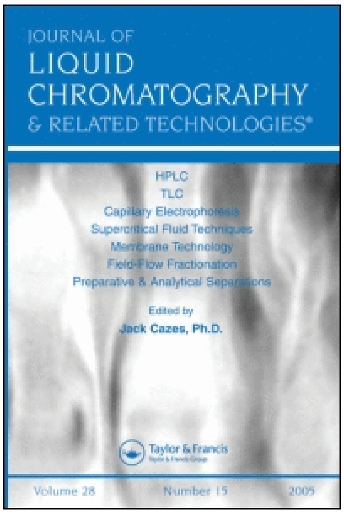

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

An Extension and New Interpretation of Ościk's Equation for Describing Liquid Chromatography with Mixed Mobile Phases. II. Partition and Adsorption Effects

M. Jaroniec[abc]; D. E. Martire[d]; J. Ościk[e]
[a] Institute for Materials Research McMaster University, Hamilton, Ontario [b] Institute of Chemistry, M. Curie-Sklodowska University, Lublin, Poland [c] Department of Chemistry, Georgetown University, Washington, D.C. [d] Department of Chemistry, Georgetown University, Washington, D. C. [e] Institute of Chemistry M. Curie-Sklodowska University, Lublin, Poland

To cite this Article Jaroniec, M. , Martire, D. E. and Ościk, J.(1986) 'An Extension and New Interpretation of Ościk's Equation for Describing Liquid Chromatography with Mixed Mobile Phases. II. Partition and Adsorption Effects', Journal of Liquid Chromatography & Related Technologies, 9: 12, 2555 — 2562

To link to this Article: DOI: 10.1080/01483918608076884

URL: http://dx.doi.org/10.1080/01483918608076884

JOURNAL OF LIQUID CHROMATOGRAPHY, 9(12), 2555-2562 (1986)

AN EXTENSION AND NEW INTERPRETATION OF OŚCIK'S EQUATION FOR DESCRIBING LIQUID CHROMATOGRAPHY WITH MIXED MOBILE PHASES. II. PARTITION AND ADSORPTION EFFECTS

M. Jaroniec[1*], D. E. Martire[2], and J. Ościk[3]
[1]Institute for Materials Research
McMaster University
Hamilton, Ontario L8N 4M1
[2]Department of Chemistry
Georgetown University
Washington, D. C. 20057
[3]Institute of Chemistry
M. Curie-Sklodowska University
20031 Lublin, Poland

ABSTRACT

Previously [J. Liquid Chromatogr. 8 (1985) 1363] it was shown that an equation having a form similar to Ościk's classical equation was derivable from a model involving solute partitioning (with no solute and solvent displacement) between a bulk-liquid mobile phase and a surface-influenced stationary liquid layer. Based on a recent general theory, we now propose a solute retention model which reveals an alternative molecular basis of Ościk's equation, which has been successfully applied to a range of liquid adsorption chromatographic systems. According to this model, solute is distributed between the

---

* Permanent address: Institute of Chemistry, M. Curie-Sklodowska University, 20031 Lublin, Poland; work done in part at: Department of Chemistry, Georgetown University, Washington D.C., 20057.

0148-3919/86/0912-2555$3.50/0

mobile and stationary phases as a consequence of a mixed mechanism, where the surface phase composition is determined by solvent competitive adsorption (displacement mechanism).

INTRODUCTION

In the previous paper of this series (1) the distribution coefficient of the s-th solute between two n-component phases, mobile and surface-influenced stationary phases, was defined as follows:

$$\ln k_{s(\underline{n}/\underline{n})} = \ln (\gamma^{\ell}_{s(\underline{n})}/\ \gamma^{\sigma}_{s(\underline{n})}) \tag{1}$$

