Calculation of the composition of sample zones in capillary zone electrophoresis
I. Mathematical model

J.L. Beckers

Eindhoven University of Technology, Laboratory of Instrumental Analysis, P.O. Box 513, 5600 MB Eindhoven, Netherlands

Abstract

A mathematical model was set up for the calculation of all parameters in sample zones in capillary zone electrophoresis. In this model, sample peaks are divided into small segments with varying sample component concentrations and all parameters of a segment can be calculated from the parameters of the preceding segment with a steady-state model, based on the mass balances of the co- and counter ions, the electroneutrality equation and the modified Ohm's law. In this way, non-steady-state electrophoretic processes can be estimated by a repeated application of a steady-state model. Although in this model only the electrodispersive effect is considered and other peak broadening effects, such as diffusion, are neglected, this model is very useful to obtain an insight into the electrophoretic separation procedure and to calculate how parameters change in a sample zone. Calculations with this model show that linear relationships are obtained between the concentration of the sample component and other parameters, such as the pH, concentrations of co- and counter ions, electric field strength and specific resistance in the sample zone, if the sample concentration is not extremely high. With this model electropherograms can be simulated on a spatial basis whereby all possible detector signals can be calculated. The combined effect of a change in pH, resulting in a change in effective mobility for weak acids and bases, and a change in the electric field strength leads to a change in the apparent mobility of the different segments of the sample peaks. For sample ions, both anions and cations, with a mobility higher than that of the co-ions of the background electrolyte a diffuse front side results from the calculations whereas tailing peaks are obtained for sample components with low mobilities.

1. Introduction

In capillary zone electrophoresis (CZE), ionic sample components migrate superimposed on a background electrolyte (BGE). Often it is stated that the influence of the presence of sample components on the composition of the BGE can be neglected if the sample concentrations are at least a factor of 100 lower than that of the BGE [1]. In that case, the composition of the BGE can be considered to be constant through the whole system. In practice, this is often not true. Component peaks often have a strong tailing or fronting character if the mobilities of the sample components differ from those of the co-ions of the BGE, whereas experimentally determined mobilities, calculated from the migration times of the top of the peaks, differ considerably from values in the literature, indicating a large influence of electrodispersive effects. Of course, these effects can be minimized by choosing a BGE with a co-ion, the mobility of which is

nearly equal to that of the sample component to be determined [1]. Nevertheless it is of interest to study whether arithmatic corrections can be carried out for electrodispersive effects. For this purpose, a mathematical model is needed to calculate all parameters in the sample zones in the electrophoretic process.

For isotachophoresis (ITP), whereby generally a steady-state is reached, steady-state models are often applied [2]. In such steady-state models the number of reduced parameters is generally four [3] and the equations needed for all calculations are the buffer balance, the isotachophoretic condition, the electroneutrality equation and the modified Ohm's law. For zone electrophoretic processes, dynamic models are generally applied, based on the continuity equations for all ionic species. Simulations of the CZE process can be carried out by means of a numerical solution of the basic transport equations [4,5]. Neglecting diffusion and generally applied for fully ionized monovalent electrolytes, Kohlrausch's regulating function can be derived from the continuity equations and solutions for zone electrophoretic processes can be given [6,7]. Such models produce for CZE the typical triangle-shaped peaks indicating that diffusional effects are significantly dominated by electrodispersive effects.

With such models, no information can be obtained about, e.g., the pH in the sample zones. Also, the application of the concept of the "eigenvalues" [8] did not lead to a simple solution for the calculation of the various parameters in the sample zones in CZE. Recently, Beckers [9] applied a steady-state mathematical model to estimate non-steady-state processes in capillary electrophoresis and from calculations with this model the character of system peaks and moving boundaries originating from discontinuities in pH and concentrations of the BGE could be explained. With this model, parameters such as the pH and the concentrations of all ionic species in system peaks could be calculated. Component peaks in CZE can be treated in a similar way. In this paper the calculation of the composition of sample peaks is considered, applying a steady-state model. With this model a computer program is set up for the simulation of electropherograms on a spatial basis.

2. Theoretical

Most mathematical models applied in CZE are based on Kohlrausch's regulating function (KRF), derived from the continuity equations for fully ionized monovalent ionic species and neglecting diffusion effects. Often the KRF is applied in the form

$$\sum_i \frac{c_i}{m_i} = \omega \qquad (1)$$

where c_i and m_i represent the ionic concentrations and absolute values of the effective ionic mobilities of all ionic constituents. The numerical value ω of the KRF is locally invariant with time [10]. Sometimes moving boundary zones can be created by the presence of discontinuities in concentrations of the co-ions and/or pH of the BGE. In such cases the ω value of KRF seems not to be locally invariant with time. Beckers [9] estimated these non-steady-state processes in capillary electrophoresis with a steady-state mathematical model. In a similar way, a mathematical model will be set up for the calculation of the parameters in sample zones in capillary zone electrophoresis.

