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### An Extension and new Interpretation of Oscik's Equation Describing Liquid Chromatography with Mixed Mobile Phases

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## AN EXTENSION AND NEW INTERPRETATION OF OŚCIK'S EQUATION DESCRIBING LIQUID CHROMATOGRAPHY WITH MIXED MOBILE PHASES

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### ABSTRACT

An extension of Ościk's original approach, which was first proposed for liquid-solid chromatography (LSC) with a multicomponent eluent in the normal-phase mode (Przem. Chem. 44, 1965, 129), leads to a new equation describing the dependence of the distribution coefficient upon mobile phase composition. This equation is also derived in terms of the expressions defining classical partitioning (J. Phys. Chem. 87, 1983, 1045). The above derivation provides a new view on the physical meaning of the parameters and indicates that Ościk's equation is more suitable for describing partition effects in reversed-phase liquid chromatography (RPLC).

### INTRODUCTION

In 1965 Ościk (1) derived an equation describing thin-layer adsorption chromatography with multicomponent mobile phases. An extensive discussion dealing with the theoretical foundations of this equation and its application for analysing chromatographic data is given in two reviews (2,3). In 1978 Jaroniec et al. (4) presented Ościk's equation in terms of distribution

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coefficients and compared it with Snyder's relationship (5). It follows from this comparison that the main terms appearing in these equations are quite different. Snyder's approach (5) implies that the total solute retention in a multicomponent stationary phase is a linear combination of independent retention contributions involving successive solute - pure solvent adsorption exchanges between the mobile ( $l$ ) and stationary ( $\sigma$ ) phases. In the case where both phases are ideal this approach gives:

$$k_{s(\underline{n}/\underline{n})} = \sum_{i=1}^n \phi_i^{\sigma} k_{s(i/i)} \quad (1)$$

where  $k_{s(\underline{n}/\underline{n})}$  and  $k_{s(i/i)}$  are the distribution coefficients of the  $s$ -th solute chromatographed in a  $n$ -component eluent and the  $i$ -th pure solvent, respectively,  $\underline{n}$  designates a multicomponent liquid mixture ( $1+2+\dots+n$ ),  $\phi_i^{\sigma}$  is the volume fraction of the  $i$ -th solvent in the stationary (surface) phase, and the subscript  $(\underline{n}/\underline{n})$  designates compositions of mobile and stationary phases, respectively. Thermodynamical justification of equation 1 made by Jaroniec et al. (4) and Martire and Boehm (6,7) shows that the solute and solvent competitive adsorption is the main physical basis of its derivation. This competitive adsorption (displacement) model of the LSC process was widely studied by Snyder (8,9).

However, the main term in Ošcik's equation has a form considerably different than equation 1; it is

$$\ln k_{s(\underline{n}/\underline{n})} = \sum_{i=1}^n \phi_i^{\sigma} \ln k_{s(i/i)} \quad (2)$$

Ošcik's equation, derived in terms of classical thermodynamics of dilute conformal solutions (1), is much too general and therefore gives scant information about the physical basis of LSC process on a molecular level. Recently, Jaroniec et al. (10) pointed out the possibility of a new interpretation of Ošcik's equation in terms of a unified formulation of the LSC process (11). This paper presents an extension of Ošcik's original equation and its new interpretation on a molecular level.

EXTENSION OF OSCIK'S EQUATION DESCRIBING LC WITH MULTICOMPONENT ELUENTS

Let us consider a chromatographic system consisting, in general, of a multicomponent mobile phase (solvents 1,2,...,n) and a multicomponent stationary phase of the same components, but under the influence of the underlying support surface assumed to be a homogeneous one (see later). We designate the composition variables (volume fractions) of the mobile phase components by  $\phi_i^k$  and those of the stationary-phase components by  $\phi_i^\sigma$ , and

$$\sum_{i=1}^n \phi_i^\rho = 1 \quad \text{for } \rho = k, \sigma. \tag{3}$$

The surface is assumed to influence the various molecular interactions in the stationary phase and, hence, to set the composition variables in that phase. Retention is taken to be governed exclusively by partitioning between a mobile phase and a stationary phase having different composition variables. Since competitive adsorption (displacement) is ignored, this treatment is not expected to be applicable to normal-phase liquid-solid (adsorption) chromatography. Instead, it is directed toward a general formulation which should be applicable to reversed-phase liquid chromatography including, under certain conditions, chemically bonded phases.