where $k_{s(\underline{n}/\underline{n})}$ denotes the distribution coefficient under consideration, $\gamma^{\ell}_{s(\underline{n})}$ and $\gamma^{\sigma}_{s(\underline{n})}$ are the activity coefficients of the s-th solute in the mobile (ℓ) and surface (σ) phases consisting of the solvents 1, 2,...,n and containing the s-th solute at infinitely low concentration. The mobile and surface-influenced stationary phases were assumed to be regular. Both phases contained the same solvents but the properties of the stationary phase differed from the bulk one because the solid surface was assumed to influence the various molecular interactions in the stationary phase and, hence, to set the composition variables in that phase. Retention was taken to be governed exclusively by partitioning between a mobile phase and a stationary phase having different composition variables. The competitive adsorption (displacement) was ignored. Such a mechanism of solute distribution between the mobile and stationary phases is quite analogous to that occurring in gas/liquid and liquid/liquid systems (2).

The final expression describing the above retention mechanism was proposed in the following form (1):

$$\ln k_{s(\underline{n}/\underline{n})} = \sum_{i=1}^{n} \phi^{\ell}_{i} \ln(\gamma^{\ell}_{s(i)}/\gamma^{\sigma}_{s(i)}) + \sum_{i=1}^{n-1} (\phi^{\sigma}_{i} - \phi^{\ell}_{i}) \ln(\gamma^{\sigma}_{s(n)}/\gamma^{\sigma}_{s(i)})$$

$$+ r_{s}\Big(\sum_{\substack{i,j=1\\ j>i}}^{n} \chi^{\sigma}_{ij}\phi^{\sigma}_{i}\phi^{\sigma}_{j} - \sum_{\substack{i,j=1\\ j>i}}^{n} \chi^{\ell}_{ij}\phi^{\ell}_{i}\phi^{\ell}_{j}\Big) \tag{2}$$

where

$$\ln(\gamma^{\ell}_{s(i)}/\gamma^{\sigma}_{s(i)}) = \ln k_{s(i/i)} = r_{s}(\chi^{\ell}_{is} - \chi^{\sigma}_{is}) \text{ for } i = 1,2,\ldots,n \tag{3}$$

$$\ln(\gamma^{\sigma}_{s(n)}/\gamma^{\sigma}_{s(i)}) = (r_s/r_i - r_s/r_n) + r_s(\chi^{\sigma}_{ns} - \chi^{\sigma}_{is}) \qquad (4)$$

and

$$\chi^{\rho}_{ij} = (z^{\rho}/kT)[\omega^{\rho}_{ij} - 0.5(\omega^{\rho}_{ii} + \omega^{\rho}_{jj})] \quad \text{for } \rho = \ell, \sigma. \qquad (5)$$

In the above, $\gamma^{\ell}_{s(i)}$ and $\gamma^{\sigma}_{s(i)}$ denote the activity coefficients of the s-th solute in the i-th solvent forming mobile (ℓ) or stationary (σ) phases, respectively; $k_{s(i/i)}$ is the distribution coefficient of the s-th solute between mobile and surface-influenced stationary phases consisting of the i-th pure solvent; ϕ^{ℓ}_i and ϕ^{σ}_i are the volume fractions of the i-th component in the mobile and stationary phases, respectively; ω^{ρ}_{ij} is a segmental energy for the interaction between the i-th and j-th components in the ρ-th phase; z^{ρ} is the lattice coordination number for the ρ-th phase; and r_i denotes the number of segments in a molecule of the i-th component. χ^{ρ}_{ij} is the usual interaction parameter.

Equation 2 may be obtained from equation 1 when the activity coefficients $\gamma^{\ell}_{s(\underline{n})}$ and $\gamma^{\sigma}_{s(\underline{n})}$ are expressed in terms of regular solution lattice theory (1). The first two terms of equation 2 are formally identical with Ościk's classical equation (3). However, it is difficult to reduce equation 2 to the expression containing only the first two terms. The last term of equation 2 may be neglected when the solvent interaction parameters χ^{ℓ}_{ij} and χ^{σ}_{ij} are equal to zero; this means that the solvent solutions forming the bulk and surface phases are energetically ideal. For such ideal solvent mixtures and a pure partition mechanism of retention, the volume fractions ϕ^{ℓ}_i and ϕ^{σ}_i ($i = 1,2,\ldots,n$) are identical, i.e., the second term of equation 2 becomes automatically equal to zero. Therefore, in the previous paper (1) we suggested that the extended form of Ościk's expression, equation 2, is applicable to describe partition effects in reversed-phase liquid chromatography including, under certain conditions, chemically bonded phases. In other words, equation 2 including an important contribution to retention arising from solvent nonideality and ignoring competitive adsorption, is better suited for describing reversed-phase liquid chromatography than liquid/solid chromatography in a normal mode.

