Mieczysław JARONIEC

Progress in the Theory of Liquid Adsorption Chromatography with
the Multicomponent Mobile Phase

Postęp w teorii adsorpcyjnej chromatografii cieczowej z wieloskładnikową fazą ruchomą

Прогресс в теории жидкостной адсорбционной хроматографии
с многокомпонентной подвижной фазой

In the beginning of the sixties, extensive theoretical investigations were started with the liquid adsorption chromatography with the mixed mobile phase. Ościk [1] and Snyder [2] were the first to consider in a quantitative way the process of liquid adsorption chromatography (LSC) with the mixed mobile phase. Ościk's formulation of the thin-layer adsorption chromatography (TLC) is analogous to that employed in the treatment of gas-liquid partition chromatography with the mixed stationary phase, which was initiated by Waksmundzki et al. [3,4]. The earlier studies by Ościk [5-8], concerning the adsorption from multicomponent liquid mixtures on solid surfaces, gave the theoretical ground for this formulation. However, Snyder's approach to LSC with the mixed mobile phase is an extension of this theoretical studies concerning the LSC with one-component eluent [9,10]. Somewhat later, an alternative approach to LSC with the mixed mobile phase was developed by Soczewiński [11,12]. The final equations resulting

from Snyder [2] and Soczewiński's approaches are similar. It follows from the comparison of these approaches that the Soczewiński's idea seems to be more general [13-15].

In the seventies, the fundamental results obtained by Oścík [1], Snyder [2] and Soczewiński [11] have been developed by many authors [13-35]. In the papers [13-35] the main factors determining the process of LSC with the mixed mobile phase are discussed; they are:

(a) nonideality of the mobile and surface phases;

(b) solute-solvent interaction in the mobile and surface phases;

(c) association between molecules of solvents in the mobile and surface phases;

(d) multilayer character of the surface phase;

(e) energetic heterogeneity of the adsorbent surface;

(f) topography of adsorption sites on the surface;

(g) differences in molecular sizes of solute and solvents.

In this paper the current state of the theory of LSC with the mixed mobile phase will be presented. Especially, the theoretical results concerning the influence of the factors mentioned in the points (a) - (g) on the LSC process will be discussed.

OŚCIK'S APPROACH TO LSC WITH THE MIXED MOBILE PHASE

The thermodynamic approach to the adsorption TLC with the mixed mobile phase on energetically homogenous solid surfaces, initiated by Oścík [1], was discussed theoretically in details [32,33] and extended to energetically heterogeneous solid surfaces [34,35]. In the reference [24] this approach has been adapted to LSC. The most general equation, resulting from Oścík's approach, may be expressed as follows [24,34]:

$$\log k'_{(n)s} = \sum_{l=1}^{L} \sum_{i=1}^{n^-} h_l \log k'_{(i)s,l} \, y_{i,l} \, +$$

$$+ \sum_{i=1}^{n-1} \Lambda_{(in)s} (y_i - x_i) + Y \tag{1}$$

where $k'_{(n)s}$ is the capacity ratio of the s-th solute chromatographed in n-component mobile phase; $k'_{(i)s,1}$ is the capacity ratio of the s-th solute for the i-th solvent and the l-th type of adsorption sites; x_i and y_i are mole fractions of the i-th solvent in the mobile and surface phases, respectively; $y_{i,1}$ is the mole fraction of the i-th solvent on the l-th type of adsorption sites; "n" is the number of solvents in the mixed mobile phase; L is the number of types of adsorption sites; n = (1,2,....,n) is n-dimensional vector used as the subscript for the symbols referring to an n-component mobile phase; h_1 is the ratio of number of adsorption sites of the l-th type to the total number of sites; $A_{(in)s}$ is the constant characterizing solute-solvent interactions and it is connected with the hypothetical rational partition coefficient for solute "s" between the i-th and n-th components of the binary solvent mixture "i + n"; and Y is the constant connected with the excess of free enthalpies of the solvent mixture in the surface and mobile phases. For energetically heterogenous solids, showing a quasi-gaussian energy distribution, equation (1) may be approximated by the following relationship [34]:

