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Effect of the organic modifier concentration on the retention in reversed-phase liquid chromatography

II. Tests using various simplified models

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Abstract

Ten simplified expressions for the retention factor, k' , that arise from either the adsorption or partition mechanism for retention in reversed-phase chromatographic columns are examined in what concerns the model they express and their performance to fit experimental data. In order to test the simplified expressions, which describe the variation of the retention of a solute with the organic modifier content in the mobile phase, a wide range of solutes in mobile phases modified with three different organic modifiers was used. It is shown that a new three-parameter expression of $\ln k'$ works more satisfactorily, since it combines simplicity, high applicability and good numerical behavior. It is also shown that the applicability of a simplified equation does not entail the validity of its model and thus no molecular information can be gained from its use. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the first part of this series of publications two models that describe the dependence of the retention of a solute on the organic modifier content in reversed-phase liquid chromatography (RPLC) were analyzed; the adsorption and the partition models [1]. Based on a semithermodynamic approach, four new expressions describing the variation of the retention factor, k' , with the organic modifier concentration were presented. The study in the first part focused on the elucidation of the retention mechanism in RPLC.

For this reason the approximations involved in the theoretical treatment were kept to a minimum. As a consequence the resulting expressions of $\ln k'$, especially those coming from the adsorption model, were extremely complicated. Such expressions for $\ln k'$ are of no practical interest, since they cannot be used to model chromatographic data.

Modeling of chromatography data is useful in two respects: first, tables with chromatographic data can be replaced by a single equation, and second, this equation can be used for optimizing separations on a certain column. It is more convenient to use equations which are as simple as possible for this purpose.

The equations used for modeling chromatographic data usually come from the theoretical treatment of

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the adsorption or partition model [2–7]. However, in order to obtain simple expressions for $\ln k'$, rather radical approximations should be adopted. For example, such an approximation is to adopt an ideal behavior for the adsorbed layer and/or the mobile phase.

In the present paper we examine the main simplified expressions of $\ln k'$ that arise from the treatment presented in Part I. In addition, we examine other three expressions from the literature. All these expressions for $\ln k'$ are applied to the data sets of Part I in an attempt to find out which of these expressions combines both simplicity and applicability. The possibility to gain some kind of physical information about the mechanism governing the retention is also examined and discussed.

2. Expressions for the retention factor in terms of the modifier volume fraction

In the treatment presented in [1] the mole fraction x of the various constituents in the chromatographic column was used as the independent variable. However, in chromatography, a handy variable is the volume fraction φ instead of the mole fraction x . The change from the mole to volume fractions can be done if the basic expressions of $\ln k'$ and the activity coefficients of the various constituents in the column are expressed in terms of volume fractions.

2.1. Basic expressions of $\ln k'$

For a mobile phase consisting of the solvent S, the organic modifier B and the eluite A, the retention factor k' may be written as:

$$\ln k' = \lim_{n_A^m \rightarrow 0} \ln \frac{n_A^s}{n_A^m} = \lim_{n_A^m \rightarrow 0} \ln \frac{n_A^s}{\varphi_A^m (M^m/r)} \quad (1)$$

Here, n_A^s , n_A^m are the numbers of moles of eluite A present on/in the stationary phase (s) and in the mobile phase (m) within the column, respectively, and φ_A^m is the site fraction of A in the mobile phase. The latter quantity is given by:

$$\varphi_A^m = \frac{rn_A^m}{M^m} = \frac{rn_A^m}{rn_A^m + nn_B^m + n_S^m} \quad (2)$$

where $M^m = rn_A^m + nn_B^m + n_S^m$ and r , n are size factors which may be defined by the following molar volume ratios: $r = V_{m,A}/V_{m,S}$ and $n = V_{m,B}/V_{m,S}$. The final expression of $\ln k'$ depends on the retention model, i.e. whether the retention is due to adsorption or partition.

If the retention mechanism is due to adsorption, Eq. (1) readily results in:

$$\ln k' = \ln k^* + \lim_{\varphi_A^m \rightarrow 0} \ln \frac{\varphi_A^s}{\varphi_A^m} \quad (3)$$

where $k^* = M^s/M^m$ and $M^s = rn_A^s + nn_B^s + n_S^s$. Note that the molar volumes of the various constituents are assumed to be the same in the mobile phase and the adsorbed layer and for this reason r and n are also the same throughout the column. The generalization in different molar volumes in the mobile phase and the adsorbed layer is straightforward.

At this point it is worth noting the following. In the present approach the molar volumes $V_{m,j}$ ($j=A, B, S$) are assumed to be constant and independent of the composition of the mobile phase or the adsorbed layer. However, we do know that in aqueous solutions the molar volumes depend on the composition and this dependence is associated with the volume contraction of the solution. Therefore, the above assumption is in fact an approximation. Within the frames of this approximation the site fraction of a component in the two phases present in the column becomes identical to its volume fraction. Indeed, the site fraction of A yields:

$$\begin{aligned} \varphi_A &= \frac{rn_A}{rn_A + nn_B + n_S} = \frac{V_{m,A}n_A}{V_{m,A}n_A + V_{m,B}n_B + V_{m,S}n_S} \\ &= \frac{V_A}{V} \end{aligned} \quad (4)$$

where V_A is the volume of A in the system, V is the total volume of the system and the ratio V_A/V is the volume fraction of A. Therefore, under the assumption of constant molar volume, the site fraction of a component becomes identical to its volume fraction.

If the retention mechanism is due to partition, the volume fraction of A in the partition layer is given by:

$$\varphi_A^s = V_A^s/V^s = V_{m,A}n_A^s/V^s \Rightarrow n_A^s = \varphi_A^s V^s/V_{m,A} \quad (5)$$

and therefore Eq. (3) is also valid for the partition mechanism but with $k^* = rV^s/(M^mV_{m,A})$.

2.2. Activity coefficients

The ratio φ_A^s/φ_A^m in Eq. (3) can be expressed as a function of the modifier volume fraction in the mobile phase, $\varphi = \varphi_B^m$, by means of the equilibrium equations valid for the partition or adsorption mechanism. However, in both cases the activity coefficients of the various constituents in the two phases present in the column should be known in terms of volume fractions. This can be done by means of the thermodynamic method proposed in [1].