2.1. Mathematical model

The shift in the baseline of the UV signal in electropherograms for a sample peak corresponds with a variation in the concentration of one of more UV-absorbing components present in the sample peak. For the derivation of a mathematical model, this shift is thought to be built up of small segments with increasing concentrations of the sample component. Calculations are started from the BGE zone with an electric field strength E_1, a pH_1 and a total concentration of the co-ions A of $c_{A,1}$. In the pure BGE solution no sample ions are present and because the composition of the BGE is known all parameters in the BGE can be calculated. For each following segment a total concentration of the sample component $c_{S,2}$ is assumed (see Fig. 1) and the other parameters E_2, pH_2 and $c_{A,2}$ are calculated with the given mathematical model. In this way, the number of
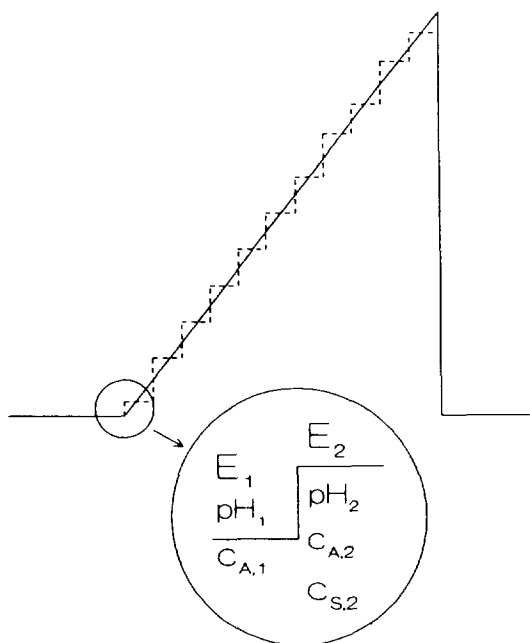
Fig. 1. For the calculation of parameters in sample peaks, the shift in the baseline is considered to be built up of small segments with increasing concentrations of the sample component. Calculations are started from the BGE with an electric field strength E_1, a pH_1 and a total concentration of the co-ions A of $c_{A,1}$. For each following segment a total concentration of the sample component $c_{S,2}$ is assumed and the other parameters E_2, pH_2 and $c_{A,2}$ are calculated with the given mathematical model.

unknown parameters in these segments is four, viz. the E_2, pH_2, $c_{A,2}$ and the concentration of the counter ions $c_{C,2}$. To calculate these parameters four equations are needed, viz., the mass balance of the co-ions A, the mass balance of the counter ions C, the modified Ohm's law and the electroneutrality equation. Analogously to a mathematical model already given [9], the mass balance of the hydrogen ions was not taken into account. In the calculations the following equations are used (see Refs. [2] and [9] for a complete description of all equations).

The principle of electroneutrality

In accordance with the principle of electroneutrality (EN), the arithmetic sum of all products of the concentration of all forms for all ionic species and the corresponding valences, present in each zone, must be zero [2].

Modified Ohm's law

According to Ohm's law, the product of the electric field strength E and electrical conductivity σ must be constant for all zones. The electrical conductivity, σ, of a zone is the sum of the values $c|mz|F$, where z and F represent the valency of the ionic species and the Faraday constant, respectively.

Mass balance of the co-ions A

The following derivation is given under the assumption that no electroosmotic flow (EOF) is present and that the mobility of the sample ions, S, m_S, is higher than that of the co-ions, m_A. In accordance with Ref. [9], all mass balances are taken over the front side of the adjacent segments. The notation m refers to the absolute values of the effective mobilities of the ionic components. The velocity of the zone boundary between the two segments 1 and 2 is determined by the velocity of the sample component S in zone 2, and this zone boundary moves in a unit of time from point 1 at time $t = 0$ (see Fig. 2A) to point 3 at time $t = 1$, over a distance $E_2 m_{S,2}$. The co-ions A present at point 2 at time $t = 0$ will just
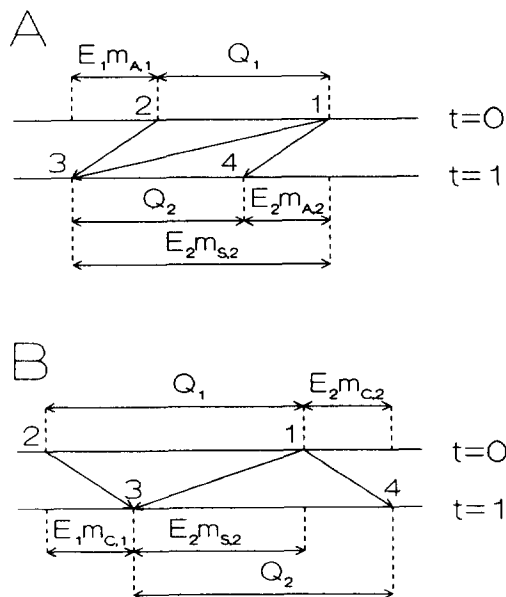

Fig. 2. Migration paths over a zone boundary between the segments 1 and 2 for (A) the co-ions A and (B) the counter ions C. For further explanation, see text.

reach the zone boundary at point 3 at time $t = 1$. The distance between point 2 and 3 is $E_1 m_{A,1}$. Co-ions in zone 2 present at point 1 at time $t = 0$ move over a distance $E_2 m_{A,2}$ to point 4 at time $t = 1$. This means that the co-ions present in zone 1 at a total concentration $c_{A,1}$ at time $t = 0$ between the points 1 and 2 will be present between the points 4 and 3 at a total concentration $c_{A,2}$ at time $t = 1$, i.e. that the amounts of the co-ions Q_1 and Q_2 are equal. Therefore, the mass balance of the co-ions over the zone boundary will be

$$c_{A,1}(E_2 m_{S,2} - E_1 m_{A,1})$$
$$= c_{A,2}(E_2 m_{S,2} - E_2 m_{A,2}) \qquad (2)$$

or

$$\frac{E_1}{E_2} = \frac{m_{S,2}}{m_{A,1}} - \frac{c_{A,2}(m_{S,2} - m_{A,2})}{c_{A,1} m_{A,1}} \qquad (3)$$

Identical equations are obtained if the co-ions have a mobility higher than that of the sample ions and are valid for both negatively and positively charged sample components even in the presence of an EOF.

