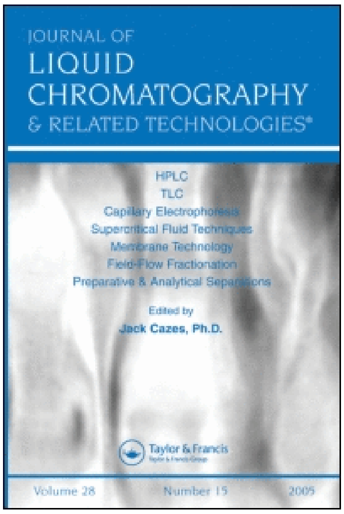

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EXTENDED THERMODYNAMIC APPROACH TO ION INTERACTION CHROMATOGRAPHY FOR LOW SURFACE POTENTIAL. USE OF THE LINEARIZED POTENTIAL EXPRESSION

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ABSTRACT

The chromatographic behaviour of charged analytes in Ion Interaction Chromatography (IIC) was theoretically investigated.

Simplified retention equations were obtained via the linearized potential expression. They can be used to model analyte retention as a function of both the mobile and stationary phase concentration of the Ion-Interaction reagent (IIR), if the surface potential is below 25 mV.

Simplified retention equations were compared to those, which can be obtained from two of the most important retention models in IIC. They reduce to stoichiometric or electrostatic retention model equations if the surface potential or pairing equilibria are respectively neglected.

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INTRODUCTION

Reversed-phase ion-interaction chromatography (IIC) is a popular separation strategy of HPLC.(1-13) We have recently put forth an exhaustive thermodynamic retention model for IIC, which is well-founded in physical chemistry. It is able to quantitatively predict retention of charged, neutral, and zwitterionic analytes(4-6,14-17) as a function of the IIR concentration both in the mobile and in the stationary phases. According to the extended thermodynamic model, retention of an analyte depends not exclusively on electrostatic interactions, but also on complex formation in both the stationary and mobile phases and on adsorption competitions for available ligand sites. The importance of chemical equilibria was recovered from stoichiometric models, but thermodynamic, and not stoichiometric equilibrium constants, were used to take into account the chemical and physical modification of the interface.

The claims for a superior theory stem, also, from the fact that new retention equations(4-6) are quantitatively able to predict experimental evidence that cannot be rationalized by the most reliable thermodynamic retention models.(8-11)

It is the aim of the present work to obtain simplified retention equations by using a linearized relationship for the surface potential.

THEORY

The basis for the present thermodynamic theory of IIC is the Stern-Gouy-Chapman model of the electrical double layer.(18) The adsorbed IIR ions are responsible for the electrical potential difference, Ψ^{o}, between the surface and the bulk solution.

We have demonstrated(4) that the course of the analyte retention, upon IIR concentration in the mobile and in stationary phase, can be described, respectively, by the following two expressions:

$$k = \phi[\mathrm{L}]_{\mathrm{T}} \frac{K_{\mathrm{EL}} \frac{\gamma_{\mathrm{E}}\gamma_{\mathrm{L}}}{\gamma_{\mathrm{EL}}} \exp\left(-z_{\mathrm{E}}\mathrm{F}\,\Psi^{o}/\mathrm{R}T\right) + K_{\mathrm{EHL}} \frac{\gamma_{\mathrm{E}}\gamma_{\mathrm{H}}\gamma_{\mathrm{L}}}{\gamma_{\mathrm{EHL}}}[H]}{\left(1 + \frac{\gamma_{\mathrm{E}}\gamma_{\mathrm{H}}}{\gamma_{\mathrm{EH}}} K_{\mathrm{EH}}[H]\right)\left(1 + K_{\mathrm{HL}} \frac{\gamma_{\mathrm{L}}\gamma_{\mathrm{H}}}{\gamma_{\mathrm{HL}}} \exp(-z_{\mathrm{H}}\mathrm{F}\,\Psi^{o}/\mathrm{R}T)[H]\right)} \tag{1}$$