The excess free energy G^e of a ternary mixture as a function of volume fractions may be expressed as:

$$\frac{G^e}{RT} = L \sum_{q=0}^p \{A_q \varphi_A \varphi_B (\varphi_A - \varphi_B)^q + B_q \varphi_A \varphi_S (\varphi_A - \varphi_S)^q + C_q \varphi_B \varphi_S (\varphi_B - \varphi_S)^q\} \quad (6)$$

where $L = rN_A + nN_B + N_S$ and N_j is the number of molecules of species $j=A, B, S$. Now the activity coefficient of component j may be derived from partial differentiation of Eq. (6) with respect to N_j . When $p = 0$, i.e. under mean field approximation [1], we obtain:

$$\ln f_A = rD_1 + rD_2\varphi_B + rD_3\varphi_B^2 \quad (7)$$

$$\ln f_B = nC_0(1 - \varphi_B)^2 \quad (8)$$

$$\ln f_S = C_0\varphi_B^2 \quad (9)$$

where $D_1 = B_0$, $D_2 = A_0 - B_0 - C_0$ and $D_3 = C_0$. It is seen that these expressions for the activity coefficients result from the corresponding Eqs. (30)–(32) of [1] by replacing x_B by φ_B and multiplying the coefficients of $\ln f_A$ by r and the coefficients of $\ln f_B$ by n . This is generally valid, that is all the expressions for the activity coefficients in terms of φ_B may result from the corresponding equations of [1] by replacing x_B with φ_B and multiplying the coefficients of $\ln f_A$ by r and the coefficients of $\ln f_B$ by n . Thus, the activity coefficient of solute A, when the excess free energy of the ternary mixture of A, B, S is

described by Eq. (6) with $p = 1$, arises from Eq. (27) of [1], which is transformed to:

$$\ln f_A = rD_1 + rD_2\varphi_B + rD_3\varphi_B^2 + rD_4\varphi_B^4 \quad (10)$$

2.3. Final expressions of $\ln k'$

Since the final expressions of $\ln k'$ depend upon the retention model, we have the following.

2.3.1. Partition model

The equilibrium process $A^s \Leftrightarrow A^m$ may be described by the following equation:

$$\ln \frac{\varphi_A^s}{\varphi_A^m} + \ln \frac{f_A^s}{f_A^m} = \ln \beta_A^p \quad (11)$$

where $\ln f_A^s = a_0$, Eq. (36) in [1], and $\ln f_A^m$ is given by either Eq. (7) or Eq. (10) depending on whether the mean field approximation is valid or not. Thus from Eqs. (3), (7), (10) and (11) we readily obtain:

$$\ln k' = a + b\varphi + c\varphi^2 \quad (\text{when } p = 0) \quad (12)$$

or

$$\ln k' = a + b\varphi + c\varphi^2 + d\varphi^3 \quad (\text{when } p = 1) \quad (13)$$

where $\varphi = \varphi_B^m$, $a = \ln k^0$, k^0 is the value of k' at $\varphi = 0$, $b = rD_2^m$, $c = rD_3^m$ and $d = rD_4^m$.

Note that the first of these equations has been previously derived by Schoenmakers et al. [3], whereas in what concerns the second equation, to our knowledge, this is the first derivation on the basis of a certain model.

2.3.2. Adsorption model

In Part I, taking into account studies on the adsorption process from aqueous solutions [8–11], we have ignored size effects and, as a first approximation, we have assumed that the adsorption process of the solute A and the modifier B from the solvent S may be expressed as:



In fact, according to [8–11], water molecules form large clusters at adsorbed layers. As a consequence each adsorbate molecule replaces from the adsorbed layer a smaller piece of a cluster of water molecules,

which always has dimensions equal to those of the adsorbate molecule. In this respect, S in Eqs. (14) and (15) denotes a solvent cluster with dimensions equal to those of A in Eq. (14) and equal to those of B in Eq. (15).

Taking into account that $\varphi_A^m \rightarrow 0$ and therefore $\varphi_A^s \rightarrow 0$, Eqs. (14) and (15) result in:

$$\ln \frac{\varphi_A^s}{\varphi_A^m} = \ln(1 - \varphi_B^s) - \ln \frac{f_A^s}{f_S^s} + \ln \frac{f_A^m}{f_S^m} + \ln \frac{\beta_A}{1 - \varphi} \quad (16)$$

$$\ln \frac{\varphi_B^s}{1 - \varphi_B^s} + \ln \frac{f_B^s}{f_S^s} = \ln \beta_B + \ln \frac{f_B^m}{f_S^m} + \ln \frac{\varphi}{1 - \varphi} \quad (17)$$

where again $\varphi = \varphi_B^m$. Note that in the present approach the surface concentrations are expressed in terms of volume fractions and not as surface coverages. Under mean field approximation, the quantities $\ln(f_A/f_S)$ and $\ln(f_B/f_S)$ are given by:

$$\begin{aligned} \ln(f_A/f_S) &= D_1 + D_2 \varphi_B \quad \text{and} \\ \ln(f_B/f_S) &= C_0(1 - 2\varphi_B) \end{aligned} \quad (18)$$

Therefore, in order to find out the dependence of $\ln k'$ upon $\varphi = \varphi_B^m$, the ratio φ_A^s/φ_A^m from Eq. (16) should be put into Eq. (3).

The value of φ_B^s , necessary in these calculations, can be obtained from the adsorption isotherm (17). However, this equation has an explicit solution with respect to φ_B^s only when $C_0^s = 0$, i.e. when the solvent and the organic modifier in the adsorbed layer exhibit an ideal behavior [1]. Under this assumption, Eq. (17) yields:

$$\varphi_B^s = A/(1 + A) \quad (19)$$

where

$$A = \frac{\beta_B^* \varphi}{1 - \varphi} \exp(-2\varphi C_0^m) \quad (20)$$

Here, $\beta_B^* = \beta_B \exp(C_0^m)$. Now Eqs. (3) and (16) give:

$$\begin{aligned} \ln k' &= \ln k^0 - \ln(1 + A) - \frac{A}{1 + A} D_2^s + \varphi D_2^m \\ &\quad - \ln(1 - \varphi) \end{aligned} \quad (21)$$

Eq. (21) has five adjustable parameters: $\ln k^0$, C_0^m , D_2^s , D_2^m and β_B^* . This number of parameters is high

enough for chromatographic studies and it can be reduced further in the following limiting cases:

If $C_0^m = 0$, then $A = \beta_B \varphi/(1 - \varphi)$ and Eq. (21) may be transformed to:

$$\ln k' = a - \ln(1 + b\varphi) - \frac{\varphi c}{1 + b\varphi} + \varphi d \quad (22)$$

where $a = \ln k^0$, $b = \beta_B - 1$, $c = \beta_B D_2^s$ and $d = D_2^m$. Eq. (22) is further reduced to:

$$\ln k' = a - \ln(1 + b\varphi) - \frac{\varphi c}{1 + b\varphi} \quad (\text{when } D_2^m = 0) \quad (23)$$

$$\ln k' = a - \ln(1 + b\varphi) + \varphi d \quad (\text{when } D_2^s = 0) \quad (24)$$

and

$$\ln k' = a - \ln(1 + b\varphi) \quad (\text{when } D_2^s = 0 \text{ and } D_2^m = 0) \quad (25)$$

Apart from the above equations, in Appendix A we develop another logarithmic expression of $\ln k'$, which may be written as:

$$\ln k' = a - \ln(1 + b\varphi) - \ln(1 + K\varphi) \quad (26)$$

To our knowledge all equations developed above, i.e. Eqs. (21)–(26), are new, except for Eq. (25), which has been previously given by Antia and Horvath [7] by assuming an ideal behavior of the mobile phase and the adsorbed layer. It is evident that the same assumptions have been adopted for the derivation of this equation in the present paper.

