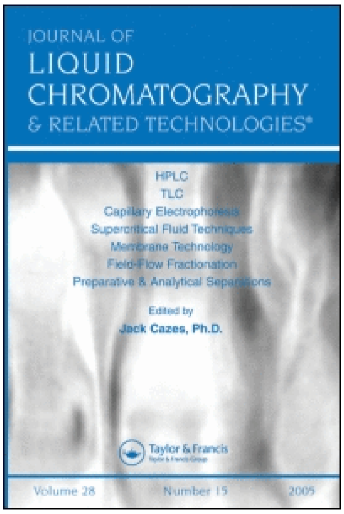

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THE DIPOLE APPROACH IN ION INTERACTION CHROMATOGRAPHY OF ZWITTERIONS. USE OF THE LINEARIZED POTENTIAL EXPRESSION FOR LOW SURFACE POTENTIAL

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ABSTRACT

The chromatographic behaviour of zwitterionic analytes in Ion Interaction Chromatography (IIC) was theoretically investigated for low surface potential.

For the first time, simplified retention equations were obtained via the linearized potential expression. They can be used to model zwitterions 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.

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INTRODUCTION

Reversed-phase ion-interaction chromatography (IIC) is a technique that makes use of a lipophilic Ion Interaction Reagent (IIR) to obtain adequate retention for poorly retained ionized solutes (1). We have recently developed an exhaustive thermodynamic retention model for IIC, which is well-founded in physical chemistry. It is able to quantitatively predict retention of charged (2–4), neutral (5–6), and zwitterionic (7) analytes as a function of the IIR concentration, both in the mobile and in the stationary phases. The model capitalized on the stoichiometric retention mechanism, because analyte retention is viewed to result from complex formation in both the stationary and mobile phases and on adsorption competitions for available ligand sites. Nevertheless, electrostatic interactions are also considered. The use of thermodynamic and not stoichiometric equilibrium constants allows one to take into account, in a thermodynamic and rigorous way, the chemical and physical modification of the interface.

It is not an overstatement to suggest that the new theory could be considered superior to the previous ones. Actually, (i) new retention equations are quantitatively able to predict experimental evidence concerning charged analytes (2) that cannot be rationalized by the most reliable thermodynamic retention models (8–11); (ii) the same approach is able to model retention of charged, neutral, and zwitterionic analytes; (iii) zwitterions retention in IIC was qualitatively and quantitatively modelled for the first time.

We have already obtained simplified retention equations for charged analytes by using a linearized relationship for the surface potential (4). Taking into account the strong interest in zwitterions, especially in the biological and therapeutical fields (12–21), the present work seeks to expand upon the earlier work and to use the same potential approximation for zwitterionic analytes retention in IIC. The purpose is to obtain simplified retention equations.

THEORY

The basis for the present thermodynamic theory of IIC is the Stern-Gouy-Chapman model of the electrical double layer (22). The adsorbed IIR ions are responsible for the electrical potential difference, Ψ^0, between the surface and the bulk solution.

It was demonstrated (5) that the following expressions describe, respectively, the course of zwitterions retention (k) upon IIR concentration in the mobile and stationary phases:

$$k = \phi[\mathrm{L}]_T \frac{\mathrm{K}_{\mathrm{LE}} \frac{\gamma_{\mathrm{L}}\gamma_{\mathrm{E}}}{\gamma_{\mathrm{LE}}} \exp\left(\left|\mathrm{N}M\Psi^0 \cdot \kappa\right|/\mathrm{R}T\right)}{\left\{1 + \mathrm{K}_{\mathrm{LH}} \frac{\gamma_{\mathrm{L}}\gamma_{\mathrm{H}}}{\gamma_{\mathrm{LH}}} \exp\left(-z_{\mathrm{H}}\mathrm{F}\Psi^0/\mathrm{R}T\right)[\mathrm{H}]\right\}} \tag{1}$$

$$k = \phi \mathrm{K}_{\mathrm{LE}} \frac{\gamma_{\mathrm{L}}\gamma_{\mathrm{E}}}{\gamma_{\mathrm{LE}}} \exp\left(\left|\mathrm{N} M \Psi^{0} \kappa\right| / \mathrm{R}T\right)\left([\mathrm{L}]_{T} - [\mathrm{LH}]\right) \tag{2}$$

In Equations (1) and (2), [H] and [LH] are, respectively, the IIR (H) concentration in the mobile and stationary phases, $[\mathrm{L}]_T$ is the total ligand surface concentration, ϕ is the column phase ratio, N is the Avogadro's number, M is a vector representing the electrical dipole moment of the analyte, κ is the inverse Debye length, K_{LE}, K_{LH}, are, respectively, the thermodynamic equilibrium constants for adsorption into the stationary phase of the analyte (E), and the IIR (H); F is the Faraday constant, R is the gas constant, T is the absolute temperature, Ψ^0 is the electrical potential difference between the surface and the bulk solution, a and b are the Freundlich isotherm constants (see below), z_{H} is the charges of the IIR; γ represents the activity coefficient for each species.

