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Migration of ions in capillary electrochromatography

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Abstract

For capillary electrochromatography (CEC) to be a generally used analytical technique the origin of the unusual, and often unwanted, peak shapes, which regularly occur for ionic compounds, must be understood. A mass balance analysis is the most fundamental approach to investigate the origin of non-linear effects during the migration of an eluite. Such an analysis shows that a CEC system composed of ionic compounds has a complex behaviour and that a variety of peak shapes for an eluite ion is expected. In this paper it is shown that the mass balance analysis is rationalised by the introduction of the non-dimensional electrochromatographic migration number Ω. This number is defined as the ratio Eu/v_0k, where E is the effective electric field strength in the eluite zone, u the mobility of the eluite, v_0 the linear velocity of the mobile phase and k the chromatographic capacity factor of the eluite. This work is focussed on the theoretical behaviour of a CEC system for analytical applications, i.e., in the limit of low eluite concentrations. Even under analytical conditions the three-component system studied in this paper shows strong peak broadening when Ω has values close to unity.

Keywords: Electrochromatography; Ions

1. Introduction

The concept for electrochromatography was introduced in 1974 when Pretorius et al. [1] proposed that the electroosmotic flow could be used to pump an eluent through a chromatographic column. Some years later Jorgenson and Lukacs applied an electric potential difference across the length of a packed capillary column and used it for the separation of non-ionic compounds [2,3]. An examination of the advantages of electrochromatography, compared to electrophoresis and chromatography, for the separation of compounds was later made in a series of papers by Knox and Grant [4–6]. Since then the potential of capillary electrochromatography (CEC) for the separation of in particular non-ionic compounds have been demonstrated by a number of research groups [7–11]. The rapidly growing interest in analytical chemistry for CEC has increased the need for a better understanding of the basic physico–chemical properties of this technique. One such important subject, which has been more closely investigated during the last years, is the generation and control of the electroosmotic flow in packed beds [12–17].

For CEC to be a generally used separation technique it must be able to efficiently separate both ionic and non-ionic compounds. However, experiments have shown that unexpected effects on the peak shape often occur for ionic compounds [18,19]. Therefore, to be able to use CEC for separation of ionic compounds a better understanding of the basic principles which governs their migration is needed.

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The basic theory for both electrophoresis and chromatography is based on a mass balance analysis [20–23]. From this analysis, and for both these techniques, the non-linear effects that are dependent on the analyte concentration in the migrating zone are generally understood (see e.g., Refs. [24,25]). Since in CEC an ionic compound migrates through the column by both a chromatographic and an electrophoretic mechanism, a mass balance analysis becomes more complex than for the individual techniques [26,27]. Consequently, the theory for CEC is a generalisation of these two theories and includes the respective theory in the limiting case of no current and of no adsorption. A mass balance analysis can be performed in either differential or finite form and the basic information gained from these two approaches is basically the same. However, from the differential form more quantitative information can be obtained about the peak shape during the migration in the column and at the point of elution from the column. The analysis in the finite form is easier to evaluate because it leads to algebraic equations instead of the set of coupled differential equations that is obtained in the differential form. This paper is a continuation of a previously published mass balance analysis in the finite form [26].

In the theory of migration of ions in CEC the coherence condition is of great importance. This term was originally introduced in chromatographic theory [21] but it also has its counterparts in electrophoretic theory, where it leads to the well-known Kohlrausch regulating function. The coherence condition is a result of a mass balance that is simultaneously made for several components. The three-component electrophoretic system in Fig. 1 is a useful starting point for understanding the implications of the coherence condition for CEC of ionic species. In this example components 1 and 2 constitute the background electrolyte and component 3 is an analyte ion which migrates through the column with the velocity v. The velocity of the analyte is determined by its electrophoretic mobility and the electric field strength in the zone containing the analyte, E. It is important to note that the electric field strength within the zone containing the analyte (i.e., component 3) is different from that outside the zone. For a given current through the column E is determined by its conductivity, i.e., by the concentration and mobility of all three components in the zone. The concentration of components 1 and 2 in the zone is determined by the electroneutrality condition in the zone in combination with the important condition that all concentration steps must move with the same velocity. This means that the concentration step that exists between the solution in the zone and outside the zone, for component 1 as well as for component 2, must move with the same velocity as component 3.