Based on classical thermodynamics of dilute conformal solutions Ošcik (1,2) expressed the standard chemical potential of the s-th solute at an infinitely low concentration in a n-component liquid phase as follows:

$$\mu_s^\rho(\underline{n}) = \sum_{i=1}^n \phi_i^\rho \mu_s^\rho(i) - G_{(\underline{n})}^{e,\rho}(\phi_1^\rho, \phi_2^\rho, \dots, \phi_n^\rho) \quad \text{for } \rho = k, \sigma \tag{4}$$

where  $\mu_s^\rho(i)$  is the standard chemical potential of the s-th solute in the i-th pure solvent forming the  $\rho$ -th phase and  $G_{(\underline{n})}^{e,\rho}$  is the excess free energy of a n-component liquid mixture forming the  $\rho$ -th phase. The function  $G_{(\underline{n})}^{e,\rho}$  was not considered by Ošcik (1). However, it represents interactions between solvent molecules in the  $\rho$ -th phase and in many chromatographic systems it introduces a significant contribution to the total solute retention (11). The function  $G_{(\underline{n})}^{e,\rho}$  may be approximated by a simple expression (11);

$$G_{(\underline{n})}^{e,\rho}(\phi_1^\rho, \phi_2^\rho, \dots, \phi_n^\rho) = \sum_{\substack{i,j=1 \\ j>i}}^n B_{ij}^\rho \phi_i^\rho \phi_j^\rho \quad \text{for } \rho = k, \sigma \tag{5}$$

where  $B_{ij}^0$  for  $i, j = 1, 2, \dots, n$  and  $j > i$  reflect the contribution from solvent nonideality.

According to reference (2) the distribution coefficients  $k_{s(n/n)}$  and  $k_{s(i/i)}$  of the  $s$ -th solute chromatographed in a  $n$ -component eluent and the  $i$ -th pure solvent, respectively, may be expressed as follows:

$$k_{s(n/n)} = \exp[-\Delta\mu_{s(n)} / (RT)] \quad ; \quad \Delta\mu_{s(n)} = \mu_{s(n)}^{\sigma} - \mu_{s(n)}^{\ell} \quad (6)$$

$$k_{s(i/i)} = \exp[-\Delta\mu_{s(i)} / (RT)] \quad ; \quad \Delta\mu_{s(i)} = \mu_{s(i)}^{\sigma} - \mu_{s(i)}^{\ell} \quad (7)$$

To derive the equation describing the dependence of the distribution coefficient  $k_{s(n/n)}$  upon mobile phase composition we should first calculate the difference of the standard chemical potentials  $\mu_{s(n)}^{\sigma}$  and  $\mu_{s(n)}^{\ell}$  (see equation 6). This difference, calculated on the basis of equations 4 and 5, is equal to:

$$\Delta\mu_{s(n)} = \sum_{i=1}^n \phi_i^{\sigma} \mu_{s(i)}^{\sigma} - \sum_{i=1}^n \phi_i^{\ell} \mu_{s(i)}^{\ell} - \sum_{\substack{i,j=1 \\ j>i}}^n B_{ij}^{\sigma} \phi_i^{\sigma} \phi_j^{\sigma} + \sum_{\substack{i,j=1 \\ j>i}}^n B_{ij}^{\ell} \phi_i^{\ell} \phi_j^{\ell} \quad (8)$$

Subtracting and adding to the right-hand side of equation 8 the following expression

$$Y = \sum_{i=1}^n \phi_i^{\ell} \mu_{s(i)}^{\sigma} \quad (9)$$

we obtain

$$\Delta\mu_{s(n)} = \sum_{i=1}^n \phi_i^{\ell} \Delta\mu_{s(i)} + \sum_{i=1}^n (\phi_i^{\sigma} - \phi_i^{\ell}) \mu_{s(i)}^{\sigma} - \sum_{\substack{i,j=1 \\ j>i}}^n B_{ij}^{\sigma} \phi_i^{\sigma} \phi_j^{\sigma} + \sum_{\substack{i,j=1 \\ j>i}}^n B_{ij}^{\ell} \phi_i^{\ell} \phi_j^{\ell} \quad (10)$$

Combining equations 6, 7 and 10, we have

$$\ln k_{s(n/n)} = \sum_{i=1}^n \phi_i^{\ell} \ln k_{s(i/i)} + \sum_{i=1}^n (\phi_i^{\sigma} - \phi_i^{\ell}) \tilde{\Lambda}_{s(i)}^{\sigma} + \sum_{\substack{i,j=1 \\ j>i}}^n \tilde{B}_{ij}^{\sigma} \phi_i^{\sigma} \phi_j^{\sigma} - \sum_{\substack{i,j=1 \\ j>i}}^n \tilde{B}_{ij}^{\ell} \phi_i^{\ell} \phi_j^{\ell} \quad (11)$$

where

$$\tilde{\Lambda}_{s(i)}^{\sigma} = -\mu_{s(i)}^{\sigma} / (RT) \quad (12)$$

and

$$\tilde{B}_{ij}^{\rho} = B_{ij}^{\rho} / (RT) \quad \text{for } \rho = \ell, \sigma \quad (13)$$