$$\log k'_{(\underline{n})s} = \sum_{i=1}^{n} \log k'_{(i)s} \, y_i^{1/m} + \sum_{i=1}^{n-1} A_{(in)s} (y_i - x_i) + Y \qquad (2)$$

where "m" is the heterogeneity parameter determining shape of the quasi-gaussian energy distribution. The mole fraction y_i may be determined by using a theoretical equation, defining the dependence between compositions of the surface and mobile phases, or experimental data of the excess adsorption. The relationships for calculating the mole fraction y_i are the following [36,37]:

$$y_i = \left(x_i / k'_{(i)s}\right)^m / \sum_{j=1}^{n} \left(x_j / k'_{(j)s}\right)^m \qquad (3)$$

and

$$y_i = N_i^e / N^s + x_i \qquad (4)$$

where N_i^e is the excess adsorption of the i-th solvent from n-component liquid mixture on energetically heterogeneous solid surface, and N^s is the capacity of the surface phase.

Now, we consider the special cases of equation (2). Assuming in equation (2) m = 1 we obtain the relationship, which is valid for energetically homogeneous solid surfaces. Such a case was considered by Ościk in 1965 [1]. However, for $m \neq 1$, $A_{(in)s} = 0$ for $i = 1,2,\ldots,n$ and Y = 0, equation (2) becomes:

$$\log k'_{(\underline{n})s} = \sum_{i=1}^{n} \log k'_{(i)s} \, y_i^{1/m} \qquad (5)$$

Equation (5) describes LSC on energetically heterogeneous solid surfaces without solute-solvent interactions. The mobile and surface phases are assumed to be ideal. For m = 1, equation (5) reduces to the following simple form:

$$\log k'_{(\underline{n})s} = \sum_{i=1}^{n} \log k'_{(i)s} \, y_i \qquad (6)$$

The above equation may be treated as a fundamental relationship in the Ościk's treatment; it assumes that $\log k'_{(\underline{n})s}$ is additive with respect to $\log k'_{(i)s}$.
The interesting case of equation (2) is obtained for m = 1, Y = 0 and $\log\left(k'_{(i)s}/k'_{(n)s}\right) + A_{(in)s} = 0$ for $i = 1,2,\ldots,n$. Then, equation (2) reduces to the following expression:

$$\log k'_{(\underline{n})s} = \sum_{i=1}^{n} \log k'_{(i)s} \, x_i \qquad (7)$$

Equation (7) for the binary mobile phases (n = 2) gives linear dependence of $\log k'_{(12)s}$ upon x_1; such a type of dependence of the capacity ratio upon composition of the mobile phase was discussed theoretically by Jandera and Churacek [20].

THEORY OF LSC WITH THE MIXED MOBILE PHASE INVOLVING IDEAS OF
SNYDER AND SOCZEWIŃSKI

Theoretical studies of Jaroniec et al. [13,14,29], basing on the conceptions of Snyder [2] and Soczewiński [11], lead to the following general expression:

$$k'_{(\underline{n})s} = q \left(x_1^r \beta_{s1} \right)^{-1} \sum_{l=1}^{L} h_l K_{s1,l} Y_{1,l}^{r} \qquad (8)$$

where

$$\beta_{s1} = (g_s/f_s) \cdot (f_1/g_1)^r$$

and $K_{s1,l}$ is the equilibrium constant describing phase exchange of molecules of the s-th solute and the 1st solvent on the l-th type of adsorption sites; f_i and g_i (i = 1,s) are the activity coefficients of the i-th component in the mobile and surface phases, respectively; "r" is the ratio of molecular sizes of the s-th solute and i-th solvent; and "q" is the proportionality factor between the distribution coefficient and the capacity ratio [2]. For a quasi-gaussian energy distribution equation (8) may be approximated by the following rela - tionship [29]:

$$k'_{(\underline{n})s} = q K_{s1} \left(x_1^r \beta_{s1} \right)^{-1} y_1^{r/m} \qquad (9)$$

where "m" is the heterogeneity parameter and y_1 is defined by equation (3). Equation (9) has been derived by using the following assumptions:

(a) mobile and surface phases are nonideal;

(b) molecular sizes of all solvents appearing in the mobile phase are identical and equal to "w";

(c) molecular size of the s-th solute, w_s, and the molecular size w are different;

(d) adsorbent surface is characterized by quasi-gaussian energy distribution;

(e) adsorption sites are randomly distributed on the surface.