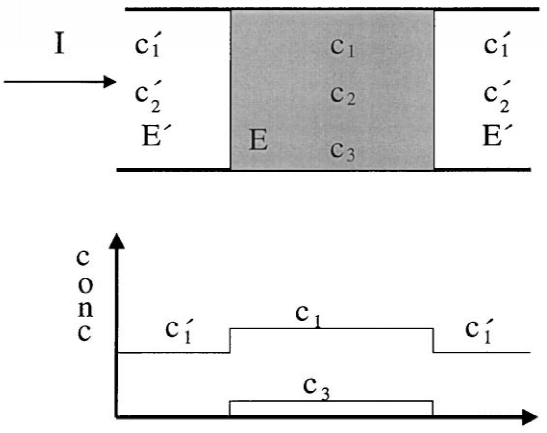

Fig. 1. Schematic representation of an electrophoretic system containing a two-component background electrolyte, components 1 and 2, and a zone containing an analyte ion, component 3. The Kohlrausch regulating function determines the concentration of components 1 and 2 within the zone. The velocity of the zone is determined by the mobility of component 3, the current I through the column and the conductivity in the zone. See also the discussion in the text.

Compared to an electrophoretic system the electrochromatographic system is more complex. The reason is that the presence of the stationary phase creates two additional requirements that the mass balance analysis must consider. Firstly, the simultaneous equilibrium for all three components between the eluent and the stationary phase must be included. Secondly, electroneutrality on the stationary phase is required. The latter condition is critical because it means that adsorption of component 3 to the stationary phase always is accompanied by a simultaneous change in the surface concentration of the other components, which in turn changes the concentration of these components in the zone containing component 3. For example, assume that the stationary phase is a cation exchanger and that both com-

ponents 1 and 3 are monovalent cations, the anionic component 2 can to a first approximation be assumed to be absent from the stationary phase surface. Under these assumptions the adsorption of component 3 is accompanied by desorption of component 1. When components 1 and 3 have different electrophoretic mobility, the conductivity in the zone will change because of the interchange of ions between the stationary phase and the eluent. This will in turn change the electrical field strength in the zone which affects the velocity of the components in the eluent, which in turn changes the concentrations of components 1 and 2, etc. Thus, to summarise, the concentrations of the different components in the zone which fulfil the coherence condition is determined by the requirement of simultaneous movement of all concentration steps in combination with the change in conductivity caused by the interchange between ions of different mobilities taking place on the stationary phase.

The aim of this study is to investigate the properties of the solution of the mass balance equation in the limit of low concentrations of component 3, i.e., the concentration range that is of interest in analytical applications. It is shown that the complex retention behaviour can be rationalised by the introduction of the non-dimensional electrochromatographic migration number. The theory is derived for an ion-exchange chromatographic system under certain assumptions and simplifications. This implies that the studied system is a model system and the objective is primarily to obtain an insight into the physical processes that determine the coherence condition for the migration of ionic analytes. Although the equations are derived for an ion-exchange system, the same principles are valid for other chromatographic systems. It has been shown, for example, that when the ionic analyte adsorbs to a non-ionic stationary phase surface the resulting equations are very similar to the equations for an ion-exchange system [26].

2. Theory

The three-component system discussed in this paper is the same as has been discussed in previous publications [26,27] and is schematically shown in Fig. 2. It consists of the sharp boundary created by a difference in eluent composition, on one side of the boundary the eluent contains two monovalent ionic species (the positively charged component 1 and the negatively charged component 2) of concentration c_1' ($=c_2'$). The stationary phase is assumed to be negatively charged, e.g., a cation exchanger, and in order to maintain electroneutrality in this phase component 1 is assumed to be non-specifically adsorbed with the surface concentration n_1'. On the other side of the boundary these two components have concentrations c_1 and c_2 and a third monovalent component is also present (positively charged component 3). Component 3 may adsorb specifically to the stationary phase and this treatment is limited to the case of a linear adsorption isotherm. Components 1 and 3 are adsorbed to the stationary phase surface with the surface concentration n_1 and n_3, respectively. To maintain electroneutrality on the stationary phase, adsorption of component 3 results in desorption of the same amount of component 1. The boundary moves along the column because of the flow of eluent [linear velocity v_0 (m/s)] and current [current density I (A/m^2)]. The values of I and v_0 are assumed to be constant through all column cross sections. The current is assumed to be transported by ions in the eluent only, i.e., there is no surface conduction. It is also assumed that the electrophoretic mobility of all three components is

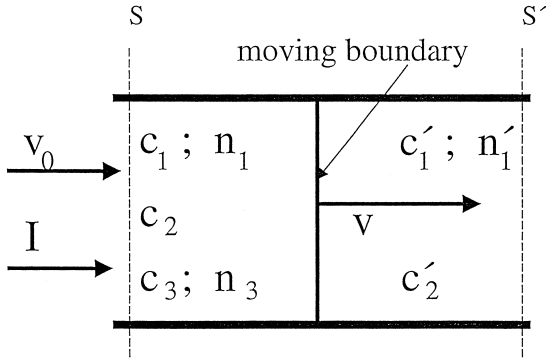

Fig. 2. Schematic representation of the three-component electrochromatographic system discussed in this paper. The system consists of a moving boundary that separates two different compositions of the eluent phase. Ions 1 and 2 are present on both sides of the boundary while component 3 is present on one side only. c_i and n_i represent the eluent and stationary phase concentration of component i, respectively.

constant and independent of the ionic strength in the mobile phase.