Eq. (24) may be considered as a limiting case of the following equation:

$$\ln k' = a + e \ln(1 + b\varphi) + \varphi d \quad (27)$$

derived from Peichang and Xiaoming [4]. The derivation of Eq. (27) was based on a rather rigorous statistical thermodynamic treatment but the final Eq. (27) with $e \neq -1$ is erroneous. Using our notation, parameter e is given by:

$$e = \sum \partial N_{B_1}^s / \partial N_A^s = \sum \partial N_{B_1}^m / \partial N_A^m \quad (28)$$

However, Eq. (A6) of [4] is derived under the assumption that $N_A^s + \sum N_{B_1}^s + N_S^s = \text{constant}$, which by differentiation with respect to N_A^s yields:

$$1 + \sum \partial N_{B_i}^s / \partial N_A^s = 0 \Rightarrow e = -1 \quad (29)$$

It is seen that Eq. (27) is an arbitrary extension of Eq. (24) made by Peichang and Xiaoming to increase the applicability of Eq. (24). The question is whether extensions that lack self-consistency are acceptable.

2.3.3. Empirical expressions

Apart from the above equations, in the present paper we used two additional equations from literature, which cannot be derived from the models presented in Part I. The first is an extension of Eq. (12) with the inclusion of a square root term:

$$\ln k' = a + b\varphi + c\varphi^2 + d\sqrt{\varphi} \quad (30)$$

and the second one is the reciprocal expression of k' :

$$1/k' = a + b\varphi + c\varphi^2 \quad (31)$$

Eq. (30) has been proposed by Schoenmakers et al. [3] to improve the performance of the quadratic Eq. (12). The square root term comes empirically from the polarity of the stationary phase. As concerns the reciprocal expression of k' , Eq. (31), it has been proposed by McCann et al. [12] totally empirically. In Appendix A we present a derivation of this equation based on a physical model within the frames of the adsorption mechanism. In particular, it is shown that if we consider only A–B interactions in the mobile phase and treat these interactions as a pseudo-reaction between A and B molecules, the adsorption model results in Eq. (26), which readily yields the reciprocal Eq. (31).

3. Approximations underlying the simplified equations for the retention factor

The derivation of the above simplified equations for k' clarifies the approximations adopted. Here, we sum up these approximations and comment on them. First we observe that the adsorption model leads to logarithmic equations for $\ln k'$, whereas the partition model results in polynomial equations for $\ln k'$. From these two categories of expressions of $\ln k'$ the most approximate are the logarithmic ones.

Before we comment on the specific approxima-

tions of each $\ln k'$ expression, we should point out that all expressions of $\ln k'$ in terms of φ are based on the assumption that the molar volumes of the eluted solute, the modifier and the solvent are constant and independent of the composition of the mobile phase or the adsorbed layer. This assumption means that the contraction of volume observed during the mixing of water with any organic modifier is ignored. This is the first significant approximation involved in all equations discussed in the present paper. In what concerns the specific approximations underlying each particular equation of $\ln k'$, we have the following.

3.1. Logarithmic expressions of $\ln k'$

Eqs. (22)–(26) are derived by assuming that $C_0^s = C_0^m = 0$. This means that we assume an ideal behavior for the mixture of the modifier and the solvent (usually water) both in the mobile phase and in the adsorbed layer. This is a radical approximation, because our treatment in Part I has shown that at least for the modifiers we used, i.e. methanol, acetonitrile and isopropanol, the above assumption is not true either for the mobile phase or the adsorbed layer. Thus, the aqueous mobile phases modified with methanol, acetonitrile and isopropanol exhibit significant positive deviations from Raoult's law, i.e. they show strong deviations from the ideal behavior. In addition, we have found that the adsorbed layer in the presence of acetonitrile and isopropanol may be described by the regular solution theory but with high values of C_0^s , which also show that the behavior of these adsorbed layers is far from being ideal. Only the adsorbed layer in the presence of methanol exhibits a behavior that may be approximately ideal ($C_0^s = 0.25$).

The differentiations among the various logarithmic expressions of $\ln k'$ concern the interactions of the eluted solute in the mobile phase and/or in the adsorbed layer. Thus, we have:

- Eq. (22) takes into account contributions only from the interactions of the solute with the solvent and the organic modifier both in the adsorbed layer and in the mobile phase via the parameters $c = \beta_B D_2^S$ and $d = D_2^m$.
- Eq. (23) takes into account the interactions of the

solute with the modifier and the solvent only in the adsorbed layer via the parameter $c = \beta_B D_2^S$.

- Eq. (24) considers only the interactions of the solute with the modifier and solvent in the mobile phase via the parameter $d = D_2^m$.
- In Eq. (25) both the adsorbed and the mobile phase behave as ideal solutions.
- Eq. (26) is based on the same approximations with those of Eq. (23). The differentiation comes from the different treatment of the solute–modifier interactions.
- Eq. (27) is an erroneous extension of Eq. (24), since, as shown above, the treatment that leads to Eq. (27) necessarily entails that $e = -1$.
- The reciprocal Eq. (31) arises directly from Eq. (26) and therefore it is subject to the same approximations with those of Eq. (26).

In all the above equations, except Eq. (31), b is closely related to β_B . Therefore, for the same column and mobile phase, b should be independent of the solute, provided that the logarithmic expression of $\ln k'$ adopted to fit the experimental data describes, even approximately, the retention behavior of the solute. However, as we have already pointed out above, the radical approximation $C_0^S = C_0^m = 0$ involved in all logarithmic expressions of $\ln k'$ makes impossible any connection between the applicability of these equations and the validity of the model they express. In other words, even if, say Eq. (25), describes an experimental system, this does not mean that for this system both the adsorbed and the mobile phase behave as ideal solutions.

3.2. Polynomial expressions of $\ln k'$

Unlike the logarithmic expressions of $\ln k'$, the polynomial ones are not subject to radical approximations. Thus, apart from the general approximation of the constant molar volumes, Eq. (12) takes into account the validity of the mean field approximation for the mobile phase, whereas Eq. (13) holds when the mobile phase cannot be described by the mean field approximation.