The effects of solute-solvent and solvent-solvent associations may be taken into account in equation (9). Then, the mole fractions x_1 and y_1, appearing in equation (9), denote the equilibrium concentrations and they should be expressed as functions of the initial composition of the mobile phase [15]. Now, we consider the special cases of equation (9).

Case 1. Assuming ideality of the surface phase ($g_s = g_1 = 1$), nonideality of the mobile phase ($f_s \neq f_1 \neq 1$), energetic homo-

geneity of the adsorbent surface $(m = 1)$, binary mobile phase $(n = 2)$, and high difference in the elution strengths of both solvents (then $y_1 = 1$ except low concentrations of x_2), equation [9] becomes the relationship derived by Slaats et al. [22]:

$$\log k'_{(12)s} = \log (q\, K_{s1}) - r \log a_1 + \log f_s \qquad (10)$$

where $a_1 = f_1 x_1$ is the activity of the 1st solvent. Equation (10) was discussed theoretically in terms of the other formalism by Jaroniec et al. [26] for r = 1 and the regular mobile phase.

Case 2. Assuming in equation (10) ideality of the mobile phase $\left(f_s = f_1 = 1\right)$, we obtain one of the most popular expressions [2,11]:

$$\log k'_{(12)s} = \log k'_{(1)s} - r \log x_1 \qquad (11)$$

The relationship (11) is known as Snyder – Soczewiński equation, although the correct analysis of the Snyder's formulation [2] leads to equation (11) with r = 1. However, the full form of this equation results from theoretical considerations of Soczewiński [11]. The relationship [11] was also obtained by Jandera and Churacek [20]; unfortunately, their considerations are not consistent and were critically discussed by Jaroniec et al. [23].

Case 3. For the purpose of prediction of the capacity ratio in the mixed mobile phases, Snyder [2] approximated $\log(K_{s1}\, g)$, appearing in equation (11), by the following expression:

$$\log \left(K_{s1}\, g\right) = C + D\left(E_s - w_s E_1\right) \qquad (12)$$

where "C" is the constant connected with volumes of the mobile and surface phases [2,20], "D" is the adsorbent surface activity function, related to the energy of adsorption of the sample on an active site of the adsorbent surface, E_s is the dimensionless free energy of adsorption of the s-th sample compound on an adsorbent of standard activity (D = 1) from n-pentane as solvent [2,20], and E_1 is the solvent strength parameter for 1-st solvent, describing the influence of the solvent on the adsorption, and it is not influenced by the properties of an adsorbent and solute. Equations (11) and (12) were wide-

ly discussed in the review articles [16, 18, 19] and extended to three-component mobile phases [17].

Case 4. Assumption in equation (9) $\beta_{s1} = 1$ (both phases are ideal) leads to the following expression:

$$\log k'_{(\underline{n})s} = \log k'_{(1)s} - (r/m)\log(y_1/x_1)^m \qquad (13)$$

Equation (13) was theoretically discussed and experimentally examined by Jaroniec and Oścık-Mendyk [29]. The mole fraction y_1 was calculated from the excess adsorption isotherm according to the relationship (4).

Case 5. Assuming in equation (13) that r = 1 we obtain:

$$\log k'_{(\underline{n})s} = \log k'_{(1)s} - (1/m)\log(y_1/x_1)^m \qquad (14)$$

The above equation describes the dependence of the capacity ratio upon the mobile phase composition for both ideal phases, identical molecular sizes of all components and heterogenous solid surfaces showing quasi-gaussian energy distribution.