Solving the mass balance equation for this three-component system gives that the velocity of the boundary is [26,27]:

$$v = \frac{v_0(2+k) + \frac{v_0 k c_3 U}{\kappa_K} + \frac{I u_3}{\kappa_K} \pm \sqrt{\left(\frac{v_0 k c_3 U}{\kappa_K} - v_0 k + \frac{I u_3}{\kappa_K}\right)^2 - \frac{4 v_0 k c_3 U}{\kappa_K} \cdot \frac{I u_3}{\kappa_K} \cdot (1+k)}}{2(1+k) \cdot \left(1 + \frac{k c_3 U}{\kappa_K}\right)} \quad (1)$$

where k is the chromatographic capacity factor of component 3, c_3 its concentration in the eluent phase and u_3 its electrophoretic mobility. U is defined as:

$$U = F u_1 u_2 \cdot \left(\frac{1}{u_3} - \frac{1}{u_1}\right) \quad (2)$$

where u_1 and u_2 are the electrophoretic mobilities of component 1 and 2, respectively. F is the Faraday constant and κ_K is defined as the conductivity of the eluent in a corresponding pure electrophoretic system containing component 3. According to electrophoretic theory its is value obtained from the Kohlrausch regulating function and is equal to:

$$\kappa_K = F\left[c_3 \cdot \frac{(u_3 - u_1)(u_3 - u_2)}{u_3} + c_1'(u_1 - u_2)\right] \quad (3)$$

where c_1' is the concentration of component 1 in the eluent phase on the side of the boundary where component 3 is absent, see also Fig. 2.

The concentration of component 1 in the eluent phase in the electrochromatographic system in Fig. 2, on the side of the boundary where component 3 is present, is obtained from a mass balance analysis [26]:

$$c_1 = \frac{c_3 \cdot \frac{u_1}{u_3} \cdot (u_3 - u_2) - \frac{v}{v - v_0} \cdot \frac{k c_3 U}{F}}{u_2 - u_1} + c_1' \quad (4)$$

From the electroneutrality condition in the eluent phase: $c_1 + c_3 = c_2$, the concentration of component 2 can easily be obtained.

The general properties of Eq. (1) have previously been analysed [27] and will briefly be discussed here. First we note that the equation has two roots which both satisfy the mass balance equation. When the sum of terms under the root sign results in a positive number both roots have real values. From a mass balance point of view this implies that two different velocities for the boundary are allowed. However, to be physically realistic, the root must also give a positive value for the concentration, c_1, which not always is the case. When the term under the root sign becomes negative both roots becomes imaginary and no real value for v exists. Another physically unrealistic solution is when the term kc_3U/κ_K becomes equal to -1, i.e.,the denominator in Eq. (1) becomes zero. This implies that the velocity approaches infinity, which gives a negative value for c_1. At low concentrations of component 3, this situation will not occur and is therefore not further discussed in this paper.

To characterise an electrochromatographic system it is rational to introduce the non-dimensional electrochromatographic migration number, Ω, defined as:

$$\Omega = \frac{I u_3}{\kappa_K v_0 k} \quad (5)$$

When Ω is introduced, Eq. (1) becomes:

$$v = \frac{v_0 k \cdot \left[\frac{2}{k} + 1 + \frac{c_3 U}{\kappa_K} + \Omega \pm \sqrt{\left(\frac{c_3 U}{\kappa_K} - 1 + \Omega\right)^2 - \frac{4 c_3 U (1+k)\Omega}{\kappa_K}}\right]}{2(1+k) \cdot \left(1 + \frac{k c_3 U}{\kappa_K}\right)} \quad (6)$$

This work is focussed on the properties of Eq. (6) when the concentration of c_3 approaches zero. In this limit, the velocity of the boundary is more or less the same as the velocity of a corresponding analytical peak and is therefore the most interesting case from an analytical point of view. The limiting case when $\Omega = 0$ (i.e., pure chromatography) and when $\Omega \to \infty$ (i.e., pure electrophoresis) have been analysed in the previous papers and shown to be consistent with chromatographic and electrophoretic theory, respectively.

