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**Relations between the Retention Equations Used in Solid-liquid  
Chromatography Applying Mixed Mobile Phases**

Zależności między równaniami retencji stosowanymi w adsorpcyjnej chromatografii cieczowej  
z wieloskładnikową fazą ruchomą

Зависимости между уравнениями удерживания, применяемыми  
в жидкостно-адсорбционной хроматографии с многокомпонентной подвижной фазой

Among various equations proposed to describe concentration equilibria in Solid-Liquid Chromatography systems, there are two which have appeared to be pretty useful. One of them is the Snyder-Soczewiński equation [1, 2]:

$$\ln \mathcal{X}_k = \text{const} - \ln x_2 \quad (1)$$

in which  $\mathcal{X}_k$  is the distribution coefficient of a solute "k", between the surface and the mobile liquid phase, being a binary solution. Further,  $x_2$  is the mole fraction of the solvent "2" in this mobile phase, while const. is a quantity independent upon the composition of the mobile phase. The theoretical considerations which led Snyder and Soczewiński to eqn. 1 were different [1, 2], but both of them concern the case when the mobile phase is composed of two solvents only.



Another useful equation was proposed by Ościk [3]:

$$\ln \mathcal{X}_k = x_1 \ln \mathcal{X}_{k,0}^{(1)} + x_2 \ln \mathcal{X}_{k,0}^{(2)} + \text{const } n_2^{(e)} \quad (2)$$

where  $\mathcal{X}_{k,0}^{(i)}$  is the appropriate distribution coefficient in the pure solvent "i", and  $n_1^{(e)}$  is the surface excess of this solvent,

$$n_1^{(e)} = \theta_1 - x_1 \quad (3)$$

Above  $\theta_1$  is the adsorption isotherm of the component "i" on the support surface.

These equations were known for a long time, and numerous examples of LC systems were reported, which could be described by either eqn. 1 or 2. At the same time it was clear that any transition from one to the other equation is possible, on the ground of the theories proposed by Snyder, Soczewiński and Ościk. It is the purpose of this paper to investigate this problem in more detail. Using methods of statistical thermodynamics and a simple lattice model of the surface phase, we shall show that both these equations are simplified forms of some more general equation.

## THEORY

When describing the properties of the surface and the mobile liquid phase on a molecular level, we shall use a lattice description formalism, which is commonly used in the theories of bulk solutions and in the theories of adsorption as well. Thus, our present model of LC systems may be described shortly as follows:

1. The mobile liquid phase (multicomponent mixture, in general) may be as well ideal as non-ideal mixture, but still a regular solution.
2. The molecules of the solvent mixture (mobile phase) and of the solute (analyzed substance) are adsorbed on a twodimensional lattice of adsorption sites, one molecule per one site.
3. All adsorption sites are energetically equivalent, i.e., the support surface is assumed to be homogeneous.



4. It is assumed that small samples of solutes are analyzed, so the concentration of solute in both the mobile and the surface phases is small. We shall, therefore, neglect the mutual interactions between solute molecules in both the mobile and the surface phases.

5. The relatively small solvent molecules adsorbed of different sites, do not interact with each other. At the same time the relatively big solute molecules may interact with other solvent admolecules.

Now, consider first the canonical, system partition function  $Q_L(M\{N_k\}, T)$ , for the case when the surface phase is ideal,

$$Q_L(M\{N_k\}, T) = \frac{M!}{\left(\prod_{k=1}^{n-1} N_k!\right) \left(M - \sum_{k=1}^{n-1} N_k\right)!} \left[ \prod_{k=1}^{n-1} q_k^{N_k} q_n^{(M - \sum_{k=1}^{n-1} N_k)} \right] \quad (4)$$