Taking into account in equation 11 the following relationship (2):

$$\sum_{i=1}^n (\phi_i^\sigma - \phi_i^l) \nu_{s(i)}^\sigma = \sum_{i=1}^{n-1} (\phi_i^\sigma - \phi_i^l) \Delta \nu_{s(in)}^\sigma ; \Delta \nu_{s(in)}^\sigma = \nu_{s(i)}^\sigma - \nu_{s(n)}^\sigma \quad (14)$$

we have

$$\ln k_{s(n/n)} = \sum_{i=1}^n \phi_i^l \ln k_{s(i/i)} + \sum_{i=1}^{n-1} (\phi_i^\sigma - \phi_i^l) \tilde{\lambda}_{s(in)}^\sigma + \sum_{\substack{i,j=1 \\ j>i}}^n \tilde{B}_{ij}^\sigma \phi_i^\sigma \phi_j^\sigma - \sum_{\substack{i,j=1 \\ j>i}}^n \tilde{B}_{ij}^l \phi_i^l \phi_j^l \quad (15)$$

The parameter  $\tilde{\lambda}_{s(in)}^\sigma$  is defined as follows:

$$\tilde{\lambda}_{s(in)}^\sigma = \tilde{\lambda}_{s(i)}^\sigma - \tilde{\lambda}_{s(n)}^\sigma = -\Delta \nu_{s(in)}^\sigma / (RT) = \ln \kappa_{s(in)}^\sigma \quad (16)$$

In the above,  $\kappa_{s(in)}^\sigma$  may be regarded as a hypothetical partition coefficient of the s-th solute between two surface-influenced solvents "i" and "n".

Equation 15 may be rewritten in other forms. The first of them contains the term given by equation 2 ; it is

$$\ln k_{s(n/n)} = \sum_{i=1}^n \phi_i^\sigma \ln k_{s(i/i)} + \sum_{i=1}^{n-1} (\phi_i^\sigma - \phi_i^l) \tilde{\lambda}_{s(in)}^l + \sum_{\substack{i,j=1 \\ j>i}}^n \tilde{B}_{ij}^\sigma \phi_i^\sigma \phi_j^\sigma - \sum_{\substack{i,j=1 \\ j>i}}^n \tilde{B}_{ij}^l \phi_i^l \phi_j^l \quad (17)$$

where

$$\tilde{\lambda}_{s(in)}^l = \tilde{\lambda}_{s(in)}^\sigma - \ln [k_{s(i/i)} / k_{s(n/n)}] \quad (18)$$

On the basis of equations 7 and 16 it is a simple matter to show that

$$\tilde{\lambda}_{s(in)}^l = \ln \kappa_{s(in)}^l = -\Delta \nu_{s(in)}^l / (RT) \quad (19)$$

where  $\kappa_{s(in)}^l$  is a hypothetical partition coefficient of the s-th solute between two bulk solvents "i" and "n".

The second form of equation 15 defines the dependence of  $k_{s(n/n)}$  upon mobile phase composition in terms of new partition coefficients of the s-th solute; it is

$$\ln k_{s(n/n)} = \sum_{i=1}^n \phi_i^l \ln k_{s(i/n)} + \sum_{i=1}^{n-1} \phi_i^\sigma \ln \kappa_{s(in)}^\sigma + \sum_{i,j=1}^n \tilde{B}_{ij}^\sigma \phi_i^\sigma \phi_j^\sigma - \sum_{i,j=1}^n \tilde{B}_{ij}^l \phi_i^l \phi_j^l \quad (20)$$

where  $k_{s(i/n)}$  represents the partition coefficient of the  $s$ -th solute between two separate pure phases; mobile phase "i" and surface-influenced stationary phase "n". It is worth mentioning that the distribution coefficient  $k_{s(i/i)}$  given by equation 7 also defines partition of the  $s$ -th solute between two separate phases where both phases contain the  $i$ -th solvent. The partition coefficient  $k_{s(i/n)}$  appearing in equation 20 is defined as follows:

$$\ln k_{s(i/n)} = -(\mu_{s(n)}^\sigma - \mu_{s(i)}^l)/(RT) = -\Delta\mu_{s(i/n)}/(RT) \quad (21)$$

Comparing equations 7, 16 and 21 we have:

$$\ln k_{s(i/n)} = \ln k_{s(i/i)} - \ln \kappa_{s(in)}^\sigma \quad (22)$$

An alternative form of equation 15 may be written if we introduce the partition coefficients  $k_{s(n/i)}$  for  $i = 1, 2, \dots, n$  defined as follows:

$$\ln k_{s(n/i)} = -(\mu_{s(i)}^\sigma - \mu_{s(n)}^l)/(RT) = -\Delta\mu_{s(n/i)}/(RT) \quad (23)$$