Mass balance of the counter ions C

The zone boundary moves in a unit of time from point 1 at time $t = 0$ (see Fig. 2B) to point 3 at time $t = 1$ over a distance $E_2 m_{S,2}$. The counter ions C present at point 2 at time $t = 0$ will just reach the zone boundary at point 3 at time $t = 1$. The distance between points 2 and 3 is $E_1 m_{C,1}$. The counter ions present at point 1 at time $t = 0$ will move over a distance $E_2 m_{C,2}$ and will reach point 4 at time $t = 1$. All counter ions C present between point 1 and 2 in zone 1 at a total concentration $c_{C,1}$ will be present in zone 2 between 3 and 4 at a total concentration $c_{C,2}$ at time $t = 1$. The amount of counter ions Q_1 and Q_2 will be equal and the mass balance of the counter ions C will therefore be

$$c_{C,1}(E_2 m_{S,2} + E_1 m_{C,1}) = c_{C,2}(E_2 m_{S,2} + E_2 m_{C,2}) \qquad (4)$$

or

$$\frac{E_1}{E_2} = \frac{c_{C,2}(m_{S,2} + m_{C,2})}{c_{C,1} m_{C,1}} - \frac{m_{S,2}}{m_{C,1}} \qquad (5)$$

Identical equations are obtained in the presence of an EOF and all equations are identical for negatively and positively charged sample components with the understanding that for negatively charged components the negative ions of the BGE are the co-ions whereas the positive ions of the BGE are the counter ions, and vice versa.

2.2. Procedure of calculation

In order to calculate all parameters in the sample zones in CZE, the set of equations described above has to be solved. Starting from the known parameters of the BGE zone, for all segments of a sample zone with a specific sample component concentration of $c_{S,2}$ the parameters E_2, pH_2, $c_{A,2}$ and $c_{C,2}$ have to be calculated from those in the preceeding segment. In Fig. 3 the relationships between the calculated ratios E_1/E_2, according to Eqs. 3 (dashed lines) and 5 (solid lines), and varying concentrations $c_{A,2}$ are given for different assumed pH_2 values for a BGE consisting of (A) 0.01 M imidazole adjusted to pH 5 by adding acetic acid and the sample component potassium at a concentration of 0.0001 M and (B) 0.01 M Tris adjusted to pH 8.0 by adding acetic acid and a sample component chloride at a concentration of 0.0001 M. All mobilities at infinite dilution and pK values of the ionic species used in the calculations are given in Table 1. Because the values of E_1/E_2 according to Eq. 3 are nearly equal for all pH_2 values, they are represented by a single dotted line, whereas the E_1/E_2 values obtained from Eq. 5 vary considerably for different $c_{A,2}$ and pH_2 values. From Fig. 3A and B, it can be concluded that for each $c_{A,2}$ value always a pH_2 value can be found whereby the values of E_1/E_2 calculated with Eqs. 5 and 3 are equal. Application of the EN and Ohm's law results in the correct pH_2 and $c_{A,2}$ values for a given $c_{S,2}$ value.

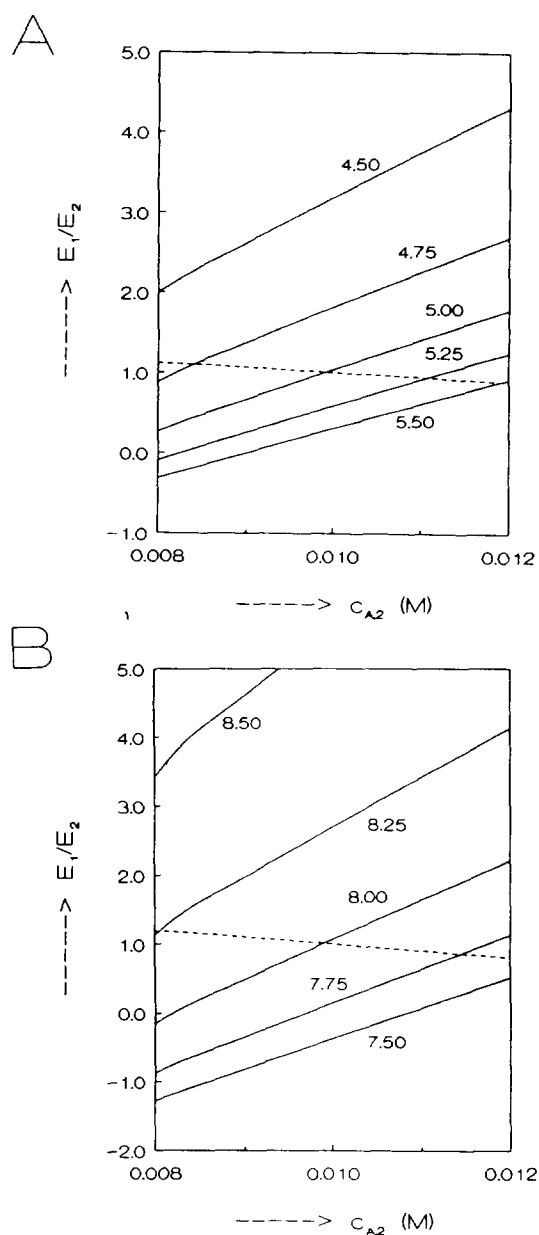The calculation of the parameters of segment 2