Similarly as in our previous paper,  $M$  is here the total number of adsorption sites,  $N_k$  is the number of admolecules of  $k$ -th kind, and  $q_k$  is the molecular partition function defined as follows:

$$q_k = q_{xk} q_{yk} q_{zk} f_{sk}^{(i)} \exp \left( \frac{\xi_k}{kT} \right) \quad (5)$$

where  $q_x$ ,  $q_y$ ,  $q_z$  are the vibrational partition functions of the vibrations parallel ( $q_x$ ,  $q_y$ ) and normal ( $q_z$ ) to the surface,  $f_{sk}^{(i)}$  is the partition function for internal vibrations, and rotational degrees of freedom of the adsorbed molecules. Further,  $\xi$  is the so-called "adsorption energy" which is just a difference between the energies of a molecule in the adsorbed and in the bulk phase, assuming that this molecule is in its lowest quantum energy states in respect to all its degrees of freedom in the adsorbed and in the bulk phase.

In case of adsorption from solutions the following conditions are fulfilled:

$$\sum_k^n N_k = M \quad (6)$$

and, consequently:



$$\mu_k^{(s)} - \mu_n^{(s)} = -kT \left( \frac{\partial \ln Q_L}{\partial N_k} \right)_{M, T, N_j \neq k} \quad (7)$$

Above,  $\mu_i^{(s)}$  is the chemical potential of the molecules of  $i$ -th kind in the surface phase. Using Stirling's approximations for  $\ln N_k!$ , and considering that:

$$\mu_k^{(s)} = \mu_k^{(b)} \quad (8)$$

where  $\mu_k^{(b)}$  is appropriate chemical potential in the bulk mobile phase, we obtain:

$$\mu_k^{(b)} - \mu_n^{(b)} = kT \ln \left[ \frac{N_k q_n}{\left( M - \sum_{i=1}^{n-1} N_i \right) q_k} \right] \quad (9)$$

Let us consider now the effects of the mutual interactions between adsorbed molecules. We shall take them into account in a simplest possible way using the well-known "Mean-Field Approximation". It is assumed in MFA, that there are no correlations between adsorbed molecules on the surface. In other words, the molecules are distributed on the surface completely at random. Thus, in a nearest neighbourhood of a certain ad molecule, there should be found on an average  $(\bar{z}^{(s)} N_i / M)$ , ad molecules of  $i$ -th kind. Here  $\bar{z}^{(s)}$  denotes the number of the nearest neighbours - adsorption sites. Let further  $w_{ij}^{(s)}$  denote the interaction energy between two molecules of  $i$ -th and  $j$ -th kind, respectively, which are the nearest neighbours. Then, every adsorbed molecule of  $k$ -th kind is subject to the action of a mean force field  $E_k^{(s)}$ :

$$E_k^{(s)} = \sum_{i=1}^n w_{ki}^{(s)} \left( \bar{z} \frac{N_i}{M} \right) \quad (10)$$

Let the set of subscripts  $k=1, 2, \dots, l$ , denote the components of the mobile phase, whereas the set  $k= (l+1), \dots, n$  denote the analyzed substances. According to our assumption (8) we have:



$$\Theta_k = \frac{N_k}{M} \rightarrow 0 \quad \text{for } k = (1+1), \dots, n \quad (11)$$

and, therefore:

$$E_k^{(s)} = \sum_{i=1}^1 E_{ki}^{(s)} \Theta_i \quad k=1,2,\dots,n \quad (12)$$

$$\text{and } E_{ki}^{(s)} = z^{(s)} w_{ki}^{(s)}.$$

For the purpose of our present work, we shall neglect the interactions between solvent molecules on the surface. At the same time, we shall assume that solute molecules may interact with solvent molecules on the surface. With this approximation, our equations are still valid, except that molecular partition functions take the form:

$$q_k = \begin{cases} q_{xk} q_{yk} q_{zk} f_{sk}^{(i)} \exp\left(\frac{\epsilon_k}{kT}\right) & \text{for } k=1,2,\dots,1 \\ q_{xk} q_{yk} q_{zk} f_{sk}^{(i)} \exp\left[\frac{\epsilon_k}{kT} + \sum_{i=1}^l \frac{E_{ki} \Theta_i^{(s)}}{kT}\right] & \text{for } k=(1+1), \dots, n \end{cases} \quad (13)$$

