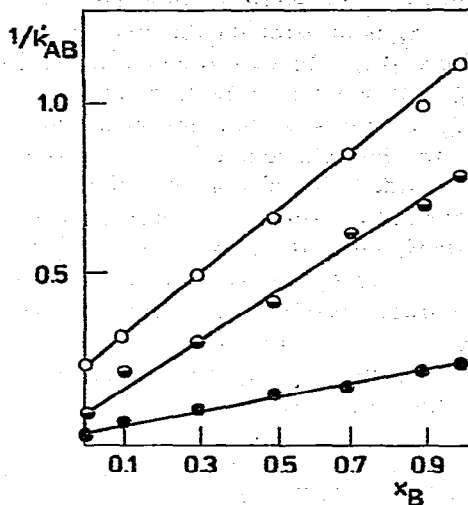
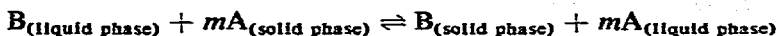


Fig. 2. Linear dependences plotted according to eqn. 8. Symbols as in Fig. 1.

without any further simplifications. Eqn. 8 has also been discussed by Soczewiński<sup>9</sup> and Scott and Kucera<sup>8</sup> by using other theoretical approaches.

In Figs. 1 and 2 the agreement of eqns. 1a and 8 with the experimental data obtained by Ościk and Chojnacka<sup>11</sup> and Różyło<sup>12</sup> is compared. It can be seen that both equations describe the experimental data at higher values of  $x_B$ , but at low concentrations of solvent B eqn. 8 gives considerably better results. These results confirm the theoretical discussion concerning the regions of applicability of eqns. 1a and 8. It is interesting, however, that eqn. 1a agrees very well with the experimental data at higher values of  $x_B$  for adsorption systems with  $n \neq 1$ . This agreement is not covered by the Snyder's treatment based upon assumptions (a)–(d); however, if A and B have very different molecular sizes, changes must be made to assumptions (a) and (d), which leads to a more general relationship for  $k'_{AB}$ .

A more generalized form of reaction in (a) can be written as



where  $m = \omega_B/\omega_A$ . This leads to the following expression for the equilibrium constant:

$$K = \frac{(1 - x_B)^m y_B}{x_B (1 - y_B)^m} \quad (11)$$

when  $m \neq 1$ , eqn. 8 cannot be solved analytically with respect to  $y_B$ , and only numerical solutions are available which are not convenient for gradient optimization.

However, in the special case when  $y_B$  approaches unity and  $K$  is sufficiently large (a large difference in concentration between the two components of the mobile phase), from eqns. 8 and 5 the following expression can be obtained:

$$\log k'_{AB} = \log \left( k'_A / K^{\frac{1}{m}} \right) - \frac{1}{m} \log x_B \quad (12)$$

for high  $x_B$  values. This equation is formally analogous to eqn. 1a where  $-1/m = b \neq -1$  (or  $n \neq 1$ ). Thus, in conclusion, it can be stated that on the basis of Snyder's theory, full mathematical justification has been found for eqn. 8, and this theory leads to the approximate eqns. 9 ( $b = -1$ ) and 12 ( $b \neq -1$ ).

#### ACKNOWLEDGEMENT

This research was supported by the Polish Academy of Sciences, Problem No. 03.10.6.03.03.

#### REFERENCES

- 1 E. Soczewiński and G. Matysik, *J. Chromatogr.*, 32 (1968) 458.
- 2 E. Soczewiński and C. A. Wachtmeister, *J. Chromatogr.*, 7 (1962) 311.
- 3 S. Hara, *J. Chromatogr.*, 137 (1977) 41.
- 4 W. Gołkiewicz, *Chromatographia*, 9 (1976) 113.
- 5 W. Gołkiewicz and E. Soczewiński, *Chromatographia*, 11 (1978) in press.
- 6 E. Soczewiński, T. Dzido and W. Gołkiewicz, *Chromatographia*, 10 (1977) 298.
- 7 P. Jandera and J. Churacek, *J. Chromatogr.*, 91 (1974) 207.
- 8 R. P. W. Scott and P. Kucera, *J. Chromatogr.*, 112 (1975) 425.
- 9 E. Soczewiński, *J. Chromatogr.*, 130 (1977) 23.
- 10 L. R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.
- 11 J. Ościk and G. Chojnacka, *J. Chromatogr.*, 93 (1974) 167.
- 12 J. K. Różyło, *Thesis*, M. Curie-Skłodowska University, Lublin, 1975.