Inspection of Eq. (6) shows that for small c_3 values two different cases are obtained; when $\Omega = 1$ and when its value is distinctly different from unity. These two cases are treated separately and the case when Ω is close to unity is discussed in the Results and Discussion section. For our purpose it is appropriate to rewrite Eq. (6) as:

$$v = \frac{v_0 k \cdot \left[\frac{2}{k} + 1 + \frac{c_3 U}{\kappa_K} + \Omega \pm \left(\frac{c_3 U}{\kappa_K} - 1 + \Omega \right) \sqrt{1 - \frac{4 c_3 U (1+k) \Omega}{\kappa_K \left(\frac{c_3 U}{\kappa_K} - 1 + \Omega \right)^2}} \right]}{2(1+k) \cdot \left(1 + \frac{k c_3 U}{\kappa_K} \right)} \quad (7)$$

When Ω is distinctly different from unity and when c_3 is small, the series expansions $\sqrt{(1-x)} \approx 1 - \frac{1}{2}x$ and $1/(1+x) \approx (1-x)$ can be applied to Eq. (7). When quadratic c_3 terms are neglected, the following expressions are obtained for the two roots:

$$\text{Root 1: } v \approx v_0 \cdot \frac{(1+k\Omega)}{1+k} \cdot \left(1 - \frac{k\Omega}{\Omega - 1} \cdot \frac{c_3 U}{\kappa_K} \right) \quad (8a)$$

$$\text{Root 2: } v \approx v_0 \cdot \left(1 + \frac{c_3 U}{\kappa_K} \cdot \frac{k}{\Omega - 1} \right) \quad (8b)$$

In the limit $c_3 \to 0$ these two roots are:

$$\text{Root 1: } v = v_0 \cdot \left(\frac{1+k\Omega}{1+k} \right) = \frac{v_0 + \frac{I u_3}{\kappa_K}}{1+k} = \frac{v_0 + E u_3}{1+k} \quad (9a)$$

$$\text{Root 2: } v = v_0 \quad (9b)$$

The last equality in Eq. (9a) follows from the fact that when $c_3 \to 0$ the conductivity in the zone or peak is almost equal to the conductivity in the eluent. In the equation, E is therefore the effective electric field in the column. Root 1 represents the case where the velocity of the peak is obtained as the sum of eluent and electrophoretic velocities divided by the effect of chromatographic retardation. Inserting Eq. (9a) into Eq. (4) gives that $c_1 \to c_1'$ when $c_3 \to 0$ and the velocity obtained from this root is therefore physically attainable. However, for the velocity according to root 2, i.e., when $v = v_0$, Eq. (4) becomes undetermined in the limit $c_3 \to 0$ because ''zero is divided by zero''. Inserting Eq. (8b) into Eq. (4) and using that $\kappa_K = c_1'(u_1 - u_2)$ in the limit $c_3 \to 0$, gives that:

$$c_1 = \Omega c_1' \quad (10)$$

Thus, in the limit of low c_3, and since Ω is positive, both roots obtained from the mass balance equation are physically attainable when Ω is distinctly different from unity.

When $\Omega = 1$ and $c_3 \to 0$ Eq. (6) gives that the velocity, v, of the boundary approaches v_0. In this limit the term under the root sign in Eq. (6) approaches the value:

$$\left(\sqrt{-\frac{4 c_3 U (1+k) \Omega}{\kappa_K}} \right)$$

A real solution to the mass balance equation can only be obtained when the term under the root sign is positive. Except for U, all other parameters are positive and U must therefore be negative which requires that $u_1 > u_3$. The case when $\Omega = 1$ is therefore divided into two separate cases; when $u_3 > u_1$ and when $u_1 > u_3$. In the former case it is not possible to find conditions that satisfy the mass balance equation for low concentrations of component 3. For an analytical peak this means a non-coherent migration of the components in the eluent which leads to a strong distortion of the peak shape. For the case $u_1 > u_3$ there is a real solution to the mass balance equation for all concentrations of component 3 and in the limit $c_3 \to 0$ this solution is $v \to v_0$. As before, in this limit ''zero is divided by zero'' in Eq. (4) and it is easily shown by series expansion that $c_1 \to c_1'$ when $c_3 \to 0$.

3. Results and discussion

A result of the analysis in the Theory section is that there is a difference between the cases when Ω is distinctly different from unity and when $\Omega = 1$. When Ω is distinctly different from unity and c_3 is very small, there are two roots for the velocity which satisfy the mass balance equation, Eqs. (8a) and (8b). For the first of these roots the concentration of c_1 that fulfil the coherence condition in the zone approaches c_1'. For the second root the coherence condition is fulfilled when $c_1 = \Omega c_1'$. From a mass balance point of view both roots are physically realistic and it is not possible at this stage to discriminate between the two. A reasonable assumption is that the starting conditions determine which of the two roots that a zone or peak will attain. If, for example, the concentration of component 1 is c_1'

when the peak starts to migrate then its velocity would be according to root 1. If, on the other hand, the concentration of component 1 is $\Omega c_1'$ then the peak velocity would be v_0. Experiments are needed to clarify whether this assumption is correct or not.