Consider now the relation between the chemical potential  $\mu_k^{(b)}$ , activity  $a_k^{(b)}$ , and the mole fraction  $x_k$  of the  $k$ -th species in the equilibrium bulk phase. We shall accept further a non-symmetrical reference system for standard chemical potentials, in which we distinguish "solvents" and the "solute substances". For the "solvents" we have:

$$\mu_k^{(b)} = \mu_{k,0}^{(b)} + kT \ln a_k^{(b)} \quad k=1,2,\dots,1 \quad (14)$$

where  $\mu_{k,0}^{(b)}$  is the standard chemical potential of the pure solvent " $k$ ". In the same reference system, for "solute" (analyzed) substances we have:

$$\mu_k^{(b)} = \mu_{k,\Theta}^{(b)} + kT \ln x_k \quad k=1+1, \dots, n \quad (15)$$

where  $\mu_{k,\Theta}^{(b)}$  is the standard chemical potential of the analyzed substance " $k$ " at its infinite dilution. Obvious-



ly, it is not equal to the standard chemical potential of the pure solute  $\mu_k^H$ . From eqns. 9, 11, 14 and 15, we obtain:

$$\theta_k = \frac{K_k a_k^{(b)}}{\sum_{i=1}^n K_i a_i^{(b)}} \quad (16)$$

where

$$K_i = q_i \exp \left( \frac{\mu_{k,s}^{(b)}}{kT} \right) \quad (17)$$

where

$$\mu_{k,s}^{(b)} = \begin{cases} \mu_{k,0}^{(b)} & \text{for } k=1,2,\dots,1 \\ \mu_{k,\theta}^{(b)} & \text{for } k=(1+1),\dots,n \end{cases} \quad (18)$$

Further,

$$a_k^{(b)} = \begin{cases} \gamma_k^x x_k & \text{for } k=1,2,\dots,1 \\ x_k & \text{for } k=(1+1),\dots,n \end{cases} \quad (19)$$

and

$$\lim_{x_k \rightarrow 1} \gamma_k = 1 \quad \text{for } k=1,2,\dots,1 \quad (20)$$

In the case when the mobile phase is a regular solution, we have

$$\mu_{k,\theta}^{(b)} = \sum_{i=1}^1 x_i \mu_{k,\theta}^{(i)} + \sum_{i < j} g_{ij}^{(e)} x_i x_j \quad (21)$$

where  $g_{ij}^{(e)} x_i x_j$  is the excess of the Gibbs free energy of mixing solvents "i" and "j". In case of a binary mobile phase  $\gamma$  has the following relation to  $g_{12}^{(e)}$ :

$$kT \ln \gamma_1 = g_{12}^{(e)} x_2^2 \quad kT \ln \gamma_2 = g_{12}^{(e)} x_1^2 \quad (22)$$

Thus, for the components of the mobile phase, we have



$$\theta_k = \frac{x_k \gamma_k q_k \exp\left(\frac{\mu_{k,0}^{(b)}}{kT}\right)}{\sum_{i=1}^L x_i \gamma_i q_i \exp\left(\frac{\mu_{i,0}^{(b)}}{kT}\right)} \quad (23)$$

whereas for the analyzed substances, we have:

$$\theta_k = \frac{x_k q_k \exp\left\{\frac{1}{kT} \left[ \sum_{i=1}^L (x_i \mu_{k,i}^{(i)} + \theta_i E_{ki}^{(s)}) + \sum_{i < j} g_{ij}^{(e)} x_i x_j \right]\right\}}{\sum_{i=1}^L x_i \gamma_i q_i \exp\left(\frac{\mu_{i,0}^{(b)}}{kT}\right)} \quad (24)$$