Case 6. Assuming in equation (13) m = 1 we have:

$$\log k'_{(n)s} = \log k'_{(1)s} - r \log (y_1/x_1) \qquad (15)$$

Equation (15) was widely discussed in the paper [13] for the binary mobile phases. The assumption in this equation is that $y_1 = 1$ leads to the relationship (11), which is known as the equation of Snyder - Soczewiński.

Case 7. Assuming in equation (9) ideality of both phases $(\beta_{s1} = 1)$, equality of molecular sizes of solute and solvents (r = 1), energetic heterogeneity of the adsorbent surface (m ≠ 1), and utilizing equation (3), we have:

$$\left(1/k'_{(\underline{n})s}\right)^m = \sum_{i=1}^{n}\left(x_i/k'_{(i)s}\right)^m \qquad (16)$$

Equation (13) may be rewritten in the following equivalent form:

$$k'_{(\underline{n})s} = \sum_{i=1}^{n} k'_{(i)s}\, y_i^{1/m} \qquad (17)$$

Equations (16) and (17) have been derived and examined   by
Jaroniec et al. [25,27,28].

Case 8. Assuming in equations (16) and (17) that m = 1
(energetically homogeneous surface) we obtain:

$$1/k'_{(\underline{n})s} = \sum_{i=1}^{n} (x_i/k'_{(i)s}) \tag{18}$$

and

$$k'_{(n)s} = \sum_{i=1}^{n} k'_{(i)s} \, y_i \tag{19}$$

Equations (18) and (19) were discussed by Jaroniec et al.[24],
and they are an extented form of Snyder's equation [2]. Equa-
tion (19) may be treated as the fundamental relationship in
the Snyder's formulation of LSC with the mixed mobile phase.
A comparative discussion of the Snyder's relationship (19) and
Ościk's equation (6) is given in the papers [24,34].

Case 9. For n = 2 (binary mobile phase) equation (18) pre-
dicts the linear dependence of $1/k'_{(12)s}$ upon x_1, which has
been discussed by Scott and Kucera [38], and directly results
from Snyder's theory of LSC [23].

CONCLUDING REMARKS

Recently, Martire and Boehm [30,31] considered LSC with the
binary mobile phase by assuming regularity of both phases   and
energetic homogeneity and heterogeneity of the adsorbent sur -
face. For this case they made detailed theoretical considera -
tions and performed extensive numerical model calculations.
In the light of our discussion, they considered equation (8)
with n = 2 by assuming the regularity of the mobile and
surface phases.

Concluding, it can be stated that almost all equations used
in LSC with the mixed mobile phase are related to the concep -
tion of Ościk [1] or Snyder - Soczewiński [2,11]. Thus, these
equations may be divided into two main groups.