On the other hand, Ościk and co-workers [see review (4) and references therein] showed that equation 2 without the last term gives a good representation for many liquid/solid chromatographic systems, in which adsorption effects seem to be significant. Theoretical derivation of equation 2 on the basis of equation 1, which describes a partition-like mechanism of retention, does not give a clear foundation to include the adsorption effects in equation 2. Thus, this problem cannot be simply resolved in terms of the theoretical formulations of liquid chromatography presented in earlier papers (1,3,4).

However, a recent general formulation of liquid/solid chromatography (2) leads to a general expression for the solute distribution coefficient and defines the so-called "pure" partition and "pure" adsorption mechanisms of retention. In this recent treatment (2) it is also noted that different "mixed" retention mechanisms may be considered as special cases of the general expression. Here we will show that, through this new approach, it is possible to include adsorption effects in equation 2 and that the resulting equation may be also used to describe liquid adsorption chromatography.

MODEL OF SOLUTE RETENTION

Let us consider a system with an energetically homogeneous solid surface, in which the s-th solute is chromatographed in an n-component mobile phase. The chromatographic process may be generally described by the equilibrium constants K_{ij} for $i,j = 1,2,\ldots,n,s$ and $i \neq j$. Each equilibrium constant is defined as follows (2):

$$K_{ij} = [(\phi_i^\sigma \gamma_{i(\underline{n})}^\sigma)/(\phi_i^\ell \gamma_{i(\underline{n})}^\ell)] \cdot [(\phi_j^\ell \gamma_{j(\underline{n})}^\ell)/(\phi_j^\sigma \gamma_{j(\underline{n})}^\sigma)]^{r_i/r_j} \qquad (6)$$

for $i,j = 1,2,\ldots,n,s$ and $i \neq j$. In the above, $\gamma_{i(\underline{n})}^\sigma$ and $\gamma_{i(\underline{n})}^\ell$ denote the activity coefficients for the n-component solvent mixture containing the s-th solute at an infinitely low concentration. Let us select the 1-st solvent as a reference solvent and assume that its adsorption properties are very similar to those of the s-th solute. Then, the equilibrium constant K_{s1} may be assumed to be equal to unity, i.e.,

$$K_{s1} = 1 \qquad (7)$$

Equation 7 indicates that in the case of liquid chromatography with the mobile phase containing the 1-st solvent only, the s-th solute is distributed between two phases according to a partition mechanism defined in the previous paper (2). Taking into account the theoretical considerations in the Ref. (2), equations 6 with i = s and j = 1 and 7 give:

$$k_{s(\underline{n}/\underline{n})} = \gamma^{\ell}_{s(\underline{n})}/\gamma^{\sigma}_{s(\underline{n})} \tag{8}$$

The assumption expressed by equation 7 requires that the equilibrium constants K_{si} and K_{1i} for i = 2,3,...,n be identical because $K_{1i} = K_{si}/K_{s1}$, i.e.,

$$K_{si} = K_{1i} \quad \text{for } i = 2,3,\ldots,n. \tag{9}$$

If the constants K_{1i} for i = 2,3,...,n are equal to unity, then the K_{si} for i = 2,3,...,n are also equal to unity, and we obtain equation 2 describing the pure partition model considered in the previous paper (1). However, if we assume that

$$K_{si} = K_{1i} \neq 1 \quad \text{for } i = 2,3,\ldots,n \tag{10}$$

(solute displacement with respect to solvents 2,3,...,n and solvent displacement), then the surface phase composition is determined by the following equation:

$$K_{ij} = [(\phi^{\sigma}_{i}\gamma^{\sigma}_{i(\underline{n})})/(\phi^{\ell}_{i}\gamma^{\ell}_{i(\underline{n})})]\cdot[(\phi^{\ell}_{j}\gamma^{\ell}_{j(\underline{n})})/(\phi^{\sigma}_{j}\gamma^{\sigma}_{j(\underline{n})})]^{r_i/r_j} \tag{11}$$

for i,j = 1,2,...,n and i ≠ j. Equation 11, even for an ideal solvent mixture ($\gamma^{\sigma}_{i(\underline{n})}$ and $\gamma^{\ell}_{i(\underline{n})}$ for i = 1,2,...,n are assumed to be equal to unity), predicts different surface phase and mobile phase compositions, i.e., $\phi^{\sigma}_{i} \neq \phi^{\ell}_{i}$ for i = 1,2,...,n.

The above considerations indicate that equation 2 may be obtained from equation 8 so that the conditions 7 and 10 are fulfilled; but then we have:

$$\ln(\gamma^{\ell}_{s(1)}/\gamma^{\sigma}_{s(1)}) = \ln k_{s(1/1)} = r_s(\chi^{\ell}_{1s} - \chi^{\sigma}_{1s}) \tag{12}$$

and

$$\ln(\gamma^{\ell}_{s(i)}/\gamma^{\sigma}_{s(i)}) = r_s(\chi^{\ell}_{is} - \chi^{\sigma}_{is}) = \ln k_{s(i/i)} - \ln K_{si}$$

$$= \ln k_{s(i/i)} - \ln K_{1i} \quad \text{for} \quad i = 2,3,\ldots,n. \qquad (13)$$

Equations 12 and 13 differ from equation 3 because they refer to a mixed model for solute transfer from the mobile phase to the surface phase, whereas, equation 3 refers to a pure solute partition model. Moreover, we have assumed here the surface phase is formed as a consequence of competitive adsorption of the solvents, which is described by equation 11. It is noteworthy that, in terms of this model, we can assume in equation 2 that $\chi^{\ell}_{ij} = \chi^{\sigma}_{ij} = 0$ for $i,j = 1,2,\ldots,n$ and $i \neq j$ (ideal solvent mixture in both phases); then, the third term in equation 2 becomes zero but the second term of this equation is different from zero because then the surface phase composition is determined by the solvent equilibrium constants $K_{ij} \neq 1$ for $i = 1, 2,\ldots,n$ and $i \neq j$, i.e.,

$$K_{ij} = (\phi^{\sigma}_i/\phi^{\ell}_i)\cdot(\phi^{\ell}_j/\phi^{\sigma}_j)^{r_i/r_j} \quad \text{for } i = 1,2,\ldots,n \text{ and } i \neq j. \qquad (14)$$

Equation 14 for $K_{ij} \neq 1$ gives $\phi^{\sigma}_i \neq \phi^{\ell}_i$ for $i,j = 1,2,\ldots,n$ and and $i \neq j$, and then equation 2 becomes an expression analogous to Ościk's classical equation:

$$\ln k_{s(\underline{n}/\underline{n})} = \sum_{i=1}^{n} \phi^{\ell}_i \ln(\gamma^{\ell}_{s(i)}/\gamma^{\sigma}_{s(i)}) + \sum_{i=1}^{n-1}(\phi^{\sigma}_i - \phi^{\ell}_i)\ln(\gamma^{\sigma}_{s(n)}/\gamma^{\sigma}_{s(i)}) \qquad (15)$$

However, in the case of the pure partition model ($K_{ij} = 1$ for $i,j = 1, 2,\ldots,n$ and $i \neq j$) and an ideal solvent mixture ($\chi^{\rho}_{ij} = 0$ for $i,j = 1, 2,\ldots,n$ and $i \neq j$) the last term in equation 15 disappears.