4. Results and discussion

The equations developed or discussed above were

tested using all the experimental data sets of [1]. Thus, we used data taken from literature [13–15] and data obtained experimentally in our laboratory [1]. The whole analysis was carried out using Microsoft EXCEL spreadsheets and SOLVER was used to fit the experimental data to the theoretical equations of $\ln k'$ or $1/k'$.

Indicative results obtained from the regression analysis of the experimental data are shown in Tables 1–5. These tables contain the values of the adjustable parameters and the standard error of the estimate σ^2 :

$$\sigma^2 = \frac{(\ln k'_{\text{calc}} - \ln k'_{\text{exp}})^2}{N - n} \quad (32)$$

where $\ln k'_{\text{calc}}$ is the calculated value of $\ln k'$ by means of a theoretical equation, $\ln k'_{\text{exp}}$ is the corresponding experimental value, N is the number of data points and n is the number of the adjustable parameters. It is evident that for the test of Eq. (31) $\ln k'$ has been replaced by $1/k'$ in Eq. (32).

Comparing plots of calculated and experimental values of $\ln k'$ vs. φ with the values of σ^2 , we readily conclude that values of $\sigma^2 < 0.02$ correspond to good fits, whereas values of $\sigma^2 > 0.05$ indicate the failure of the theoretical expression of $\ln k'$ to describe the experimental data.

From the values of σ^2 , some of which are listed in Tables 1–5, we conclude that Eqs. (25) and (26) are the least satisfactory. They fit only the retention data of the catechol-related compounds, except the retention of 5-hydroxytryptophol. The most unexpected result is that the reciprocal Eq. (31) seems to fit all experimental data perfectly. However, if we use the fitted values of k' to calculate $\ln k'$ values and then recalculate σ^2 using $\ln k'$ instead of $1/k'$, we realize that the applicability of Eq. (31) is deceptive, since the low values of σ^2 , which correspond to Eq. (31), come from the fact that the values of $1/k'$ are low enough, yielding low values of σ^2 .

In contrast, there are five other equations that work satisfactorily, since they describe well all the experimental data. These are Eqs. (13), (22), (23), (27) and (30). If we use the values of σ^2 as the only criterion for the fitting performance of an equation, we can hardly distinguish which of them is the most appropriate for modeling the retention data. How-

Table 1

Fitted parameters of the equations used for modelling the retention data of two benzene and eight phenol derivatives in aqueous mobile phases modified with methanol. Experimental data from [13]

	Solutes ^a									
	1	2	3	4	5	6	7	8	9	10
Eq. (22)										
<i>a</i>	5.156	5.173	5.013	5.303	5.749	4.818	4.706	5.145	5.238	3.714
<i>b</i>	0.010	0.058	0.077	0.090	0.062	0.086	0.091	-0.054	0.097	0.074
<i>c</i>	26.798	26.980	25.018	19.975	20.844	27.027	29.254	1.550	12.079	25.032
<i>d</i>	18.643	19.677	17.745	12.744	13.249	19.553	21.642	-3.756	5.525	19.103
σ^2	0.007	0.018	0.006	0.004	0.022	0.007	0.006	0.015	0.002	0.006
Eq. (23)										
<i>a</i>	5.178	5.165	5.013	5.310	5.740	4.820	4.711	5.145	5.242	3.711
<i>b</i>	0.475	0.252	0.341	0.315	0.185	0.429	0.518	-0.016	0.201	0.436
<i>c</i>	8.143	7.120	7.120	7.141	7.457	7.331	7.480	5.269	6.496	5.697
σ^2	0.007	0.017	0.006	0.004	0.019	0.007	0.008	0.013	0.002	0.007
Eq. (24)										
<i>a</i>	5.400	4.996	4.801	5.388	5.715	4.565	4.417	5.155	5.288	3.707
<i>b</i>	9.309	-0.001	-0.001	4.926	2.557	-0.001	-0.001	-0.001	3.206	3.933
<i>d</i>	-3.917	-6.016	-5.719	-4.088	-5.251	-5.612	-5.474	-5.331	-4.251	-2.826
σ^2	0.012	0.032	0.029	0.007	0.022	0.039	0.048	0.013	0.003	0.011
Eq. (25)										
<i>a</i>	13.276	5.299	5.188	13.594	13.834	5.008	4.892	5.500	13.545	3.908
<i>b</i>	227 994.2	65.266	61.581	218 566.5	243 429.3	62.143	60.007	47.746	191 664.7	31.345
σ^2	0.950	0.993	0.794	0.875	1.381	0.717	0.643	0.698	0.836	0.333
Eq. (26)										
<i>a</i>	13.627	5.555	5.393	9.720	20.391	5.186	5.051	5.628	9.021	3.970
<i>b</i>	880.715	11.856	11.063	101.521	20 325.2	10.920	10.550	8.986	67.714	6.574
<i>K</i>	880.715	11.856	11.063	101.521	20 325.3	10.920	10.550	8.986	67.714	6.574
σ^2	0.203	0.427	0.303	0.210	0.435	0.255	0.213	0.316	0.213	0.097
Eq. (27)										
<i>a</i>	5.150	5.173	5.013	5.296	5.748	4.818	4.705	5.155	5.235	3.713
<i>b</i>	0.108	0.074	0.097	0.093	0.079	0.124	0.116	-0.001	0.074	0.096
<i>d</i>	39.298	34.949	31.931	29.667	24.354	29.712	37.363	-5.597	22.815	32.014
<i>e</i>	-440.77	-574.65	-404.73	-398.24	-403.73	-300.34	-387.49	-375.18	-396.08	-394.49
σ^2	0.007	0.018	0.006	0.004	0.022	0.007	0.006	0.015	0.002	0.006
Eq. (12)										
<i>a</i>	5.147	5.175	5.013	5.298	5.752	4.817	4.704	5.145	5.235	3.713
<i>b</i>	-8.144	-7.357	-7.313	-7.257	-7.654	-7.504	-7.629	-5.253	-6.602	-5.965
<i>c</i>	2.348	1.491	1.772	1.609	1.218	2.104	2.396	-0.085	1.035	1.710
σ^2	0.005	0.015	0.005	0.003	0.018	0.005	0.005	0.013	0.002	0.005
Eq. (13)										
<i>a</i>	4.859	5.035	4.937	5.064	5.183	4.749	4.642	5.159	5.121	3.639
<i>b</i>	-5.390	-4.792	-5.922	-5.013	-2.205	-6.251	-6.494	-5.514	-5.510	-4.605
<i>c</i>	-4.188	-6.019	-2.301	-3.717	-11.714	-1.565	-0.929	0.679	-1.558	-2.271
<i>d</i>	4.357	5.564	3.017	3.550	8.621	2.717	2.463	0.566	1.728	2.949
σ^2	0.0017	0.0015	0.0011	0.0005	0.0005	0.0024	0.0027	0.0145	0.0015	0.0012
Eq. (30)										
<i>a</i>	3.820	5.039	4.948	4.023	2.871	4.778	4.665	5.259	4.620	3.639
<i>b</i>	-15.944	-10.38	-8.763	-14.748	-24.597	-8.369	-8.494	-2.725	-10.214	-7.609
<i>c</i>	5.310	3.100	2.544	4.453	7.651	2.564	2.856	-1.430	2.406	2.585
<i>d</i>	6.323	1.702	0.816	6.072	13.734	0.486	0.487	-1.422	2.928	0.926
σ^2	0.0019	0.0091	0.0038	0.0002	0.0017	0.0055	0.0051	0.0088	0.0014	0.0032
Eq. (31)										
<i>a</i>	0.138	0.052	0.050	0.123	0.156	0.047	0.043	0.050	0.135	0.042
<i>b</i>	-1.202	-0.808	-0.721	-0.996	-1.329	-0.692	-0.606	-0.620	-1.063	-0.310
<i>c</i>	2.673	2.172	2.005	2.015	2.507	2.131	2.055	1.404	2.013	1.819
$\sigma^2(1/k')$	0.0011	0.0014	0.0011	0.0009	0.0014	0.0011	0.0006	0.0017	0.0016	0.0002
$\sigma^2(\ln k')$	1.1547	1.1217	0.9786	0.8973	0.9580	0.7687	1.2103	2.0482	1.1832	0.0700