REFERENCES

1. Ościk J.: Przem. Chem. 44, 129 (1965).
2. Snyder L. R.: Principles of Adsorption Chromatography.
   Marcel Dekker, New York 1968.
3. Waksmundzki A., Soczewiński E., Suprynowicz Z.: Coll.Cze-
   choslov. Chem. Commun. 27, 2001 (1962).
4. Waksmundzki A., Suprynowicz Z.: J. Chromatogr. 18, 232(1965).
5. Ościk J.: Bull. Acad. Sci. Polon. ser. chim. 9, 29 (1961).
6. Ościk J.: Bull. Acad. Sci. Polon. ser. chim. 9, 33 (1961).
7. Ościk J.: Przem. Chem. 40, 281 (1961).
8. Ościk J.: Ann.Univ.Mariae Curie-Skłodowska, sectio AA, 17,
   115 (1962).
9. Snyder L. R.: J. Chromatogr. 8, 178 (1962).
10. Snyder L. R.: J. Chromatogr. 16, 55 (1964).
11. Soczewiński E.: Anal. Chem. 41, 179 (1969).
12. Soczewiński E.: J. Chromatogr. 130, 23 (1977).
13. Jaroniec M., Różyło J.K., Ościk - Mendyk B.: J. Chromatogr.
    179, 237 (1979).
14. Jaroniec M., Patrykiejew A.: J. Chem. Soc. Faraday I 76,
    2486 (1980).
15. Jaroniec M., Piotrowska J.: JHRC &CC 3, 257 (1980).
16. Snyder L. R.: Anal.Chem. 46, 1384 (1974).
17. Paanakker J.E., Kraak J. C., Poppe H.: J. Chromatogr. 149,
    111 (1978).
18. Snyder L. R., Poppe H.: J. Chromatogr. 184, 363 (1980).
19. Perry J. A.: J. Chromatogr. 163, 117 (1979).
20. Jandera P., Churacek J.: J. Chromatogr. 91, 207 (1974).
21. Jandera P., Churacek J.: J. Chromatogr. 170, 1 (1979).
22. Slaata E. H., Kraak J. C., Brugman W. J. T., Poppe H.: J.
    Chromatogr. 149, 255 (1978).
23. Narkiewicz J., Jaroniec M., Borówko M., Patrykiejew A.: J.
    Chromatogr. 157, 1 (1978).
24. Jaroniec M., Narkiewicz J., Borówko M.: Chromatographia 11,
    581 (1978).
25. Borówko M., Jaroniec M.: Chromatographia 12, 672 (1979).
26. Jaroniec M., Klepacka B., Narkiewicz J.: J. Chromatogr. 170,
    299 (1979).
27. Jaroniec M., Różyło J.K., Gołkiewicz W.: J. Chromatogr. 178,
    27 (1979).
28. Jaroniec M., Różyło J. K., Jaroniec J. A., Ościk-Mendyk B.:
    J. Chromatogr. 188 (1980) 27.
29. Jaroniec M., Ościk - Mendyk B.: J. Chem. Soc. Farady I 77,
    (1981).
30. Martire D. E., Boehm R. E.: J. Liquid Chromatogr. 3, 753
    (1980).
31. Martire D. E., Boehm R. E.: J. Phys. Chem. 84, 3520 (1980).
32. Ościk J.: in: Physical Adsorption from Multicomponent Pha-
    ses. M. M. Dubinin ed. , Nauka, Moscow 1972, pp. 138-147,
    in Russian.
33. Ościk J., Różyło J. K.: Chromatographia 4, 516 (1971).
34. Różyło J. K., Ościk J., Ościk-Mendyk B., Jaroniec M.: JHRC
    &CC, 4, 17 (1981).
35. Ościk J., Różyło J. K., Ościk-Mendyk B., Jaroniec M.: Chro-
    matographia, 14, 95 (1981).

36. Jaroniec M.: J. Res. Inst. Catalysis 28, 31 (1980).
37. Jaroniec M.: Thin Solid Films 71, 273 (1980).
38. Scott R. P. W., Kucera P.: J. Chromatogr. 112, 425 (1975).

STRESZCZENIE

Przedstawiono najważniejsze osiągnięcia w teorii adsorpcyj-
nej chromatografii cieczowej z wieloskładnikową fazą ruchomą.
Opis teoretyczny procesu adsorpcyjnej chromatografii cieczowej
bazuje na fundamentalnych badaniach Ościka, Snydera i Socze-
wińskiego. Wyniki tych badań, po ich rozszerzeniu i odpowied-
niej modyfikacji, doprowadziły do wyprowadzenia wielu równań
opisujących zależność współczynnika pojemnościowego od składu
fazy ruchomej. Obecnie dokonano klasyfikacji tych równań oraz
dokładnie przedyskutowano założenia leżące u ich podstaw.

Резюме

В данной работе представлены наиболее важные достижения
в теории жидкостной адсорбционной хроматографии с многокомпо-
нентной подвижной фазой. Актуальное теоретическое описание про-
цесса жидкостной адсорбционной хроматографии основывается на
фундаментальных исследованиях Осцика, Снайдера и Сочевинского.
Расширены и соответственно модифицированы результаты этих исс-
ледований довели до выведения уравнений описывающих зависимость
коэффициента распределения от состава подвижной фазы. Представ-
лено классификацию этих уравнений и проведено точную дискуссию
предположений, на которых эти уравнения основаны.