The coefficient  $k_{s(n/i)}$  describes partition of the  $s$ -th solute between two separate pure phases; mobile phase "n" and surface-influenced stationary phase "i". Returning to equation 15, we write it in terms of the partition coefficients  $k_{s(n/i)}$  ( $i = 1, 2, \dots, n$ ) as follows:

$$\ln k_{s(n/n)} = \sum_{i=1}^n \phi_i^\sigma \ln k_{s(n/i)} + \sum_{i=1}^{n-1} \phi_i^l \ln \kappa_{s(ni)}^l + \sum_{i,j=1}^n \tilde{B}_{ij}^\sigma \phi_i^\sigma \phi_j^\sigma - \sum_{i,j=1}^n \tilde{B}_{ij}^l \phi_i^l \phi_j^l \quad (24)$$

The relation between  $k_{s(i/i)}$  and  $k_{s(n/i)}$  is analogous to that given by equation 22; it is

$$\ln k_{s(n/i)} = \ln k_{s(i/i)} - \ln \kappa_{s(ni)}^l ; \quad \ln \kappa_{s(ni)}^l = -\ln \kappa_{s(in)}^l \quad (25)$$

Equation 15 and its other forms (equations 17, 20 and 24) contain four terms. In all equations the third and fourth terms are identical and they define the contribution to the total solute retention resulting from interactions between solvent molecules in mobile and surface-influenced stationary phases.

The first term, giving a greatest contribution to the total solute retention, is expressed by a sum, in which each term is a simple product of the volume fraction of the  $i$ -th solvent and logarithm of the suitable distribution coefficient of the  $s$ -th solute between two separate pure phases. However, the second term contains distribution coefficients of the  $s$ -th solute between two pure solvents contained in the bulk phase or surface-influenced stationary phase. The mathematical forms of the first and second terms depend upon definition of the distribution coefficients of the  $s$ -th solute.

It is worth mentioning another form of equation 15, which may be useful to obtain equations for liquid/liquid chromatography and LC with chemically bonded phases. Introducing hypothetical partition coefficients of the  $s$ -th solute between the  $i$ -th pure solvent forming the bulk phase and a  $n$ -component surface-influenced eluent consisting of the equilibrium mixture ( $1+2+\dots+n$ ), we can obtain

$$\ln k_{s(n/n)} = \sum_{i=1}^n \phi_i^l \ln k_{s(i/n)} - \sum_{\substack{i,j=1 \\ j>i}}^n \tilde{B}_{ij}^l \phi_i^l \phi_j^l \quad (26)$$

where

$$\ln k_{s(i/n)} = -(\nu_{s(n)}^\sigma - \nu_{s(i)}^l) / (RT) = -\Delta\nu_{s(i/n)} / (RT) . \quad (27)$$

It is a simple matter to show that

$$\sum_{i=1}^n \phi_i^l \ln k_{s(i/n)} = \sum_{i=1}^n \phi_i^l \ln k_{s(i/i)} + \sum_{i=1}^{n-1} (\phi_i^\sigma - \phi_i^l) \ln \kappa_{s(in)}^\sigma + \sum_{\substack{i,j=1 \\ j>i}}^n \tilde{B}_{ij}^\sigma \phi_i^\sigma \phi_j^\sigma . \quad (28)$$

Equation 26 has a very simple form, which is convenient for analysing partition phenomenon of a solute between two separate phases containing components, which are immiscible with those appearing in the neighbouring phase. As an example of chromatographic systems fulfilling the above assumption we can indicate RPLC systems with chemically bonded phases, in which solvents are excluded from the stationary phase. Also liquid/liquid chromatographic systems usually contain liquid components in the stationary phase, which are virtually immiscible with those appearing in the mobile phase.



INTERPRETATION OF OSCIK'S EXTENDED EQUATION IN TERMS OF REGULAR SOLUTION  
LATTICE THEORY

In the previous section we extended Ošcik's original expressions for the standard chemical potentials of the  $s$ -th solute at an infinitely low concentration in  $n$ -component bulk and surface solutions (see equation 4). It has been shown that this extension leads to a new equation 15 describing the dependence of the distribution coefficient of the  $s$ -th solute upon mobile phase composition. This section shows that equation 15 and its equivalent forms (equations 17, 20, 24 and 26) may be justified in terms of a regular solution theory approach.

Let us consider the chromatographic system defined in the beginning of the previous section. The mobile and surface-influenced stationary phases are assumed to be regular. Thus, nonideality of these phases may be described in terms of regular solution lattice theory. From a straightforward extension of this theory, we have

$$\ln \gamma_s^\rho(\underline{n}) = \sum_{i=1}^n \phi_i^\rho \ln \gamma_s^\rho(i) - r_s \sum_{\substack{i,j=1 \\ j>i}}^n \chi_{ij}^\rho \phi_i^\rho \phi_j^\rho \quad \text{for } \rho = \ell, \sigma \quad (29)$$