In the Theory section it is shown that when $\Omega=1$ it is necessary to discriminate between two cases; when $u_1>u_3$ and when $u_1<u_3$. A real solution to the mass balance equation is possible only in the former case, this contrasts to the case when $u_3>u_1$ where no real solution exists in the limit $c_3\rightarrow 0$. The velocity of the boundary when Ω is close to unity is analysed in this section by numerical calculations. For the solution of the mass balance equation to be physically attainable, two criteria must be fulfilled; the expression for the velocity, Eq. (1), must have real values and at the same time the concentration c_1 corresponding to this velocity must be positive. The two velocity roots, with the corresponding concentrations of component 1, for two different cases are analysed as a function of the concentration of component 3 at low concentrations. In all the calculations Ω is varied by varying the current through the column keeping the rest of the parameters constant.

In Fig. 3a the velocities according to root 1 for the case $u_1>u_3$ for different Ω values are shown as a function of the concentration of component 3. The c_1 values that correspond to the velocities in Fig. 3a are shown in Fig. 3b. Fig. 3a shows that when $\Omega>1$ the velocity of the boundary increases when c_3 increases. The reason for this is understood from Fig. 3b that shows that when c_3 increases the concentration of component 1, c_1, decreases. This leads to a decrease in the conductivity in the zone and a corresponding increase of the electric field strength, which in turn increases the velocity of the boundary. When $\Omega<1$ there is a small decrease in the velocity when the concentration of component 3 increases due to a small increase of the zone conductivity. All these calculated functions are well represented by the approximate Eq. (8a). When $\Omega=1$ this approximate function is not valid and the velocity increases strongly and non-linearly when c_3 approaches zero. The presence of this increase is visualised more clearly in Fig. 3b which shows the strong decrease in the concentration of component 1 in the zone, resulting in a corresponding decrease in the electrolyte conductivity.

In Fig. 4a the velocities calculated from root 2 for the same parameters as in Fig. 3a are shown. For low c_3 values the velocity is close to v_0 for all the Ω values in accordance to Eq. (8b). As the concentration of component 3 increases the velocity increases or decreases almost linearly in accordance to this equation. It is interesting to note that the velocity is almost independent of the Ω value and is always close to v_0. The constant velocity is achieved by creating a zone with a conductivity, which regulates the velocity to v_0 irrespective of the amount of current that passes through the column. For example, in Fig. 4 the Ω value varies between 0.5 and 2 but the velocity of the boundary is almost the same. This is achieved by creating an electric field strength, in the zone where component 3 is present, which is constant and independent of the current. It is interesting to compare the velocity plot for $\Omega=1$ between the two roots in Figs. 3a and 4a, respectively. Both plots intersect at $v=v_0$ and show a strong non-linear increase and decrease, respectively, when c_3 increases. The same intersection point means that both roots are physically equivalent at low c_3 values for a component with $\Omega=1$ and it is possible for one part of the peak to follow root 1 and another part to follow root 2, this will cause a strong broadening of the peak.

Numerical examples of the two roots that are obtained for the case when $u_3>u_1$ are shown in Fig. 5a (root 1) and Fig. 6a (root 2). The parameters are the same as in Figs. 3 and 4 except that the u_1 and u_3 values are interchanged. In the limit $c_3\rightarrow 0$ both roots show the same pattern as in Figs. 3 and 4, i.e., the velocity is well described by Eq. (9a) for root 1 and Eq. (9b) for root 2. The concentration of component 1 also follows the same pattern since $c_1\rightarrow c_1'$ for root 1 and $c_1\rightarrow\Omega c_1'$ for root 2 in the limit $c_3\rightarrow 0$. When c_3 increases the discussion in the Theory section showed that when Ω approaches unity the range of c_3 values that gives real velocity values becomes more and more limited. This is clearly seen in the figures where the curves becomes interrupted at successively lower c_3 values the closer Ω is to unity. When $\Omega=1$ the solution of the mass balance equation gives an imaginary value for the velocity also for vanishingly small concentrations of component 3 and this case can therefore not be presented in the figures. The calculated c_1 values that correspond to the two velocity roots are shown in Figs. 5b and 6b,