Fig. 3. Calculated relationships between the ratios E_1/E_2, according to Eqs. 3 (dashed lines) and 5 (solid lines), and varying concentrations $c_{A,2}$ are given for different assumed pH_2 values for a BGE consisting of (A) 0.01 M imidazole adjusted to pH 5 by adding acetic acid and the sample component potassium at a concentration of 0.0001 M and (B) 0.01 M Tris adjusted to pH 8.0 by adding acetic acid and a sample component chloride at a concentration of 0.0001 M. The values of E_1/E_2 according to Eq. 3 are nearly equal for all pH_2 values. The numbers refer to the corresponding pH_2 values. For further information, see text.

Table 1
Ionic mobilities at infinite dilution, m (m²/V·s), and pK values for ionic species used in the calculations

Ionic species[a]	$m \cdot 10^9$	pK
Acetic acid	−42.4	4.76
Benzoic acid	−33.6	4.203
Formic acid	−56.6	3.75
Histidine	29.7	6.03
Hydrochloric acid	−79.1	−2.0
Imidazole	50.4	6.953
Lithium	40.1	14.0
MES	−28.0	6.095
Potassium	76.2	14.0
TBA	25.0	>9.0
Tris	29.5	8.10

[a] MES = 2 − (N-Morpholino)ethanesulphonic acid; TBA = tetrabutylammonium; Tris = Tris(hydroxymethyl)amino-methane.

starting from these of the BGE is as follows (see Fig. 4). The concentration of the sample component, $c_{S,2}$, is assumed. Then a pH_2 is assumed whereby all pH-dependent parameters, such as the effective mobilities, can be calculated. Further, a $c_{A,2}$ is assumed whereby the total concentration of the counter ions $c_{C,2}$ can be calculated from the EN equation. Iterating between a low and a high value of $c_{A,2}$ the correct value of $c_{A,2}$ can be found whereby the values of E_1/E_2 are equal, applying Eqs. 3 and 5. The correct value for pH_2 can be found by iterating between a high and a low pH_2 until the modified Ohm's law is obeyed. The parameters for each following segment can be calculated with the same procedure starting from the parameters of the preceding segment.

2.3. Significance of the mathematical model

With a computer program, based on the foregoing mathematical model several parameters for sample zones in CZE are calculated. In the calculations corrections are made for activity coefficients and the mobility dependence according to Debye–Huckel–Onsager. In Fig. 5A the relationship is given between the concentration of the sample component c_S and the calculated pH in the sample zone for (1) potassium as
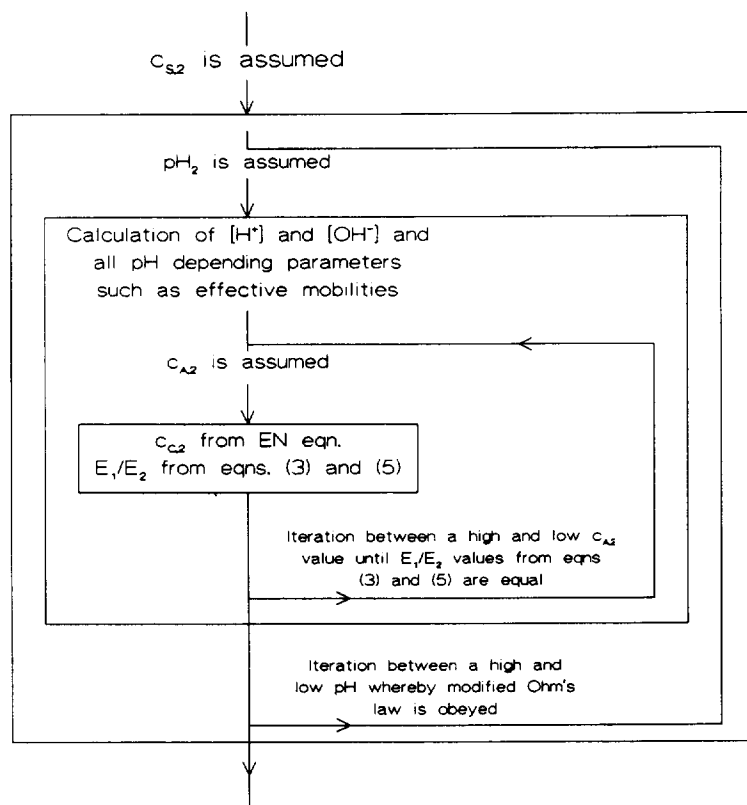
Fig. 4. Calculation procedure for the parameters in sample zones in capillary zone electrophoresis. In the calculation the mass balances of the co- and counter ions, the EN equation and the modified Ohm's law are used.