^a Solutes: 1 = 2,4-dinitrophenol, 2 = 2-chlorophenol, 3 = 2-methylphenol, 4 = 2-nitrophenol, 5 = 3-chlorophenol, 6 = 3-nitrophenol, 7 = 4-nitrophenol, 8 = benzene, 9 = nitrobenzene, 10 = phenol.

Table 2

Fitted parameters of the equations used for modelling the retention data of two benzene and six phenol derivatives in aqueous mobile phases modified with acetonitrile. Experimental data from [13]

	Solutes ^a							
	1	2	3	4	5	6	7	8
Eq. (22)								
<i>a</i>	5.172	5.126	4.998	4.837	4.726	5.284	5.288	3.684
<i>b</i>	0.270	0.271	0.853	0.523	0.566	0.128	0.196	0.874
<i>c</i>	28.739	30.297	15.469	20.195	19.333	27.760	26.151	11.924
<i>d</i>	17.312	18.795	3.675	8.493	7.656	19.550	16.590	2.945
σ^2	0.0003	0.0019	0.0010	0.0006	0.0009	0.0039	0.0016	0.0003
Eq. (23)								
<i>a</i>	5.540	5.187	5.035	4.892	4.779	5.300	5.447	3.715
<i>b</i>	1.919	1.698	1.812	1.871	1.907	0.675	1.136	1.997
<i>c</i>	14.831	12.672	12.516	12.808	12.752	8.203	10.650	9.334
σ^2	0.005	0.013	0.003	0.008	0.008	0.005	0.004	0.002
Eq. (24)								
<i>a</i>	11.750	5.174	5.052	4.8944	4.781	5.323	8.032	3.735
<i>b</i>	17 931.0	21.074	22.288	22.8215	22.821	8.075	275.491	15.616
<i>d</i>	-2.867	-2.887	-2.637	-2.6377	-2.571	-3.402	-2.880	-1.589
σ^2	0.030	0.058	0.033	0.045	0.045	0.013	0.013	0.015
Eq. (25)								
<i>a</i>	12.991	3.836	5.118	4.953	4.841	5.472	13.307	3.836
<i>b</i>	25 995	42.996	98.700	100.05	96.801	67.796	229 826.5	42.996
σ^2	0.731	1.170	0.472	0.487	0.462	0.630	0.700	0.155
Eq. (26)								
<i>a</i>	15.787	5.377	5.220	5.065	4.944	5.626	16.712	3.777
<i>b</i>	3196.73	14.587	13.631	13.819	13.475	11.308	229 061.3	7.335
<i>K</i>	3196.73	14.587	13.631	13.819	13.475	11.308	69.696	7.335
σ^2	0.045	0.117	0.071	0.077	0.070	0.189	0.077	0.008
Eq. (27)								
<i>a</i>	5.134	5.123	4.999	4.836	4.725	5.281	5.272	3.684
<i>b</i>	0.251	0.373	1.463	0.842	0.917	0.138	0.212	1.499
<i>d</i>	42.704	31.128	6.627	13.436	12.252	39.212	35.369	5.161
<i>e</i>	-214.85	-114.77	-13.213	-30.490	-26.701	-343.70	-212.38	-10.045
σ^2	0.0003	0.0019	0.0010	0.0006	0.0009	0.0038	0.0015	0.0003
Eq. (12)								
<i>a</i>	5.079	5.089	4.900	4.769	4.653	5.277	5.241	3.606
<i>b</i>	-10.768	-11.050	-10.550	-10.843	-10.756	-8.185	-9.286	-8.173
<i>c</i>	5.392	5.919	5.595	5.906	5.885	2.931	3.928	4.396
σ^2	0.0006	0.0024	0.0064	0.0033	0.0040	0.0030	0.0011	0.0037
Eq. (13)								
<i>a</i>	5.165	5.124	4.990	4.834	4.723	5.249	5.213	3.676
<i>b</i>	-11.594	-11.69	-12.187	-12.038	-12.047	-7.671	-9.017	-9.445
<i>c</i>	7.352	7.799	10.398	9.406	9.666	1.428	3.291	8.121
<i>d</i>	-1.307	-1.393	-3.558	-2.592	-2.801	1.114	0.425	-2.759
σ^2	0.0002	0.0018	0.0010	0.0004	0.0007	0.0029	0.0012	0.0004
Eq. (30)								
<i>a</i>	5.448	5.097	4.998	4.831	4.719	5.270	5.064	3.687
<i>b</i>	-8.597	-10.88	-8.371	-9.472	-9.299	-8.339	-10.327	-6.381
<i>c</i>	4.567	5.831	4.438	5.178	5.109	3.014	4.324	3.443
<i>d</i>	-1.760	-0.093	-1.224	-0.771	-0.820	0.0087	0.844	-1.008
σ^2	0.0004	0.0028	0.0032	0.0022	0.0028	0.0035	0.0012	0.0014
Eq. (31)								
<i>a</i>	0.009	-0.007	0.004	-0.009	-0.010	0.025	0.053	0.0002
<i>b</i>	-0.231	0.025	-0.053	0.102	0.134	-0.355	-0.493	0.508
<i>c</i>	1.907	1.411	1.502	1.579	1.646	1.255	1.643	1.0704
$\sigma^2(1/k')$	0.0009	0.0009	0.0004	0.0013	0.0013	0.0005	0.0007	0.001
$\sigma^2(\ln k')$	0.3594	0.0713	0.0565	0.0334	0.0253	1.2642	0.0631	3.262

^a Solutes: 1=2,4-dinitrophenol, 2=2-chlorophenol, 3=2-methylphenol, 4=3-nitrophenol, 5=4-nitrophenol, 6=benzene, 7= nitrobenzene, 8=phenol.