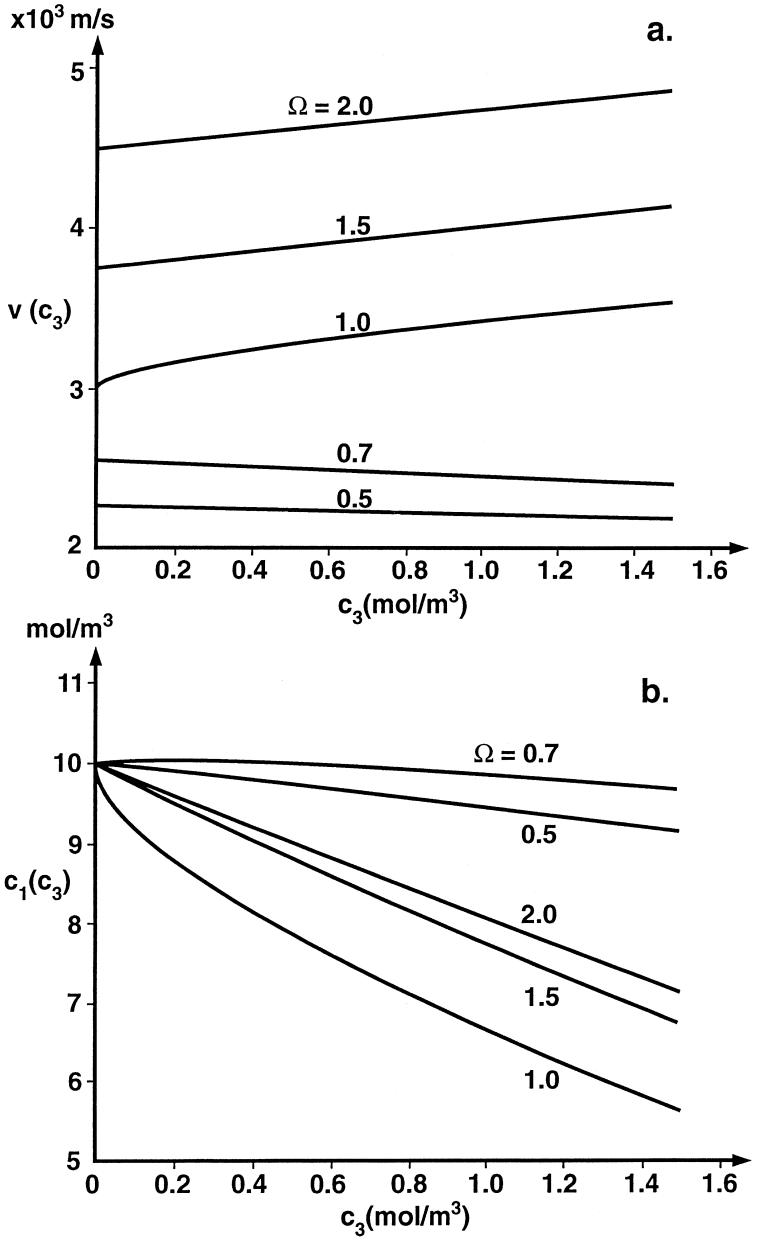

Fig. 3. (a) Calculations according to root 1 of Eq. (6) for the velocity of the moving boundary as a function of the concentration of component 3 with Ω as the parameter. (b) The concentration of component 1 in the zone which satisfies the coherence condition, as a function of the concentration of component 3, with Ω as the parameter. In both figures the parameters in Eq. (6) have the following values: $k=1$, $v_0=3\cdot10^{-3}$ (m/s), $u_1=8\cdot10^{-8}$ (m^2/V s), $u_2=-6\cdot10^{-8}$ (m^2/V s), $u_3=5\cdot10^{-8}$ (m^2/V s), $c_1'=10$ (mol/m^3).

respectively. The physical interpretation of an imaginary value for the velocity is that no concentration of component 1 exists which can satisfy the coherence condition. In analytical applications this implies that the peak will broaden in an uncontrolled and unpredicted manner.