$$k = \phi \frac{K_{\mathrm{EL}} \frac{\gamma_{\mathrm{E}}\gamma_{\mathrm{L}}}{\gamma_{\mathrm{EL}}} \exp\left(-z_{\mathrm{E}}\mathrm{F}\,\Psi^{o}/\mathrm{R}T\right) + \frac{K_{\mathrm{EHL}}}{a^{1/b}} \frac{\gamma_{\mathrm{E}}\gamma_{\mathrm{H}}\gamma_{\mathrm{L}}}{\gamma_{\mathrm{EHL}}}[\mathrm{LH}]^{1/b}}{\left(1 + \frac{K_{\mathrm{EH}}}{a^{1/b}} \frac{\gamma_{\mathrm{E}}\gamma_{\mathrm{H}}}{\gamma_{\mathrm{EH}}}[\mathrm{LH}]^{1/b}\right)} \left([L]_{\mathrm{T}} - [\mathrm{LH}]\right) \tag{2}$$

where a, b, are constants related to the Freundlich adsorption isotherm, z_{E}, z_{H} are, respectively, the charges of the analyte E and of the IIR H, [H] and [LH] are, respectively the mobile phase and stationary phase concentration of the IIR; K_{EHL} is the thermodynamic equilibrium constant for ion-pair formation in the stationary phase, K_{EH} is the thermodynamic equilibrium constant for ion-pair formation in the eluent, K_{HL} is the thermodynamic equilibrium constant for adsorption of the IIR onto the stationary phase, $[L_T]$ estimates the total ligand surface concentration.

To obtain an expression for a practical test, as a first approximation we may assume that the activity coefficients ratios are almost constant.

The solution of the Poisson-Boltzmann equation for a planar surface(4) gives the following rigorous relationship for the surface e potential (Ψ^o):

$$\Psi^O = \frac{2RT}{F}\ln\left\{\frac{[\mathrm{LH}]|z_H|F}{\left(8\varepsilon_0\varepsilon_r RT\sum_i c_{0i}\right)^{\frac{1}{2}}} + \left[\frac{([\mathrm{LH}]z_H F)^2}{8\varepsilon_0\varepsilon_r RT\sum_i c_{0i}} + 1\right]^{\frac{1}{2}}\right\} \tag{3}$$

where ε_o is the electrical permitivity of vacuum, ε_r is the dielectric constant of the mobile phase, and Σc_i is the mobile phase concentration (mol/m^3) of electrolyte ions, which are assumed to be singly charged. Ψ^o must be considered positive or negative, according to the charge status of the IIR.

For low surface potentials the above expression can be linearized(9) and approximated by:

$$\Psi^o = \frac{z_H[\mathrm{LH}]F}{\kappa\varepsilon_o\varepsilon_r} \tag{4}$$

where κ is the inverse Debye length. For the sake of simplicity we will indicate:

$$g = \frac{z_H F}{\kappa\varepsilon_o\varepsilon_r} \tag{5}$$

where g (V m^2/mol) is a constant that can be evaluated from experimental conditions.

In a number of cases, if the IIR concentration in the mobile phase is not too high the rigorous potential modified Langmuir adsorption isotherm reduces to an empirical Freundlich isotherm:(20)

$$[\mathrm{LH}] = a[\mathrm{H}]^b \tag{6}$$

where *a* and *b* are constants that depend on experimental conditions.

By substitution of equations (4), (5), (6) into equation (1), we obtain the following relationship between the retention factor and the mobile phase concentration of IIR:

$$k = \frac{c_1 \exp\left(-z_{\mathrm{E}} \frac{\mathrm{F}}{\mathrm{R}T} ga[H]^b\right) + c_2[H]}{(1 + c_3[H])\left(1 + c_4[H]\exp\left(-z_{\mathrm{H}} \frac{\mathrm{F}}{\mathrm{R}T} ga[H]^b\right)\right)} \tag{7}$$

where:

$$c_1 = \phi[\mathrm{L}]_{\mathrm{T}} K_{\mathrm{EL}} \frac{\gamma_{\mathrm{E}}\gamma_{\mathrm{L}}}{\gamma_{\mathrm{EL}}} \tag{8}$$