Table 3

Fitted parameters of the equations used for modelling the retention data of clarithromycin and roxythromycin in aqueous mobile phases modified with methanol and acetonitrile. Experimental data from [1]

	Solutes ^a			
	1	2	3	4
Eq. (22)				
<i>a</i>	10.310	12.065	28.855	29.001
<i>b</i>	0.053	0.121	9.262	7.888
<i>c</i>	12.897	15.446	315.493	282.948
<i>d</i>	0.992	0.759	5.551	6.405
σ^2	0.0001	0.0002	0.0013	0.0016
Eq. (23)				
<i>a</i>	10.287	12.068	30.478	33.783
<i>b</i>	0.054	0.129	17.730	17.304
<i>c</i>	11.836	14.694	517.946	568.953
σ^2	$9.3 \cdot 10^{-5}$	0.0002	0.0111	0.0123
Eq. (24)				
<i>a</i>	10.623	12.393	6.439	7.055
<i>b</i>	4.238	8.834	0.001	0.001
<i>d</i>	-9.972	-11.238	-8.797	-9.795
σ^2	$9.6 \cdot 10^{-5}$	0.0002	0.0825	0.0999
Eq. (25)				
<i>a</i>	11.816	12.208	12.366	12.877
<i>b</i>	20 145.53	22 300.52	44 799.54	63 215.28
σ^2	0.705	0.930	0.646	0.854
Eq. (26)				
<i>a</i>	19.249	20.165	20.397	21.254
<i>b</i>	8899.18	12 138.00	19 342.13	23 544.30
<i>K</i>	4025.28	5514.99	8455.60	13 859.33
σ^2	0.664	0.891	0.333	0.479
Eq. (27)				
<i>a</i>	10.254	11.930	21.778	21.834
<i>b</i>	-0.374	-0.534	17.890	12.687
<i>d</i>	-13.584	-16.738	15.614	18.325
<i>e</i>	-5.008	-4.987	-12.061	-14.553
σ^2	0.0001	0.0002	0.0020	0.0027
Eq. (12)				
<i>a</i>	10.289	12.114	11.149	12.211
<i>b</i>	-11.882	-14.855	-30.818	-33.899
<i>c</i>	0.598	1.700	24.467	26.781
σ^2	$9.3 \cdot 10^{-5}$	0.0002	0.0041	0.0058
Eq. (13)				
<i>a</i>	2.604	3.073	16.144	18.780
<i>b</i>	21.546	24.474	-66.214	-80.443
<i>c</i>	-47.496	-54.891	105.448	133.267
<i>d</i>	22.889	26.938	-59.980	-78.869
σ^2	$4 \cdot 10^{-5}$	$6.4 \cdot 10^{-5}$	0.0014	0.0007
Eq. (30)				
<i>a</i>	13.537	16.423	48.703	51.475
<i>b</i>	-2.295	-2.299	144.320	148.959
<i>c</i>	-1.741	-1.325	-41.541	-42.042
<i>d</i>	-10.532	-13.883	-153.533	-160.413
σ^2	0.0001	0.0002	0.0012	0.0004
Eq. (31)				
<i>a</i>	2.640	2.599	-0.042	0.027
<i>b</i>	-8.665	-8.466	-0.109	-0.460
<i>c</i>	7.200	6.946	0.9719	1.340
$\sigma^2(1/k')$	$9.4 \cdot 10^{-5}$	0.0001	$3.5 \cdot 10^{-5}$	$6.3 \cdot 10^{-6}$
$\sigma^2(\ln k')$	0.029	0.066	0.010	0.005

^a Solutes: 1=clarithromycin in methanol–water, 2=roxythromycin in methanol–water, 3=clarithromycin in acetonitrile–water, 4=roxythromycin in acetonitrile–water.

Table 4

Fitted parameters of the equations used for modelling the retention data of the catechol-related compounds in aqueous mobile phases modified with isopropanol. Experimental data from [1]