sample ions and (2) tetrabutylammonium (TBA) ions applying a BGE consisting of 0.01 M lithium ions adjusted to pH 5 by adding acetic acid. From Fig. 5A, it can be concluded that the pH in sample zones changes linearly with increasing concentrations of the sample components, whereby the pH in the zone decreases for sample components with a mobility lower than that of the co-ions in the BGE and increases for higher mobilities. This is in accordance with ITP, where the pH decreases for sample components with lower mobilities in cationic systems. In Fig. 5B, the relationships are given between c_S and (3, 4) the calculated ionic concentrations of the co-ions lithium and (5, 6) counter ions acetate for (3, 5) the sample component potassium and (4, 6) TBA, respectively. As expected from Kohlrausch's law, the ionic concentration of the co-ion lithium decreases for both sample com-

ponents. Because the transfer ratio, representing the number of co-ions replaced by one sample ion [11], is smaller than unity for potassium, because its mobility is higher than that of the co-ions, the decrease in concentration of the co-ions lithium is smaller than for TBA (transfer ratio > 1) at the same c_S. Further, the total ionic strength and the total concentration of the counter components increase in the case of potassium sample ions. Because of these effects, potassium ions would give a peak and TBA a dip on applying the indirect UV mode with UV-absorbing counter ions [12]. In Fig. 5C the ratios of the electric field strengths in sample zone and BGE, E_S/E_{BGE}, are given as a function of the concentrations c_S for (1) potassium and (2) TBA. For sample components with a mobility higher than that of the co-ions the E gradient decreases, whereas it increases for larger c_S values for
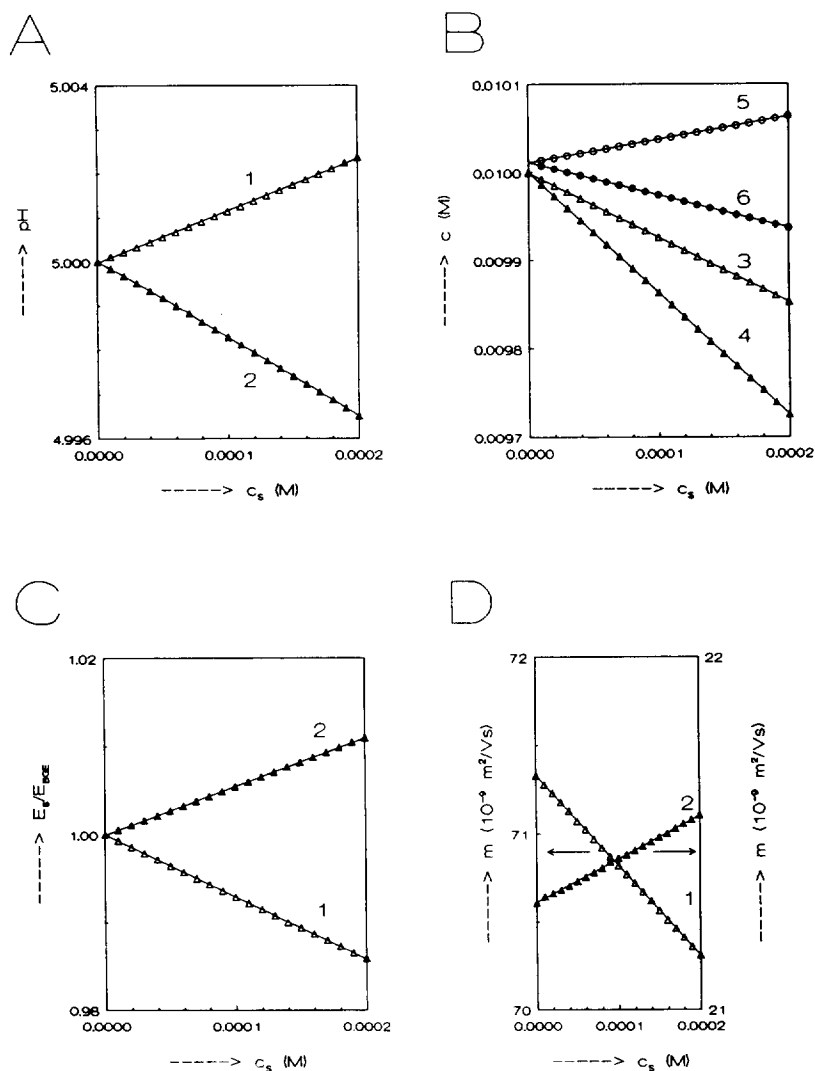
Fig. 5. Calculated relationships between the concentration of the sample component c_s and (A) pH, (B) ionic concentrations of counter and co-ions, (C) ratio E_s/E_{BGE} and (D) apparent mobility of the sample components in the sample zones applying a BGE consisting of 0.01 M lithium adjusted to pH 5 by adding acetic acid for (1) the sample component potassium with a mobility higher than that of the co-ions and (2) sample component TBA with a lower mobility. Ionic concentrations of the co-ions and counter ions are respectively (3, 5) for the sample component potassium and (4, 6) for the sample component TBA. For further explanation, see text.