This means that c_1 is the retention factor when the IIR is not present in the eluent (k_o) and it can be obtained by experimental results;

$$c_2 = \phi[\mathrm{L}]_{\mathrm{T}} K_{\mathrm{EHL}} \frac{\gamma_{\mathrm{E}}\gamma_{\mathrm{H}}\gamma_{\mathrm{L}}}{\gamma_{\mathrm{EHL}}} \tag{9}$$

$$c_3 = K_{\mathrm{EH}} \frac{\gamma_{\mathrm{E}}\gamma_{\mathrm{H}}}{\gamma_{\mathrm{EH}}} \tag{10}$$

$$c_4 = K_{\mathrm{HL}} \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{L}}}{\gamma_{\mathrm{HL}}} \tag{11}$$

If k_o is known, equation (7) is a three-parameter equation. As it may be observed from the second term in the right factor of the denominator, the potential that develops at the stationary phase always run counter further adsorption of the IIR, since the *g* constant is of the same sign of z_H. From the first term in the numerator, it is clear that, if the charge status of the eluite and the IIR is the same, *k* is expected to decrease with increasing IIR concentration, while the opposite is predicted for oppositely charged analyte and IIR.

By substitution of equations (4), (5), (6) into equation (2), we obtain the following relationship between the retention factor and the stationary phase concentration of IIR:

$$k = \frac{d_1 \exp\left(-z_E \frac{F}{RT} g[LH]\right) + d_2[LH]^{1/b}}{\left(1 + d_3[LH]^{1/b}\right)} \left(d_4 - [LH]\right) \qquad (12)$$

where:

$$d_1 = \phi K_{EL} \frac{\gamma_E \gamma_L}{\gamma_{EL}} \qquad (13)$$

This means that d_1 is equal to (k_o / d_4), hence, it is not an additional fitting parameter, if k_o is known; if [HL] is negligible with respect to $[L]_T$, this term is included in d_1, hence, $d_1 = c_1 = k_o$

$$d_2 = \phi \frac{K_{EHL}}{a^{1/b}} \frac{\gamma_E \gamma_H \gamma_L}{\gamma_{EHL}} \qquad (14)$$

If [HL] is negligible with respect to $[L]_T$, this term is included in d_2, hence, $d_2 = c_2 / (a^{1/b})$

$$d_3 = \frac{K_{EH}}{a^{1/b}} \frac{\gamma_E \gamma_H}{\gamma_{EH}} \qquad (15)$$

Hence, $d_3 = c_3 / (a^{1/b})$

$$d_4 = [L]_T \qquad (16)$$

Again, the fitting of equation (12), if k_o is known, requires the optimisation of only three parameters. The analyte retention is predicted to increase (decrease) with increasing IIR surface concentration, if its charge status is the opposite (same) of the IIR one.

Eqs (7) and (12), which are well founded in physical chemistry, can be used to model and predict analyte retention in IIC when the surface potential is below the threshold of 25 mv and the linearized equation (4) for surface potential, is a good approximation.

If the charge status of the analyte and IIR are the same, ion pair equilibria in both the stationary and mobile phases do not apply, hence, the c_2 and c_3 terms in Eq. (7), and d_2 and d_3 terms Eq. (12), are missing.(4) In this case, Eq (1) reduces to Eq. (26) of reference(8) and Eq. (2) becomes:

$$k = d_1 \exp\left(-z_{\mathrm{E}} \frac{\mathrm{F}}{\mathrm{R}T} g[\mathrm{LH}]\right)\left(d_4 - [\mathrm{LH}]\right) \qquad (17)$$

If adsorption competitions are missing as well, Eqs (1) and (2) further reduce both to Eq. (4a) of reference (8).

On the other hand, if surface potential is not taken into account, Eq. (1) reduces to Eq. (2) of the stoichiometric model of Knox and Hartwick,(7) except that their equilibria contain the counter ions necessary to ensure the balance of electrical neutrality. The present approach, which underlines the importance of a charged stationary phase to which the eluite ion migrates without a counter ion, is better founded in experimental evidence.(3,11)

It is also rewarding to see that, if the analyte is neutral, Eqs (1) and (2) reduce to the previously developed retention equations for uncharged eluates under the same potential approximation (see Eqs. (30) and (36) of reference (5)).

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