	Solutes ^a								
	1	2	3	4	5	6	7	8	9
Eq. (22)									
<i>a</i>	2.233	2.892	4.357	2.391	2.331	2.635	3.280	2.922	3.300
<i>b</i>	29.912	30.726	37.436	30.197	35.383	39.921	34.824	49.264	60.369
<i>c</i>	72.234	101.192	87.758	86.481	79.709	80.597	120.152	130.528	63.320
<i>d</i>	2.865	4.473	-1.431	4.664	1.583	1.428	3.729	3.038	-1.099
σ^2	0.0017	0.0010	0.0016	0.0015	0.0016	0.0028	0.0013	0.0062	0.0009
Eq. (23)									
<i>a</i>	2.269	2.944	4.337	2.438	2.353	2.657	3.328	2.958	3.280
<i>b</i>	58.076	64.127	29.789	81.476	49.499	56.856	59.844	86.803	42.144
<i>c</i>	65.058	102.449	86.827	73.039	77.894	77.890	127.101	132.433	68.757
σ^2	0.0046	0.0096	0.002	0.012	0.0024	0.0033	0.0074	0.0123	0.0014
Eq. (24)									
<i>a</i>	2.311	3.007	4.439	2.485	2.407	2.705	3.406	3.013	3.328
<i>b</i>	160.118	254.188	204.085	201.697	180.510	183.536	325.263	336.094	150.783
<i>d</i>	-0.508	-1.080	-4.637	0.197	-1.430	-1.054	-2.245	-0.858	-1.849
σ^2	0.008	0.0005	0.0011	0.017	0.009	0.0082	0.035	0.029	0.0016
Eq. (25)									
<i>a</i>	2.331	3.041	4.574	2.477	2.458	2.744	3.464	3.037	3.398
<i>b</i>	172.149	290.612	357.366	196.340	219.002	212.007	418.911	371.409	195.777
σ^2	0.007	0.032	0.126	0.017	0.019	0.014	0.0648	0.0333	0.0174
Eq. (26)									
<i>a</i>	2.272	2.926	4.388	2.416	2.361	2.667	3.316	2.929	3.314
<i>b</i>	204.918	579.986	2690.535	243.677	320.544	282.776	4923.649	1027.983	260.182
<i>K</i>	-0.188	-0.526	-0.879	-0.220	-0.352	-0.281	-0.920	-0.653	-0.283
σ^2	0.008	0.015	0.070	0.012	0.0095	0.007	0.0252	0.0137	0.0101
Eq. (27)									
<i>a</i>	2.243	2.906	4.369	2.402	2.342	2.644	3.298	2.938	3.305
<i>b</i>	65.413	72.118	84.640	68.563	78.349	85.583	85.060	122.556	111.496
<i>d</i>	5.512	8.449	1.215	7.975	4.067	3.798	8.025	6.149	-0.188
<i>e</i>	-1.719	-2.047	-1.642	-1.888	-1.622	-1.541	-2.060	-1.672	-1.182
σ^2	0.0015	0.0005	0.0011	0.0014	0.0012	0.0018	0.0005	0.0062	0.0007
Eq. (12)									
<i>a</i>	1.893	2.444	3.933	1.995	1.942	2.236	2.749	2.302	2.898
<i>b</i>	-40.162	-48.283	-47.351	-43.067	-42.402	-42.315	-53.146	-49.919	-38.930
<i>c</i>	127.439	160.363	139.830	142.932	132.512	133.780	176.515	166.317	114.780
σ^2	0.069	0.136	0.120	0.114	0.104	0.0986	0.185	0.251	0.097
Eq. (13)									
<i>a</i>	2.107	2.717	4.189	2.250	2.181	2.448	3.060	2.679	3.125
<i>b</i>	-62.924	-77.245	-74.508	-70.114	-67.634	-64.816	-86.090	-89.920	-63.034
<i>c</i>	448.573	568.953	522.960	524.496	488.479	451.215	641.290	730.645	454.839
<i>d</i>	-1087.637	-1383.835	-1297.608	-1292.304	-1205.611	-1075.107	-1574.128	-1911.299	-1151.733
σ^2	0.012	0.020	0.016	0.012	0.014	0.0245	0.0302	0.0264	0.0149
Eq. (30)									
<i>a</i>	2.339	3.021	4.471	2.509	2.440	2.731	3.420	3.066	3.386
<i>b</i>	-5.348	-3.342	-5.376	-3.016	-3.599	-3.768	-0.858	9.635	-0.894
<i>c</i>	43.062	51.443	38.098	45.861	38.465	40.354	49.789	21.982	22.594
<i>d</i>	-9.290	-11.993	-11.201	-10.688	-10.355	-10.287	-13.954	-15.893	-10.150
σ^2	0.008	0.0135	0.0111	0.015	0.011	0.0066	0.0154	0.0309	0.0078
Eq. (31)									
<i>a</i>	0.036	-0.044	0.005	0.011	0.030	-0.0002	-0.069	0.012	0.035
<i>b</i>	21.088	20.443	2.949	23.054	21.439	17.392	19.551	21.317	5.602
<i>c</i>	-21.983	-31.445	13.930	-40.181	-3.966	-15.036	-22.711	-14.860	10.921
$\sigma^2(1/k')$	0.0042	0.0074	0.00016	0.0064	0.0031	0.0123	0.0093	0.0263	0.0003
$\sigma^2(\ln k')$	0.251	0.181	0.017	0.029	0.240	0.0612	0.744	0.406	0.0016

^a Solutes: 1=5-hydroxyindole-3-acetic acid, 2=5-hydroxytryptamine, 3=5-hydroxytryptophol, 4=5-hydroxytryptophan, 5=homovanillic acid, 6=4-hydroxy-3-methoxyphenylglycol, 7=N ω -methylserotonin, 8=3-methoxytyramine, 9=L-tryptophan.

Table 5
Fitted parameters of Eq. (23) used for modelling the retention of the catechol-related compounds with $b = 59$

	Solutes ^a								
	1	2	3	4	5	6	7	8	9
Eq. (23)									
a	2.271	2.926	4.527	2.390	2.386	2.664	3.324	2.861	3.340
c	65.13	99.33	122.79	71.93	81.85	78.56	126.19	112.63	78.82
σ^2	0.0039	0.0084	0.0208	0.0115	0.0026	0.0028	0.0064	0.0149	0.0028

^a Solutes as in Table 4.

ever, we can distinguish the least satisfactory, which is Eq. (13). We observe from Table 4 that this equation does not describe absolutely satisfactorily the retention of the catechol-related solutes. In general, all non-logarithmic expressions of $\ln k'$ exhibit small or great problems in the description of the retention of the catechol-related compounds. This is clearly supported by the shape of the plots of $\ln k'$ vs. φ in Fig. 1.

From the rest of the equations with the good fitting performance, i.e. Eqs. (22), (23), (27) and (30), Eq. (27) exhibits the worst numerical behavior. Depending on the initial estimates of the adjustable parameters, the Solver is usually trapped in local minima other than the global one or even worse it may not converge to a solution. Note also that parameter e usually departs strongly from the value of -1 . The numerical behavior normally depends on the number of the adjustable parameters: the fewer these parameters are, the easier it is for the Solver to find the solution. The same is valid for the simplicity of the fitted equation. Taking into account all these criteria, we readily conclude that Eq. (23) is the best of the equations studied.

As shown above, the model which Eq. (23) is based on is the adsorption model that assumes an ideal behavior for the mixture of the modifier and solvent both in the mobile phase and in the adsorbed layer and additionally it takes into account the interactions of the solute with the modifier and solvent only in the adsorbed layer via parameter c . It is evident that the applicability of this equation is not related to the validity of its model, since the mixtures of the modifier and solvent of all systems studied exhibit significant deviations from the ideal behavior [1]. Therefore, from the application of Eq. (23) to a

certain data set no molecular information can be gained.

However, it is interesting to point out the following. As we have already shown above, parameter b would be independent of solute if Eq. (23) represented the physical reality in an RPLC column, since it is related to the free energy of adsorption of the modifier on the stationary phase. Despite the fact that the model of Eq. (23) definitely does not describe the molecular behavior of the mobile phase or the adsorbed layer, we found that b may be handled as a parameter characteristic of the adsorption of modifier on the stationary phase. Indeed, if we calculate the mean value of b for each of the data set studied in the present paper and then, using this value of b , recalculate parameters a and c , we observe that the two-parameter Eq. (23) describes satisfactorily all data sets. Table 5 shows the results of fitting the two-parameter Eq. (23) to the retention of the catechol-related compounds, where σ^2 has relatively higher values. If we compare the results of this table with the corresponding ones of Table 4, we note that the two-parameter Eq. (23) gives comparable and, in some cases, better results than those of its three-parameter version. Therefore, Eq. (23) can be used as two-parameter equation with high applicability if we have determined the value of b from experiments with other solutes chromatographed under the same conditions concerning column and mobile phase.