where  $\gamma_s^\rho(\underline{n})$  and  $\gamma_s^\rho(i)$  are activity coefficients of the  $s$ -th solute at infinite dilution in a  $n$ -component liquid mixture and the  $i$ -th pure solvent, respectively, forming the  $\rho$ -th phase, where the subscripts  $\ell$  and  $\sigma$  refer to the mobile and surface-influenced stationary phases, respectively. The definition of the above activity coefficients is based on the convention that  $\gamma_s^\rho \rightarrow 1$  as  $\phi_s^\rho \rightarrow 1$ . The parameter  $\chi_{ij}^\rho$  is defined as follows:

$$\chi_{ij}^\rho = (z^\rho/kT) [\omega_{ij}^\rho - 0.5(\omega_{ii}^\rho + \omega_{jj}^\rho)] = (z^\rho \Delta\omega_{ij}^\rho)/(kT) \quad \text{for } \rho = \ell, \sigma \quad (30)$$

where  $\omega_{ij}^\rho$  is a segmental energy for the interaction between the  $i$ -th and  $j$ -th components in the  $\rho$ -th phase,  $\Delta\omega_{ij}^\rho$  is the corresponding interchange energy and  $z^\rho$  is the lattice coordination number for the  $\rho$ -th phase. The activity coefficient  $\gamma_s^\rho(i)$  is equal to:

$$\ln \gamma_s^\rho(i) = (1 - r_s/r_i) + r_s \chi_{is}^\rho \quad \text{for } i = 1, 2, \dots, n-1 \text{ and } \rho = \ell, \sigma \quad (31)$$

and

$$\ln \gamma_{s(n)}^{\ell} = (1 - r_s/r_n) + r_s \chi_{ns}^{\ell} \quad (32)$$

$$\ln \gamma_{s(n)}^{\sigma} = (1 - r_s/r_n) + r_s \chi_{ns}^{\sigma} + \Delta_n \quad (33)$$

The symbol  $\chi_{is}^{\rho}$  is the well-known interaction parameter, which is related to the segmental interchange energy of the  $i$ -th solvent and  $s$ -th solute and is defined by an equation analogous to equation 30. The parameter  $r_i$  ( $i=1,2,\dots,n$ ) denotes the number of segments in a molecule of the  $i$ -th component. In the expression defining the activity coefficient of the  $s$ -th solute and the  $n$ -th pure solvent forming the surface-influenced stationary phase we have included a correction term  $\Delta_n$ . This is to permit in the theory the possibility that  $n$ -th component is a chemically bonded phase (CBP); in such case, of course,  $\phi_n^{\ell} = 0$  and  $\Delta_n \neq 0$ . In other cases  $\Delta_n = 0$ . The simple correction of the form shown is strictly valid when the CBP is "collapsed" or nearly so, implying little uptake of the solvent components by the stationary phase, i.e.,  $\phi_i^{\sigma}$  is small ( $i \neq n$ ) (11). In this collapsed-chain limit  $\Delta_n$  depends only on the surface coverage and intrinsic flexibility of the CBP chains, and on the nature of the solute.

In classical partitioning, the distribution coefficient of the  $s$ -th solute between two phases: mobile and surface-influenced stationary phases consisting of the solvents  $1,2,\dots,n$ , is defined as follows (11,12):

$$\ln k_{s(n/n)} = \ln(\gamma_{s(n)}^{\ell}/\gamma_{s(n)}^{\sigma}) \quad (34)$$

Combining equations 29 and 34 we have

$$\begin{aligned} \ln k_{s(n/n)} = & \sum_{i=1}^n \phi_i^{\ell} \ln(\gamma_{s(i)}^{\ell}/\gamma_{s(i)}^{\sigma}) - \sum_{i=1}^n (\phi_i^{\sigma} - \phi_i^{\ell}) \ln \gamma_{s(i)}^{\sigma} + \\ & r_s \sum_{\substack{i,j=1 \\ j>i}}^n \chi_{ij}^{\sigma} \phi_i^{\sigma} \phi_j^{\sigma} - r_s \sum_{\substack{i,j=1 \\ j>i}}^n \chi_{ij}^{\ell} \phi_i^{\ell} \phi_j^{\ell} \end{aligned} \quad (35)$$

The expression  $\ln(\gamma_{s(i)}^{\ell}/\gamma_{s(i)}^{\sigma})$  denotes the solute partition coefficient between a mobile phase of the  $i$ -th pure solvent and a stationary, surface-influenced phase containing this same pure solvent. Taking into account in equation 35 that

$$\sum_{i=1}^{n-1} (\phi_i^{\sigma} - \phi_i^{\ell}) = \phi_n^{\ell} - \phi_n^{\sigma} \quad (36)$$

we obtain

$$\ln k_{s(\underline{n}/\underline{n})} = \sum_{i=1}^n \phi_i^{\ell} \ln(\gamma_{s(i)}^{\ell} / \gamma_{s(i)}^{\sigma}) + \sum_{i=1}^{n-1} (\phi_i^{\sigma} - \phi_i^{\ell}) \ln(\gamma_{s(n)}^{\sigma} / \gamma_{s(i)}^{\sigma}) + r_s \left( \sum_{\substack{i,j=1 \\ j>i}}^n \chi_{ij}^{\sigma} \phi_i^{\sigma} \phi_j^{\sigma} - \sum_{\substack{i,j=1 \\ j>i}}^n \chi_{ij}^{\ell} \phi_i^{\ell} \phi_j^{\ell} \right). \tag{37}$$

The symbol  $\ln(\gamma_{s(n)}^{\sigma} / \gamma_{s(i)}^{\sigma})$  represents a hypothetical partition coefficient of the s-th solute between two pure surface-influenced phases, "i" and "n".