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

The rigorous relationship for the solution of the Poisson–Boltzmann equation for a planar surface (see Equation (16) of reference (7) is a very complicated expression. For low surface potential it may be linearized (9) and approximated by the following much simpler relationship:

$$\Psi^{0} = \frac{z_{\mathrm{H}}[\mathrm{LH}]\mathrm{F}}{\kappa \varepsilon_{0} \varepsilon_{\mathrm{r}}} \tag{3}$$

where ε_0 is the electrical permitivity of vacuum, ε_{r} is the dielectric constant of the mobile phase, Σc_{i} is the mobile phase concentration (mol/m^3) of electrolyte ions, which are assumed to be singly charged, and κ is the inverse Debye length. Ψ^0 must be considered positive or negative, according to the charge status of the IIR.

For the sake of simplicity we will indicate:

$$g = \frac{z_{\mathrm{H}}\mathrm{F}}{\kappa \varepsilon_{0} \varepsilon_{r}} \tag{4}$$

where g (V m^2/mol) is a constant that can be evaluated from the composition of the mobile phase.

When the rigorous potential modified Langmuir adsorption isotherm reduces to an empirical Freundlich isotherm (23)

$$[\mathrm{LH}] = a[\mathrm{H}]^{b} \tag{5}$$

(a and b are constants that depend on experimental conditions) by substitution of Equations (3), (4), and (5) into Equation (1) we obtain the following relationship between the retention factor and the mobile phase concentration of IIR:

$$k = \frac{c_{1} \exp\left(\left|c_{2} \frac{\kappa}{\mathrm{R}T} g a [\mathrm{H}]^{b}\right|\right)}{\left(1 + c_{3}[\mathrm{H}] \exp\left(-z_{\mathrm{H}} \frac{\mathrm{F}}{\mathrm{R}T} g a [\mathrm{H}]^{b}\right)\right)} \tag{6}$$

where

$$c_1 = \phi[\mathrm{L}]_T \mathrm{K}_{\mathrm{EL}} \frac{\gamma_{\mathrm{E}}\gamma_{\mathrm{L}}}{\gamma_{\mathrm{EL}}} \tag{7}$$

This means that c_1 has a precise physical meaning: it is the retention factor when the IIR is not present in the eluent (k_0) and it can be obtained by experimental results;

$$c_2 = \mathrm{N}M \tag{8}$$

$$c_3 = \mathrm{K}_{\mathrm{HL}} \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{L}}}{\gamma_{\mathrm{HL}}} \tag{9}$$

If k_0 is known, Equation (6) is a two-parameter equation.

As it may be observed from the numerator, the potential that develops at the stationary phase always favors zwitterions adsorption, since the electrical dipole, aligned with the field lines by a torque moment, approaches the charged surface with the similarly charged head as far as possible from it. The force acting on the dipole, in the non-uniform electrical field that develops, is always attractive and k is expected to increase with increasing IIR concentration of either charge (24), as long as adsorption competitions are negligible.

By substitution of Equations (3) and (4) into Equation (2), we obtain the following relationship between the retention factor and the stationary phase concentration of IIR:

$$k = d_1 \exp\left(\left| d_2 \frac{\kappa}{\mathrm{R}T} g[\mathrm{LH}] \right|\right)\left(d_3 - [\mathrm{LH}]\right) \tag{10}$$

where:

$$d_1 = \phi \mathrm{K}_{\mathrm{EL}} \frac{\gamma_{\mathrm{E}}\gamma_{\mathrm{L}}}{\gamma_{\mathrm{EL}}} \tag{11}$$

This means that d_1 is equal to (k_0/d_4), hence, it is not an additional fitting parameter, if k_0 is known; if [HL] is negligible with respect to $[\mathrm{L}]_T$, this term is included in $d_{1,}$ hence, $d_1 = c_1 = k_0$

$$d_2 = \mathrm{N}M \equiv c_2 \tag{12}$$

$$d_3 = [\mathrm{L}]_T \tag{13}$$

Again, the fitting of Equation (10), if k_0 is known, requires the optimization of only two parameters.

Equations (6) and (10), which are well founded in physical chemistry, are predictive in their own right, since the estimates of the fitting parameters have important physical meaning.

They can be used to model analyte retention in IIC when the surface potential is below the threshold of 25 mV and the linearized Equation (3) gives a good approximation of the surface potential. This can be reasonably expected on the basis of the application experimental conditions, if short chain IIR or high organic modifier concentrations are used. Low surface potentials can also be predicted if the ionic strength is high or the stationary phase capacity is low (8).

We have already shown (7) that none of the previously developed retention models for IIC (8–11,23) is able to predict, via retention equations, the behavior of zwitterions.

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