Up to now the equation with the widest use in studies about the modifier effect on the retention of solutes was Eq. (12). This is really a very simple equation that fits retention data very well for most data sets studied in the present paper. In our study it failed completely to describe the data set of the catechol-related compounds. Therefore, we should be

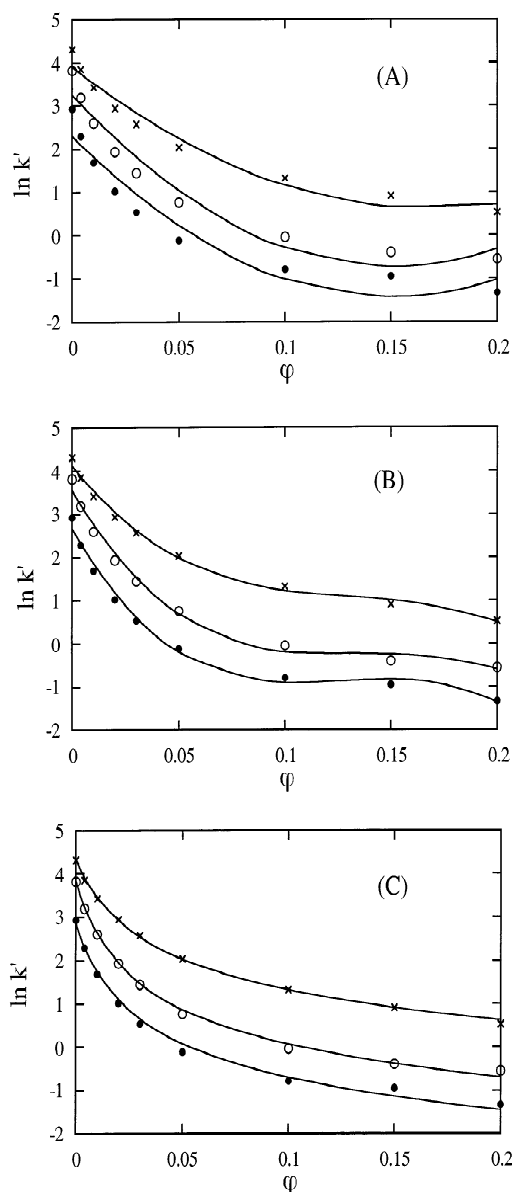


Fig. 1. Retention plots of 3-methoxytyramine (●), N ω -methylserotonin (○) and L-tryptophan (×) in isopropanol–water mobile phase. Curves have been calculated from (A) Eq. (12), (B) Eq. (13) and (C) Eq. (23) using the relevant parameters of Tables 4 and 5. Data of N ω -methylserotonin and L-tryptophan have been shifted along the y axis by +0.5 and +1, respectively.

careful when we adopt this equation, especially in studies on the combined effect of modifier concentration and pH on the retention of a solute.

Preliminary tests of the validity of this equation at certain pH values should be necessary before its adaptation.

To sum up, the tests of ten simplified equation for the retention of solutes in reversed-phase chromatographic columns have shown that Eq. (23) is the most satisfactory combining simplicity, accuracy and good numerical behavior. Good fitting results are also obtained from Eqs. (22) and (30), which, however, contain four adjustable parameters. Eq. (12), which has been used widely up to now, does not describe all experimental systems. Finally, the applicability of a simplified equation does not entail the validity of its model and for this reason no molecular information can be gained from the use of this equation.

Appendix A

A phenomenological approach of the solute–modifier interactions is to assume the existence of the following equilibrium:



in the mobile phase and/or in the adsorbed layer. It is evident that strong attractive interactions between A and B molecules will shift the equilibrium of Eq. (A.1) to the right.

We assume that the A–B interactions are limited to the mobile phase and all other interactions have a negligible contribution to the retention mechanism, which occurs via the adsorption mechanism. Due to the pseudo-equilibrium (A.1), the retention factor is now given by:

$$\begin{aligned} \ln k' &= \lim_{n_A^m \rightarrow 0} \ln \frac{n_A^s}{n_{A,\text{total}}^m} = \lim_{n_A^m \rightarrow 0} \ln \frac{n_A^s}{n_A^m + n_M^m} \\ &= \lim_{n_A^m \rightarrow 0} \ln \frac{\varphi_A^s M^s / r}{M(\varphi_A^m / r + \varphi_M^m / r')} \end{aligned} \quad (\text{A.2})$$

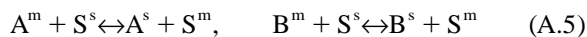
which yields:

$$\ln k' = \ln k^* + \lim_{\varphi_A^m \rightarrow 0} \ln \frac{\varphi_A^s}{\varphi_A^m / r + \varphi_M^m / r'} \quad (\text{A.3})$$

From the equilibrium (A.1) we have:

$$K_\varphi = \frac{\varphi_M^m}{\varphi_A^m \varphi_B^m} \quad (\text{A.4})$$

However, apart from Eq. (A.1), the following two adsorption processes take place:



which are described by:

$$\frac{\varphi_A^s}{1 - \varphi_B^s} = \beta_A \frac{\varphi_A^m}{1 - \varphi}, \quad \frac{\varphi_B^s}{1 - \varphi_B^s} = \beta_B \frac{\varphi}{1 - \varphi} \quad (\text{A.6})$$

Note that we have assumed that the A–B interactions are described via Eq. (A.1) and all the other interactions have a negligible contribution to the retention mechanism. For this reason there are no activity coefficients in Eqs. (A.4), (A.6). If Eqs. (A.4), (A.6) are substituted into Eq. (A.3), we readily obtain:

$$\ln k' = \ln k^0 - \ln(1 + \beta\varphi) - \ln(1 + K\varphi) \quad (\text{A.7})$$

where $\beta = \beta_A - 1$ and $K = K_\varphi r/r'$. It is seen that we have derived Eq. (26).

Eq. (A.7) may also be written as:

$$\ln k' = -\ln \left\{ \frac{1}{k^0} + \frac{(\beta + K)}{k^0} \varphi + \frac{\beta K}{k^0} \varphi^2 \right\} \quad (\text{A.8})$$

which yields the reciprocal equation:

$$1/k' = a + b\varphi + c\varphi^2 \quad (\text{A.9})$$

where $a = 1/k^0$, $b = (\beta + K)/k^0$ and $d = \beta K/k^0$.

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