Equation 37 is formally identical to equation 15 based on an extension of Ošcik's treatment. Comparing these equations, we can define the parameters appearing in Ošcik's equation by means of the molecular parameters used in the regular lattice theory. This comparison gives:

$$\ln k_{s(i/i)} = \ln(\gamma_{s(i)}^{\ell} / \gamma_{s(i)}^{\sigma}) = r_s (\chi_{is}^{\ell} - \chi_{is}^{\sigma}) \quad \text{for } i = 1, 2, \dots, n \tag{38}$$

$$\ln \kappa_{s(in)}^{\sigma} = \bar{A}_{s(in)}^{\sigma} = \ln(\gamma_{s(n)}^{\sigma} / \gamma_{s(i)}^{\sigma}) = (r_s / r_i - r_s / r_n) + \Delta_n + r_s (\chi_{ns}^{\sigma} - \chi_{is}^{\sigma}) \tag{39}$$

$$\bar{B}_{ij}^{\rho} = r_s \chi_{ij}^{\rho} \quad \text{for } i, j = 1, 2, \dots, n; \quad j > i \quad \text{and } \rho = \ell, \sigma. \tag{40}$$

For practical purposes, it is useful to recast equation 37. Then, we rewrite it as follows:

$$\ln k_{s(\underline{n}/\underline{n})} = \sum_{i=1}^n \phi_i^{\ell} \ln(\gamma_{s(i)}^{\ell} / \gamma_{s(n)}^{\sigma}) + \sum_{i=1}^{n-1} \phi_i^{\sigma} \ln(\gamma_{s(n)}^{\sigma} / \gamma_{s(i)}^{\sigma}) + r_s \left( \sum_{\substack{i,j=1 \\ j>i}}^n \chi_{ij}^{\sigma} \phi_i^{\sigma} \phi_j^{\sigma} - r_s \sum_{\substack{i,j=1 \\ j>i}}^n \chi_{ij}^{\ell} \phi_i^{\ell} \phi_j^{\ell} \right) \tag{41}$$

where  $(\gamma_{s(i)}^{\ell} / \gamma_{s(n)}^{\sigma})$  denotes the hypothetical partition coefficient  $k_{s(i/n)}$  appearing in equation 20 and  $(\gamma_{s(n)}^{\sigma} / \gamma_{s(i)}^{\sigma})$  is equal to the partition coefficient  $\kappa_{s(in)}^{\sigma}$  defined by equation 39. This first coefficient, defined in terms of the parameters of regular solution lattice theory, is

$$\ln k_{s(i/n)} = \ln(\gamma_{s(i)}^{\ell} / \gamma_{s(n)}^{\sigma}) = (r_s / r_n - r_s / r_i) - \Delta_n + r_s (\chi_{is}^{\ell} - \chi_{ns}^{\sigma}). \tag{42}$$

Comparison of Ošcik's extended formulation of LC with mixed mobile phases to that describing classical partitioning in terms of the regular solution lattice theory shows that both formulations are equivalent; this means that

Ošcik's original and extended equations are not expected to be applicable to normal-phase LSC but they are more suitable for describing RPLC including, under certain conditions, chemically bonded phases. Moreover, the regular solution lattice theory makes possible definition of the parameters appearing in Ošcik's original equation on a molecular level.

## SIMPLIFIED EQUATIONS AND THEIR DISCUSSION

It follows from discussion presented in the previous section that equation 15 and its other forms (equations 17, 20, 24 and 26) should be capable of describing reversed-phase LSC systems (RP LSC) and, as we shall see, reversed-phase liquid chromatographic systems with chemically bonded phases (RPLC-CBP). In the first case, the surface influence provides the driving force that determines the composition of the stationary phase. In the second case, the influence of the underlying support surface should be only a secondary effect. The above equations may appear to be formidable, but under certain realizable conditions, they simplify considerably.