The distribution coefficient  $\mathcal{X}$  is just the ratio of the concentrations (mole fractions) of the analyzed substance in the surface, and the mobile phase, so we have:

$$\mathcal{X}_k(\{x_i\}) = \frac{\theta_k(\{x_i\})}{x_k} \quad (25)$$

Let us consider now the form of the distribution coefficient  $\mathcal{X}_k$  when the mobile phase is the pure solvent  $j^4$ . We shall denote it by  $\mathcal{X}_{k,0}^{(j)}$ . From eqn. 24, in the limit  $x_j \rightarrow 1$ , we obtain:

$$\mathcal{X}_{k,0}^{(j)} = \frac{q_k \exp\left[\frac{1}{kT} (\mu_{k,\theta}^{(j)} + E_{kj}^{(s)})\right]}{q_j \exp\left(\frac{\mu_{j,0}^{(b)}}{kT}\right)} \quad (26)$$

So, it can easily be deduced that the distribution coefficient  $\mathcal{X}_k(\{x_i\})$  in the mixture  $\{x_i\}$  of the solvents, may be expressed by means of appropriate distribution coefficients in pure solvents  $\mathcal{X}_{k,0}^{(j)}$ .

$$\mathcal{X}_k(\{x_i\}) = \left\{ \prod_{i=1}^L [\mathcal{X}_{k,0}^{(i)}]^{x_i} \left[ \frac{\theta_i}{x_i \gamma_i} \right]^{x_i} \left[ \exp \frac{E_{ki}^{(s)}}{kT} \left( \frac{\theta_i}{x_i} - 1 \right) \right]^{x_i} \right\} \cdot \left\{ \prod_{1 \leq i < j} \left[ \exp \left( \frac{g_{ij}^{(e)}}{kT} x_i x_j \right) \right] \right\} \quad (27)$$



For the case of binary liquid mobile phases, eqn. 27 can be rewritten to the form:

$$\ln x_k = x_1 \ln x_{k,0}^{(1)} + x_2 \ln x_{k,0}^{(2)} + \frac{E_{k1}^{(s)}}{kT} n_1^{(e)} + \frac{E_{k2}^{(s)}}{kT} n_2^{(e)} + \quad (28)$$

$$+ x_1 \ln \frac{\theta_1}{x_1 \gamma_1} + x_2 \ln \frac{\theta_2}{x_2 \gamma_2} + \frac{g_{12}^{(e)}}{kT} x_1 x_2$$

where  $n_i^{(e)}$  is the surface excess of the component "i" which, for our model of adsorbed phase, takes the form:

$$n_1^{(e)} = -n_2^{(e)} = \frac{x_1 \gamma_1 - x_1 (x_1 \gamma_1 + x_2 \gamma_2 x_2^{(1)})}{x_1 \gamma_1 + x_2 \gamma_2 x_2^{(1)}} \quad (29)$$

and where

$$x_2^{(1)} = \frac{K_2}{K_1} = \left[ x_1^{(2)} \right]^{-1} \quad (30)$$

## RESULTS AND DISCUSSION

Let us assume that:

a) the standard chemical potentials  $\mu_{k,\theta}^{(1)}$  and  $\mu_{k,\theta}^{(2)}$  are equal;

b) the interactions in the adsorbed phase between solute and solvent molecules can be neglected, i.e.,  $E_{k1}^{(s)} = E_{k2}^{(s)} = 0$ .

With these simplifications, eqn. 28 can be rewritten to the form:

$$\ln x_k = \ln x_{k,0}^{(1)} - \ln (x_1 \gamma_1 + x_2 \gamma_2 x_2^{(1)}) + \quad (31)$$

$$+ \frac{g_{12}^{(e)}}{kT} x_1 x_2$$

Let us assume further that the mobile phase is ideal, i.e.,  $\gamma_1 = \gamma_2 = 1$ . Then, from eqn. 31, we obtain:

$$\ln x_k = \text{const} - \ln (1 + x_2 (x_2^{(1)} - 1)) \quad (32)$$



Let us assume at last, that the second component is much more strongly adsorbed than the component "1", i.e., that  $\chi_2^{(1)} \gg 1$ . Eqn. 32 reduces then to Soczewiński-Snyder eqn. 1

$$\ln \chi_k = \ln \frac{\chi_k^{(1)}}{\chi_2^{(1)}} - \ln x_2 \quad (33)$$

In Fig. 1A we have shown the experimental data by Ościk and Chojnacka [4] (benzene-cyclohexane as the mobile phase and Alumina G as adsorbent) plotted according to eqn. 33. One can observe there some serious deviations from a linear behaviour vs.  $\ln x_2$ , what means that eqn. 33 is rather a poor approximation.