sample components with a low mobility. Because the E gradient in the potassium zone decreases for higher concentrations of the sample component and because the ionic mobility of potassium is nearly constant, the apparent velocity of the potassium ions ($v = mE$) decreases. This results in the well known triangle-shaped peaks, because the higher concentrations of the sample peak migrate at a lower velocity. This explains the diffuse fronting peaks for sample components with a mobility higher than that of the co-ions and sharp tailing peaks for sample components with a lower mobility. If the mobilities of sample components and co-ions are different, Gaussian peaks can only be obtained by applying very sensitive detectors and for sample com-

ponent zones at very low concentrations. In that case the variations in electric field strength are so small that the contribution of peak broadening by diffusion is larger than that by electrodispersion. In Fig. 5D the effect of varying E gradients in the zone is shown. In Fig. 5D the relationship between the product of ionic mobility and E_S/E_{BGE} ratio which can be considered to be the apparent mobility of a specific segment of the sample peak and correcting in this way for the effect of varying E, and the concentration of the sample component c_S is given (if an EOF is present the apparent mobility can be presented as $m_i E_S/E_{BGE} + m_{EOF}$). It can clearly be seen that if mobilities are calculated from the top of sample peaks, for components with a high mobility too low mobilities are obtained, whereas for "slow" components an overestimation of the mobilities will be obtained.

In Fig. 6 the same parameters as described in Fig. 5 for cations are given for the anionic sample components (1) chloride and (2) MES applying a BGE consisting of 0.01 M formic acid adjusted to pH 6 by adding histidine. As shown in Fig. 6A, the pH decreases in sample peaks for a sample component with a mobility higher than that of the co-ions of the BGE, whereas the pH increases for components with a mobility lower than that of the co-ions, just as in anionic ITP. In Fig. 6B the lines (3, 4) represent the calculated total concentrations of the co-ions (left-hand scale) and (5, 6) the total concentrations of the counter ions histidine (right-hand scale). Because the pK value of the component MES is about 6, and the pH in the sample zone varies the total concentrations are given. From Fig. 6B it can be seen that the concentrations of the co-ions decrease with increasing concentrations of the sample components. This effect is larger for sample components with a low mobility. The concentration of the counter ions can both increase and decrease. If the mobility of the sample components is high, the transfer ratio is low and the ionic strength increases, through which the total concentration of the counter ions increases. For sample components with a high mobility the ratio E_S/E_{BGE} decreases (see Fig. 6C), resulting in a decrease in the apparent

mobility ($m_i E_S/E_{BGE}$) at higher sample concentrations c_S (see Fig. 6D). With this model the typical triangle-shaped character of sample peaks can be understood. For the sample component MES an irregularity is observable in all graphs at a c_S of about 0.00016 M, probably connected with its pK value of about 6.1.

3. Discussion

The basis of the mathematical model described is that sample zones are divided into segments with a specific sample concentration and calculations show that these segments are characterized by a specific mobility. Because the apparent mobilities of these segments vary by a combined effect of a variation in effective mobility, due to a varying pH in the sample peak, and in the ratio E_S/E_{BGE}, the for CZE typical triangle-shaped sample peaks are obtained. According to this model, the apparent mobility depends on the local concentration of the sample component c_S, as already indicated by several workers [8,10]. The beginning of the diffuse side of a sample peak, calculated on a spatial basis, at time t is positioned at the point

$$x = vt = m_{app,BGE} E_{BGE} t \qquad (6)$$

where $m_{app,BGE}$ is the apparent mobility of the sample component in the BGE ($c_S = 0$) and E_{BGE} is the electric field strength in the BGE. The position of a segment i with a specific concentration of the sample component can be calculated according to