Let first consider RPLSC systems with nearly ideal mixing of solvent components in the mobile phase. Then

$$\tilde{B}_{ij}^l = r_s X_{ij}^l = 0 \text{ for } i, j = 1, 2, \dots, n \text{ and } j > i. \quad (43)$$

If the solvent mixture is also nearly ideal in the stationary phase, i.e.,

$$\tilde{B}_{ij}^s = r_s X_{ij}^s = 0 \text{ for } i, j = 1, 2, \dots, n \text{ and } j > i \quad (44)$$

and, as was mentioned earlier, the competitive adsorption is ignored, we observe no surface bias on the composition of the stationary phase and, hence,

$$\phi_i^s = \phi_i^l \text{ for } i = 1, 2, \dots, n. \quad (45)$$

Under above conditions given by equations 43, 44 and 45, equation 15 becomes the well-known relationship expressed by equation 2. The coefficients  $k_{s(i/i)}$  can be different than unity and different for different solvents, even though equations 43 and 44 are fulfilled. This is because these coefficients reflect solute-solvent interactions, which are perturbed by the solid surface.

Nevertheless, if we assume that these solute-solvent interactions are not

perturbed by the solid surface, these coefficients become equal to unity and then  $k_{s(n/n)} = 1$  too; this means that in the case of systems with nearly ideal mixing of solvent components in the mobile and stationary phases and non-perturbed solute-solvent interactions in the stationary phase, the distribution coefficient  $k_{s(n/n)}$  may be different than unity only when solute and solvent displacement effects are included.

For binary eluents equation 2 gives a very simple relationship:

$$\ln k_{s(12/12)} = a + b \phi_1^k \quad (46)$$

where

$$a = \ln k_{s(2/2)} \quad \text{and} \quad b = \ln(k_{s(1/1)}/k_{s(2/2)}) \cdot \quad (47)$$

The linear relationship given by equation 46 has been discussed theoretically and applied for analysing chromatographic data by many authors (e.g., 10,13-16). The linear dependence of the logarithm of  $k_{s(12/12)}$  upon  $\phi_1^k$  given by equation 46 is, besides the Snyder-Soczewiński equation (9), one of the most popular relationships used for characterizing chromatographic systems. On the other hand, the equations in question relate to very simple models of the LC process (2,11,17,18), which do not reflect many important features of real chromatographic systems. The source of a good representation of a great number of chromatographic systems by these equations in a wide concentration region must lie elsewhere. Our studies show that theoretical dependence of  $k_{s(12/12)}$  vs.  $\phi_1^k$  calculated for different chromatographic models may often be well represented by the equations mentioned above in a limited concentration region (18). This means that the linear parameters appearing in these equations evaluated by fitting the experimental data have different physical meaning than those resulting from the above-mentioned simple models. In other words, the interpretation of the linear parameters in question is very difficult because they can be discussed in terms of different models of the LC process.

Now, we consider possibility of application of equation 20 (equation 41 is its analog in the regular-solution lattice formulation) for describing RPLSC and RPLC-CBP systems with nonideal eluents satisfying the following condition:

$$B_{ij}^{-\ell} = r_s X_{ij}^{\ell} > 0 \text{ for } i, j = 1, 2, \dots, n \text{ and } j > i. \quad (48)$$

This condition implies that the solvent components are not exceptionally compatible due to relatively weak unlike (ij) interactions (e.g., in a binary mixture: H<sub>2</sub>O + THF). Consider the situation where component "n" is preferentially extracted into the stationary phase. Then,  $\phi_i^{\sigma} = 0$  for  $i = 1, 2, \dots, n-1$  and equation 20 gives

$$\ln k_{s(n/n)}^{\ell} = \sum_{i=1}^n \phi_i^{\ell} \ln k_{s(i/n)} - r_s \sum_{\substack{i, j=1 \\ j > i}}^n X_{ij}^{\ell} \phi_i^{\ell} \phi_j^{\ell}. \quad (49)$$

This equation describes the actual partitioning of the s-th solute between a mobile phase consisting of 1+2+...+n and a stationary phase of essentially pure "n". Application of equation 49 suggests a surface influence in causing  $\phi_n^{\sigma}$  to approach unity (hence, RPLSC systems) and requires the presence of the n-th solvent in the entire system.

One special case of equation 49 seems to be most interesting. It refers to the situation where  $\phi_n^{\ell} = 0$ ; it can occur if the n-th component is a CBP near the collapsed-chain limit or a high molecular weight hydrocarbon in contact with a polar solvent mixture (such that  $\phi_i^{\sigma} = 0$  for  $i = 1, 2, \dots, n-1$ ). Here, the "surface influence" is incidental to the formation of the stationary phase. Accordingly

$$\ln k_{s(n-1/n)}^{\ell} = \sum_{i=1}^{n-1} \phi_i^{\ell} \ln k_{s(i/n)} - r_s \sum_{\substack{i, j=1 \\ j > i}}^{n-1} X_{ij}^{\ell} \phi_i^{\ell} \phi_j^{\ell} \quad (50)$$

which is the Martire-Boehm expression applicable to liquid/liquid partition chromatography and RPLC-CBP in the above-mentioned limit. In the case of binary eluents equation 50 becomes (11):

$$\ln k_{s(12/3)}^{\ell} = \phi_1^{\ell} \ln k_{s(1/3)} + \phi_2^{\ell} \ln k_{s(2/3)} - r_3 X_{12}^{\ell} \phi_1^{\ell} \phi_2^{\ell} \quad (51)$$

or

$$\ln k_{s(12/3)}^{\ell} = a^* + b^* \phi_1^{\ell} + c^* (\phi_1^{\ell})^2 \quad (52)$$

where

$$a^* = \ln k_{s(2/3)}^{\ell}, \quad b^* = \ln(k_{s(1/3)}^{\ell} / k_{s(2/3)}^{\ell}) - r_3 X_{12}^{\ell}, \quad c^* = r_3 X_{12}^{\ell} \quad (53)$$