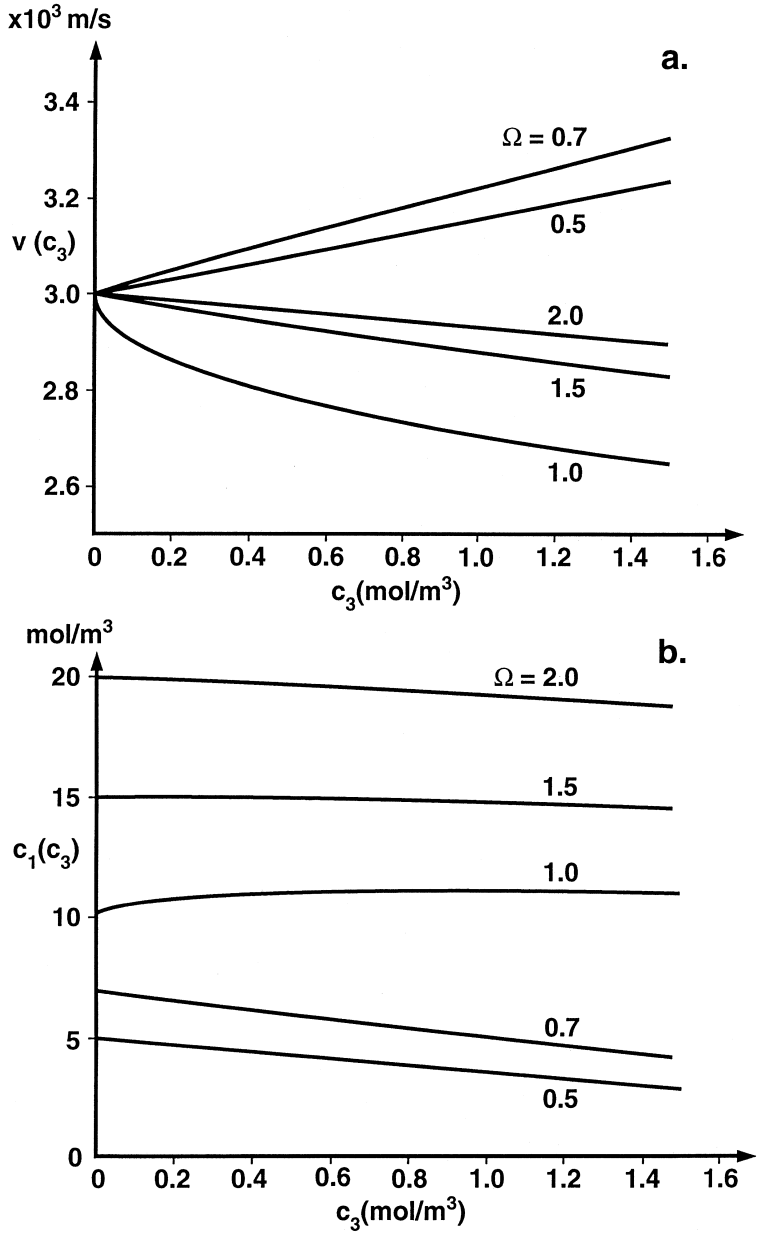

Fig. 4. (a) and (b) The same calculations as in Fig. 3a and b but according to root 2 of Eq. (6).

4. Conclusions

A mass balance analysis for a moving boundary of ionic species in electrochromatography results in a complex behaviour. The complexity is due to the simultaneous requirement of coherence and equilibrium with the stationary phase in combination with the electroneutrality condition in both the eluent and on the stationary phase. In the limit of low analyte concentration, the introduction of the electrochromatographic migration number Ω, defined by Eq. (5), facilitates the analysis of the equations which