In Fig. 1 we have shown the behaviour of the more general equation 31. The constant  $\chi_2^{(1)}$  was assumed to be equal to  $\chi_k^{(1)} / \chi_k^{(2)}$ , and its average value was used in calculation, found by averaging the following values in Table 1.

Table 1

Solute	$\chi_2^{(1)} = \chi_k^{(1)} / \chi_k^{(2)}$
Quinoline	15.17
6-Methylquinoline	14.79
2,6-Dimethylquinoline	12.22
Acridine	13.00
Average	13.80

Looking to the Fig. 1B we can see, that also the more general eqn. 31 does not lead to a satisfactory agreement with the experiment. Thus, we are going now to investigate the applicability of Ościk's eqn. 2.

This equation is obtained from our general eqn. 28, by assuming that the individual adsorption isotherms of solvents  $\theta_i$ 's are linear functions of appropriate bulk activities  $x_i \bar{\chi}_i$ 's. We should mention at this moment, that in his original development Ościk [3] takes also the differences in bulk and surface molar volumes of solvents into account. However, it does not make any serious difference in our particular case of the benzene-cyclohexane mixture. The full Ościk's equation has the form:



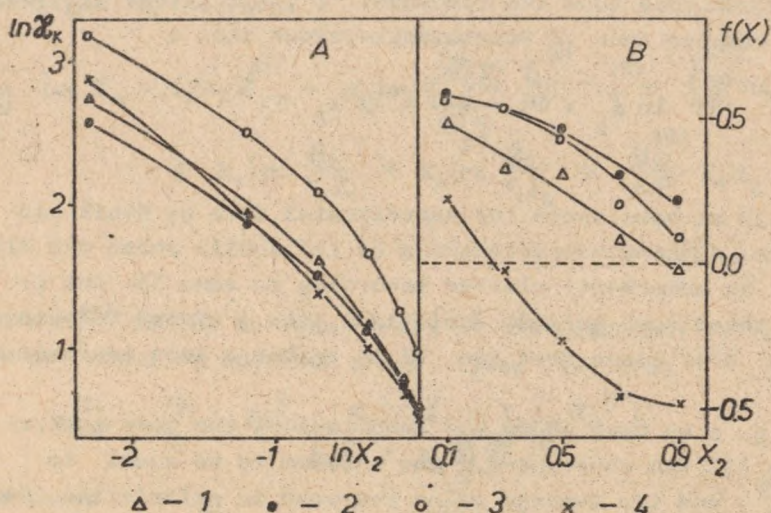


Fig. 1. A - the experimental data by Ościk and Chojnacka [4] plotted according to eqn. 33; B - the function  $f(x) = \ln X_k - \ln X_k^{(1)} - \ln(x_1 T_1 + x_2 T_2 X_2^{(1)}) - a_{12} x_1 x_2$  plotted against  $x_2$ , provided that  $X_2^0 = 13.8$ ; 1 - quinoline, 2 - methylquinoline, 3 - 2,6-dimethylquinoline, 4 - acridine

$$\ln X_k = x_1 \ln X_k^{(1)} + x_2 \ln X_k^{(2)} + \text{const } n_1^{(e)} + \frac{V_z^0}{V_r} \frac{\Delta G_{12}^{(e)}}{kT} \quad (34)$$

where  $V_z^0$  and  $V_r$  are molar volumes of the solute and of the solvent mixture, whereas  $\Delta G_{12}^{(e)}$  is the difference between the excesses of the free energies of mixing solvents in bulk and surface phase, respectively. Since we assume that the surface phase is ideal, this term is very close to our term  $a_{12} x_1 x_2$ .