The relationship given by equation 52, representing a quadratic dependence of logarithm of the distribution coefficient on the volume fraction  $\phi_1^l$ , is frequently used for analysing chromatographic data (12-13), particularly in reversed-phase systems.

In the general case of RPLC-CBP systems, in which the stationary phase contains solvent molecules, i.e.,  $\phi_i^\sigma \neq 0$  for  $i = 1, 2, \dots, n$  and  $\phi_n^l = 0$ , equation 26 gives:

$$\ln k_{s(n-1/n)} = \sum_{i=1}^{n-1} \phi_i^l \ln k_{s(i/n)} - r_s \sum_{i,j=1}^{n-1} \chi_{ij}^l \phi_i^l \phi_j^l \quad (54)$$

where

$$\sum_{i=1}^{n-1} \phi_i^l \ln k_{s(i/n)} = \sum_{i=1}^{n-1} \phi_i^l \ln k_{s(i/i)} + \sum_{i=1}^{n-1} (\phi_i^\sigma - \phi_i^l) \ln \kappa_s^\sigma + r_s \sum_{i,j=1}^n \chi_{ij}^\sigma \phi_i^\sigma \phi_j^\sigma \quad (55)$$

Equation 55 becomes the expression for the distribution coefficient  $k_{s(i/in)}$  at  $\phi_j^l = 0$  for  $j = 1, 2, \dots, n$  and  $j \neq i$ , and  $\phi_j^\sigma = 0$  for  $j = 1, 2, \dots, n-1$  and  $j \neq i$ ; it is

$$\ln k_{s(i/in)} = \ln k_{s(i/i)} + (\phi_i^{\sigma(n)} - 1) \ln \kappa_s^\sigma + r_s \chi_{in}^\sigma \phi_i^\sigma \phi_n^\sigma \quad (56)$$

where

$$\phi_n^{\sigma(i)} + \phi_i^{\sigma(n)} = 1 \quad \text{for} \quad \phi_i^l = 1. \quad (57)$$

Expressing  $\ln k_{s(i/i)}$  by means of  $\ln k_{s(i/in)}$  (see equation 56) and combining it with equation 15 for  $\phi_n^l = 0$ , we have

$$\ln k_{s(n-1/n)} = \sum_{i=1}^{n-1} \phi_i^l \ln k_{s(i/in)} + \sum_{i=1}^{n-1} (\phi_i^\sigma - \phi_i^l \phi_i^{\sigma(n)}) \ln \kappa_s^\sigma + r_s \sum_{i,j=1}^n \chi_{ij}^\sigma \phi_i^\sigma \phi_j^\sigma - r_s \sum_{i=1}^{n-1} \chi_{in}^\sigma \phi_i^\sigma \phi_n^{\sigma(i)} \phi_i^l - r_s \sum_{i,j=1}^{n-1} \chi_{ij}^l \phi_i^l \phi_j^l \quad (58)$$

Equation 58 describes RPLC-CBP systems and when the solvents are excluded from the stationary phase it reduces to equation 49 because  $k_{s(i/in)}$  becomes

$$k_{s(i/n)} \quad \text{and} \quad \phi_i^\sigma = \phi_i^{\sigma(n)} = 0 \quad \text{for } i = 1, 2, \dots, n-1.$$

It must be emphasized that the equations derived above for RPLC-CBP and classical liquid/liquid partition chromatography do not take into account possible contributions arising from interfacial effects. This problem will be treated in future papers (19,20).

#### SUMMARY

We have extended Ościk's original derivation to include an often important contribution to retention arising from solvent nonideality, and have described a novel, complementary treatment based on a regular-solution lattice theory. The two approaches are seen to yield equivalent equations for solute retention. Since the later approach, which is based on a pure partitioning model, leads to expressions in terms of molecular parameters, we have provided a molecular basis for Ościk's parameters. Moreover, it is now clear that Ościk's approach applies to a partitioning mode of retention, without "displacement" or "competitive adsorption", and, hence, is better suited for describing partition effects in reversed-phase liquid chromatography with solid, liquid and chemically bonded stationary phases, as is demonstrated in the previous section.

In a forthcoming paper (19), a generalized treatment, incorporating concurrent partition and adsorption effects, and applicable to normal- and reversed-phase systems, will be presented.

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