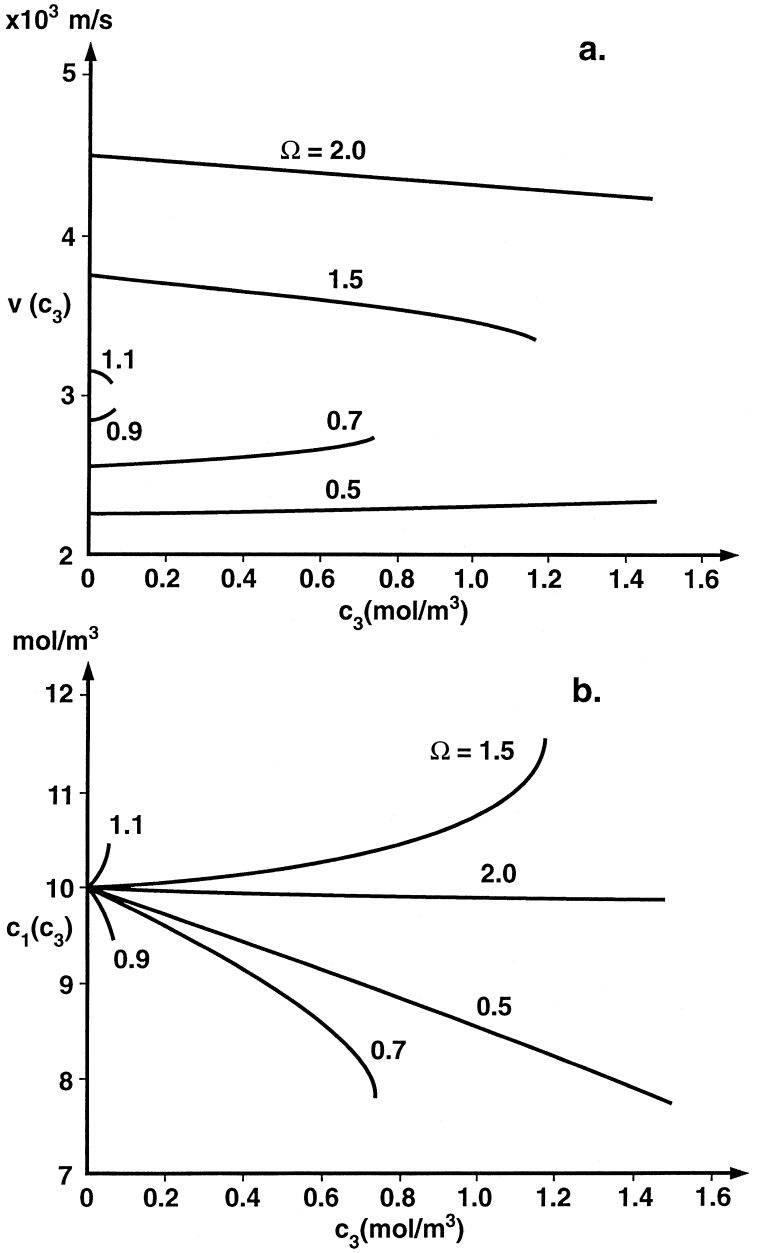

Fig. 5. (a) Calculations according to root 1 of Eq. (6) for the velocity of the moving boundary as a function of the concentration of component 3 with Ω as the parameter. (b) The concentration of component 1 in the zone which satisfies the coherence condition, as a function of the concentration of component 3, with Ω as the parameter. In both figures the parameters in Eq. (6) have the same values as in Figs. 3 and 4 except that the values for u_1 and u_3 are interchanged, i.e.,: $k=1$, $v_0=3\cdot10^{-3}$ (m/s), $u_1=5\cdot10^{-8}$ (m^2/V s), $u_2=-6\cdot10^{-8}$ (m^2/V s), $u_3=8\cdot10^{-8}$ (m^2/V s), $c_1'=10$ (mol/m^3).

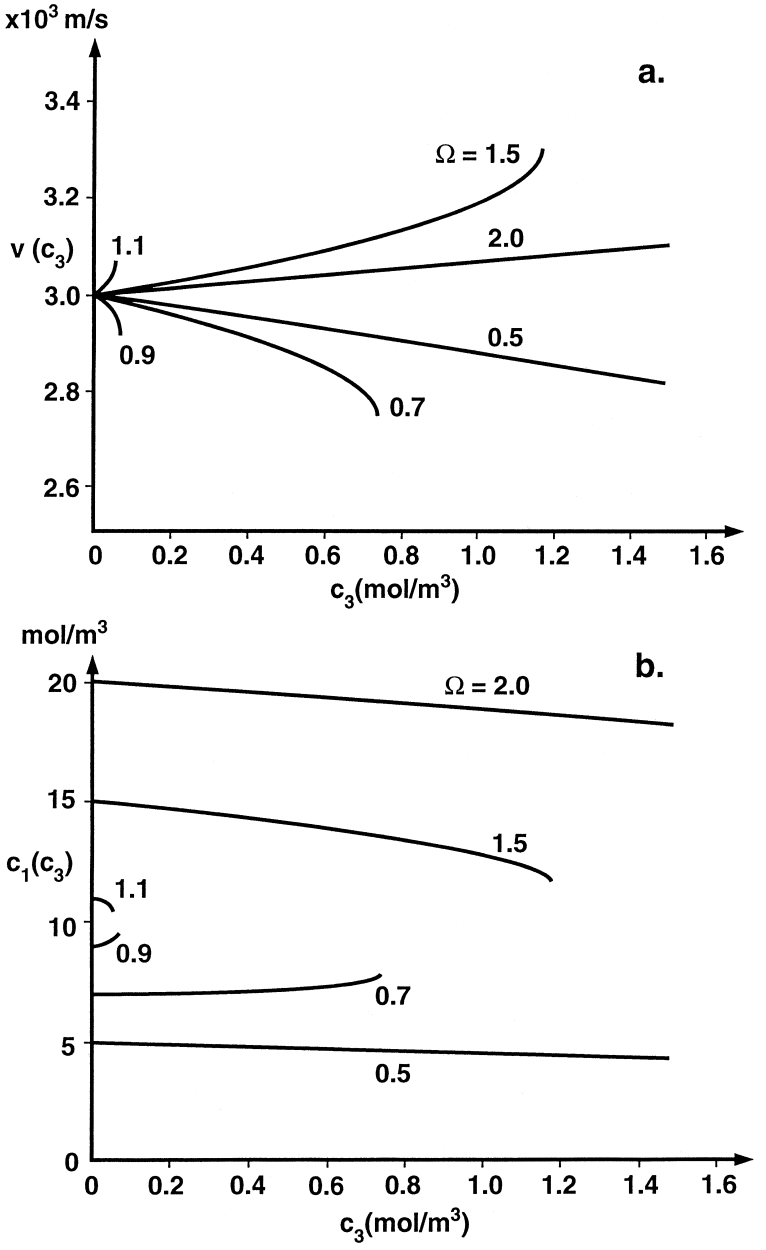

Fig. 6. (a) and (b) The same calculations as in Fig. 5a and b but according to root 2 of Eq. (6).

emerge from the mass balance analysis. For example, the theory shows that the case $\Omega = 1$ requires a special treatment. For this special case, and when the mobility of the analyte is higher than that of its co-ion in the eluent, it is not possible to obtain a stable peak that moves along the column. Also when

the mobility of the analyte is lower than the co-ion, uncontrollable effects on the peak shape may occur when $\Omega = 1$.

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