Let  $F_k(x)$  denote the function,

$$F_k(x) = \ln X_k - x_1 \ln X_k^{(1)} - x_2 \ln X_k^{(2)} - a_{12} x_1 x_2 \quad (35)$$

According to Ościk's eqn. 34,  $F_k$ 's should be proportional to  $n_1^{(e)}$ . In Fig. 2A, we have shown  $F_k$ 's for the investigated chromatography systems, whereas in B - these functions, normalized so that their maxima be still at 0.63.



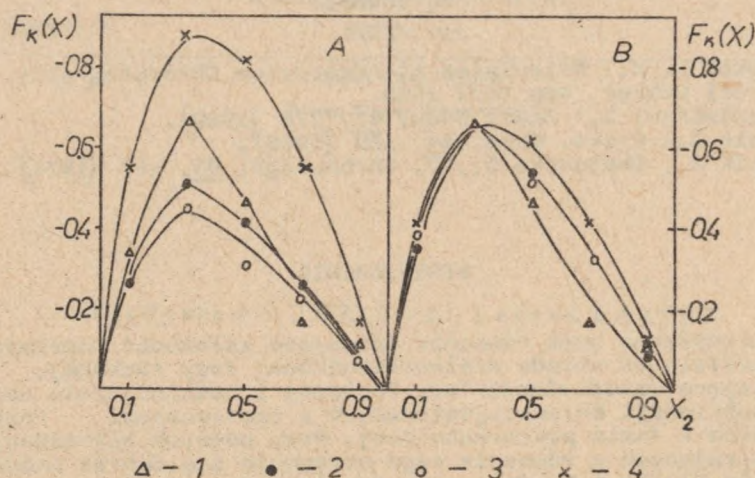


Fig. 2. A - the functions  $F_k$ 's from eqn.35 plotted against  $x_2$ ; B - normalized functions; for explanation see Fig. 1

We can see that the normalized excess isotherms overlap each other pretty well. This is an evidence that the term  $\text{Const. } n_1^{(e)}$  is very important, i.e., that the interactions between solvent and solute molecules on the surface play an important role.

Of course, one should expect that the full equation 28, will be the most adequate description of solid-liquid chromatography systems. In order to demonstrate it we would have to perform calculations of best-fit type, with respect to the two parameters:  $\chi_2^{(i)}$  and  $\text{Const} = (E_{k1}^{(s)} - E_{k2}^{(s)})/kT$ . However, we are not sure if, having six experimental points, makes such a best-fit calculation reliable.

Moreover, we feel that the present approach should be developed further, to take other important physical factors into account. For instance:

- 1) interactions between solvent molecules on the surface;
- 2) differences in the surface areas occupied by solute and solvent molecules;
- 3) surface non-uniformity;
- 4) multilayer adsorption.

We are continuing our investigation along these lines.



## REFERENCES

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## STRESZCZENIE

Wyprowadzono nowe równanie opisujące zależność współczynnika rozdziału od składu wieloskładnikowej fazy ruchomej, uwzględniające nieidealność fazy ruchomej i oddziaływania cząsteczek substancji chromatografowanych z cząsteczkami rozpuszczalników w fazie powierzchniowej. Przy pewnych założeniach upraszczających z równania tego otrzymuje się dobrze znane równania Ościka i Snydera - Soczewińskiego.

## Резюме

Выведено новое уравнение описывающее зависимость коэффициента распределения от состава многокомпонентной подвижной фазы. Это уравнение учитывает неидеальность подвижной фазы и взаимодействие между молекулами разделяемого вещества и растворителей в неподвижной фазе. При некоторых предположениях из этого уравнения можно получить хорошо известные уравнения Осьчика и Снейдера-Сочевинского.