$$x_i = v_i t = m_{app,i} E_{BGE} = m_{eff,i} E_i \qquad (7)$$

where $m_{app,i}$ is the effective mobility of a segment i recalculated to the applied electric field strength of the BGE, E_{BGE}. The calculations of the positions of the segments i are repeated until the summation of all products of the concentrations of the sample component c_i, length of the corresponding segment Δx_i and capillary area $A = \Sigma c_i \Delta x_i$ A is equal to the total injected amount of the sample component. In this treatment the back and front sides of the component
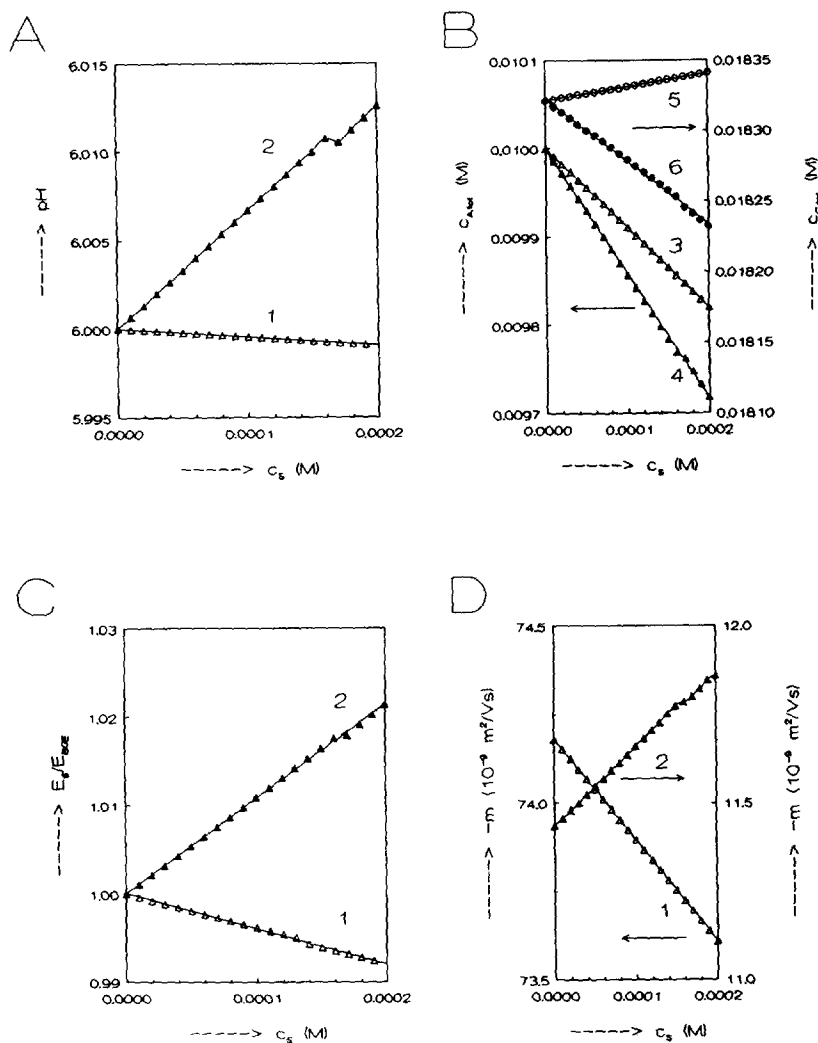
Fig. 6. Calculated relationships between the concentration of the sample component c_S and (A) pH, (B) total concentrations of counter and co-ions, (C) ratio E_S/E_{BGE} and (D) apparent mobility of the sample components in the sample zones applying a BGE consisting of 0.01 M formic acid adjusted to pH 6 by adding histidine for the sample component (1) chloride with a mobility higher than that of the co-ions and (2) MES with a lower mobility. Total concentrations of the co-ions and counter ions are respectively (3,5) for the sample component chloride and (4,6) for the sample component MES. For further explanation, see text.

peaks are assumed to be sharp and this model will only be valid if diffusion effects are negligible compared with the electrodispersive character of the sample peak. The electropherograms calculated in this way have a spatial character. As an example, sample peaks present in a capillary tube after a 300-s CZE separation, are calculated, for cations with mobilities of (1) 75, (2) 65, (3) 50, (4) 35 and (5) $25 \cdot 10^{-9}$

$m^2/V \cdot s$, respectively. All sample pK values are assumed to be 7. The BGE in the simulation was 0.01 M imidazole adjusted to pH 4.2 by adding benzoic acid. The results of the calculations are given in Fig. 7.

In Fig. 7A the concentrations of the sample components are given as function of the position of the peaks after a separation time of 300 s. It can be clearly seen that the calculated peaks are
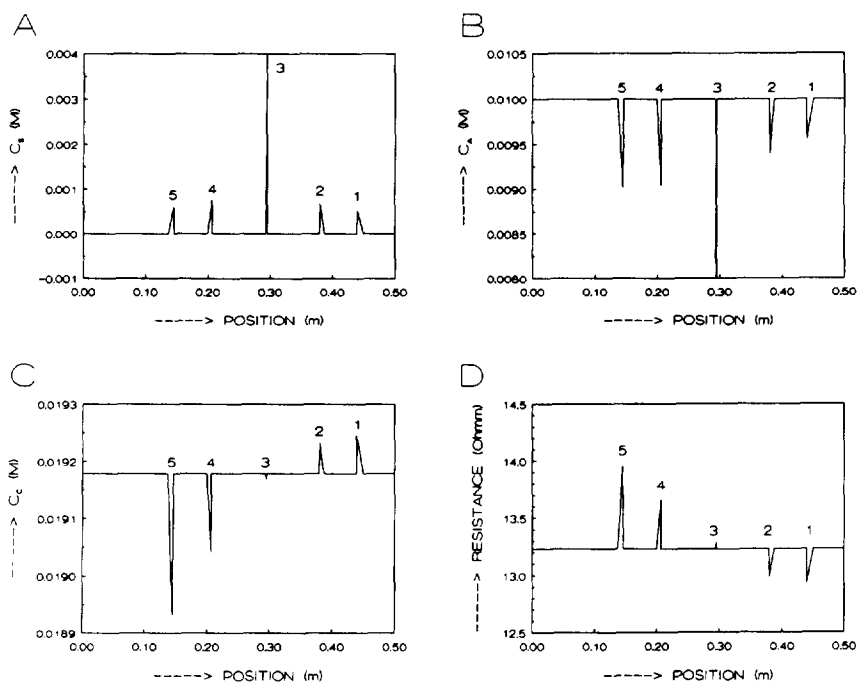
Fig. 7. Calculated (A) concentrations of the sample components, (B) concentrations of the co-ions A, (C) concentrations of the counter ions C and (D) zone resistances for sample peaks of cations with mobilities of (1) 75, (2) 65, (3) 50, (4) 35 and (5) $25 \cdot 10^{-9}$ m^2/V·s and a pK value of 7 as a function of the position in the separation capillary, applying a BGE consisting of 0.01 M imidazole adjusted to pH 4.2 by adding benzoic acid. The sample zones are calculated after a separation time of 300 s. Further simulation conditions: capillary diameter, 75 μm; capillary length, 0.467 m; injection–detection distance, 0.4 m; applied voltage, 10 kV; amounts injected for all sample compounds, $1 \cdot 10^{-11}$ mol. For further explanation, see text.