Let us consider a special case of equation 15 when $n = 2$ (binary solvent mixture). Then, equation 15 becomes

$$\ln k_{s(\underline{2}/\underline{2})} = \phi^{\ell}_1 \ln k_{s(1/1)} + \phi^{\ell}_2 \ln k_{s(2/2)} + (\phi^{\sigma}_1 - \phi^{\ell}_1) \ln(\gamma^{\sigma}_{s(2)}/\gamma^{\sigma}_{s(1)})$$

$$- \phi^{\ell}_2 \ln K_{12} \qquad (16)$$

The last term in equation 15 is a consequence of equation 13. For systems showing strong solute-solvent interactions, ideal solvent behaviour and K_{12} close to unity the last term in equation 16 may be negligible and then this equation reduces to Ościk's expression (3):

$$\ln k_{s(\underline{2}/\underline{2})} = \phi_1^{\ell} \ln k_{s(1/1)} + \phi_2^{\ell} \ln k_{s(2/2)}$$

$$+ \ (\phi_1^{\sigma} - \phi_1^{\ell}) \ln(\gamma_{s(2)}^{\sigma}/\gamma_{s(1)}^{\sigma}) \qquad (17)$$

If additionally we assume identical molecular sizes of solvent molecules ($r_1 = r_2 = r$), then ϕ_1^{σ} may be calculated according to an Everett-type equation (4):

$$\phi_1^{\sigma} = K_{12}(\phi_1^{\ell}/\phi_2^{\ell})/[1 + K_{12}(\phi_1^{\ell}/\phi_2^{\ell})] \qquad (18)$$

where $\phi_i^{\sigma} = x_i^{\sigma}$ and $\phi_i^{\ell} = x_i^{\ell}$ for i = 1,2 and x_i^{ρ} denotes the mole fraction of the i-th solvent in the ρ-th phase ($\rho = \ell, \sigma$).

Equation 17 combined with Everett's equation 18 was linearized and its linear form was applied successfully to describe several chromatographic systems also showing adsorption effects (5,6). Thus, the above chromatographic model combining solvent competitive adsorption (equation 18) and a mixed mechanism of the solute transfer (equation 16) gives a reasonable answer the question of when Ościk's equation 17 may be used to describe chromatographic systems showing adsorption effects. Equation 17 seems to be useful for practical applications because it involves competitive solvent adsorption which is frequently important in the case of a mixed mechanism of solute transfer. Although the pure displacement model seems to be adequate to represent the solute transfer in liquid adsorption chromatography in the normal mode (4,6) and the pure partition model is useful to describe reversed-phase liquid chromatography (7-9), there are chromatographic systems showing both adsorption and partition effects and then equation 16 or other equations involving mixed models of solute and solvent transfer should be employed (2).

ACKNOWLEDGMENTS

This material is based on work supported at Georgetown University (D.E.M. and, in part, M.J.) by the National Science Foundation under Grant CHE-8305045. One of the authors (M.J.) wishes also to thank McMaster University for partial support of this research.

REFERENCES

1. Martire, D.E. and Jaroniec, M., J. Liquid Chromatogr., 8, 1985, 1363.
2. Jaroniec, M. and Martire, D.E., J. Chromatogr., 351, 1986, 1.
3. Ościk, J., Przem. Chem., 44, 1965, 129.
4. Jaroniec, M. and Ościk, J., Journal of HRC & CC, 5, 1982, 3.
5. Ościk, J., Jaroniec, M. and Malinowska, I., J. Liquid Chromatogr., 6, 1983, 81.
6. Jaroniec, M., Martire, D.E. and Borówko, M., Advances Colloid Interface Sci., 22, 1985, 177.
7. Martire, D.E. and Boehm, R.E., J. Phys. Chem., 87, 1983, 1045.
8. Martire, D.E. and Boehm, R.E., J. Liquid Chromatogr., 3, 1980, 753.
9. Boehm, R.E. and Martire, D.E., J. Phys. Chem., 84, 1980, 3620.