fronting if the sample components have a mobility higher than that of the co-ions (peaks 1 and 2) and tailing if their mobilities are lower (peaks 4 and 5). For a component with a mobility nearly equal to that of the co-ions (peak 3), a very sharp sample zone is obtained, because in the mathematical model peak broadening due to diffusion is neglected. In fact, the calculated sample concentrations in Fig. 7A represent the simulated electropherogram obtained on applying the direct UV mode, if the effect of the molar absorptivities is included. In Fig. 7B the calculated concentrations of the co-ions A are given for the different sample peaks in the capillary tube after the 300-s separation. Peak 3 is sharp again, whereas peaks 1 and 2 are fronting and 4 and 5 are tailing. It is notable that peaks 4 and 5 are larger than peaks 1 and 2, because the transfer ratios of components 4 and 5 are larger

than those of components 1 and 2 [11]. All components are present as negative peaks, as can be expected because Fig. 7B represents the classical "indirect UV" mode [12].

In Fig. 7C, the concentrations of the counter ions C are given for the sample peaks after the 300-s separation. As explained earlier [12], the sample peaks for components with a mobility higher than that of the co-ions are positive, whereas those for lower mobilities are negative. The reason is simple. The transfer ratio for sample components with a mobility higher than that of the co-ions is smaller than unity, i.e., in the sample peak the ionic strength increases, as can be seen in Fig. 7C. If the counter ions C are the only UV-absorbing ions of the BGE in the electropherogram, negative and positive peaks are the result, as shown in Fig. 7C. For components with a mobility nearly equal to that of

the co-ions, the transfer ratio is unity, i.e. the concentration of the counter ions is constant. In Fig. 7D the specific zone resistances in the sample peaks are given for the 300-s separation. For sample components with a high mobility (peaks 1 and 2) the zone resistances decrease whereas for components with low mobilities the zone resistances increase (peak 4 and 5). It is satisfying that the results of this mathematical model, based on mass balances, correspond with the results of a total different model based on Kohlrausch's regulation function as described in Ref. [12].

4. Conclusions

All parameters of the sample zones in CZE can be calculated by a mathematical model, whereby non-steady-state processes in CZE can be estimated by repeated application of a steady-state model to sample zones divided into segments. The calculations are started from the diffuse side of the peak, where the composition of the sample peak differs only slightly from that of the BGE and it is assumed that Ohm's law, the electroneutrality and the mass balances of the co-ions and counter ions must be obeyed. Calculations with this model show that linear relationships are obtained between concentrations of the sample ions and parameters such as the pH, concentrations of co- and counter-ions, E gradients and specific resistance in the sample zone on a spatial basis. The combined effect of the change in pH, resulting in a changing effective mobility for weak acids and bases, and the change in the electric field strength E leads to a change in apparent mobility of the different segments of the sample peaks. For sample ions, both anions and cations, with a mobility higher than that of the co-ions of the BGE a diffuse

front-side results from the calculations whereas tailing peaks are obtained for sample components with low mobilities, as is known from experiments.

Applying this model, simulated electropherograms on a spatial basis can be calculated. The limitations of the described mathematical model are obvious. In this model, peak broadening effects due to the diffusion and differences in temperature in the radial and axial directions are neglected. In this model all sample peaks are considered apart, and initial effects connected with the co-migration of the different sample components and the effect of, e.g., sample stacking cannot be treated. In Part II this mathematical model will be used for the simulation of electrophoregrams on a temporal basis, through which simulated and measured electropherograms can be compared to check the model.

References

[1] F. Foret, S. Fanali, L. Ossicini and P. Boček, *J. Chromatogr.*, 470 (1989) 299.
[2] J.L. Beckers and F.M. Everaerts, *J. Chromatogr.*, 480 (1989) 69.
[3] F.M. Everaerts, J.L. Beckers and Th.P.E.M. Verheggen, *Isotachophoresis –Theory, Instrumentation and Applications*, Elsevier, Amsterdam, 1976.
[4] M. Bier, O.A. Palusinksi, R.A. Mosher and D.A. Saville, *Science*, 219 (1983) 1281.
[5] R.A. Mosher, D.A. Saville and W. Thormann, *The Dynamics of Electrophoresis*, VCH, Weinheim, 1992.
[6] F.E.P. Mikkers, F.M. Everaerts and Th.P.E.M. Verheggen, *J. Chromatogr.*, 169 (1979) 1.
[7] W. Thormann, *Electrophoresis*, 4 (1983) 383.
[8] H. Poppe, *Anal. Chem.*, 64 (1992) 1908.
[9] J.L. Beckers, *J. Chromatogr. A*, 662 (1994) 153.
[10] F.E.P. Mikkers, *Thesis*, Eindhoven University of Technology, Eindhoven, 1980.
[11] M.W.F. Nielen, *J. Chromatogr.*, 588 (1991) 321.
[12] J.L. Beckers, *J. Chromatogr. A*, 679 (1994) 153.