Modelling of the migration effect occurring at an ISFET-based coulometric sensor–actuator system

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Abstract

The migration effect, in addition to diffusion, occurring at an ion-selective field-effect transistor (ISFET)-based coulometric sensor–actuator system has been studied. A diffusion–migration model is presented, based on the numerical solution of the Nernst–Planck equations of which a digital simulation is realized. Corresponding experiments were carried out and compared with the simulation. The results are in good agreement with the simulation.

Typical titration times of this system were found to be 0.5–10 s, corresponding to fully dissociated acid concentrations of 0.5×10^{-3} – 6.5×10^{-3} mol l⁻¹ with excess of supporting electrolyte. Both the simulation and experimental results show that if the concentration of the supporting electrolyte is ≥ 20 times higher than that of the species to be titrated, the deviation caused by migration is less than 5% and within the experimental error when pure diffusion is considered. At relatively low concentrations of supporting electrolyte, the migration effect should be taken into account to determine the concentrations of titrated species.

Keywords: Ion-selective field-effect transistor; Migration effect

The theoretical study of a coulometric sensor–actuator system based on an ion-sensitive field-effect transistor (ISFET) is a fundamental contribution to the development of coulometric sensor–actuators and the application of these devices. The advantage of the integration of an ISFET and an actuator is that it is possible to eliminate the long-term drift of the ISFET by operating it in a dynamic way and, as coulometry is an absolute method, regular calibration is not necessary. For the correct operation of the coulometric sensor–actuator, it is of importance to understand fully the dynamic behaviour of the coulometric sensor–actuator system.

The coulometric sensor–actuator is made by depositing a planar noble metal electrode on top of an ISFET closely shaped around the gate area

(Fig. 1). The ISFET works as a fast pH sensor. By coulometrically generating protons or hydroxyl ions at the electrode, the local pH in the vicinity of the ISFET can be changed or controlled, depending on the purpose of the application. For example, when an acid–base titration is performed [1], the electrode operates under current control and the ISFET indicates the equivalence point. By recording the time needed to reach the equivalence point, the concentration of base or acid can thus be calculated. Another application of this sensor–actuator system is the construction of a pH-static enzyme sensor [2]. In this instance, the ISFET detects the pH change resulting from the enzymatic reaction in the membrane which covers the sensor–actuator. The output of the ISFET is fed into the computer, which controls

Fig. 1. (a) Top view and (b) cross-section of the coulometric sensor-actuator device. The active area of the actuator is $1 \times 1 \text{ mm}^2$.

the current flowing through the actuator. The resulting protons or hydroxyl ions thus generated can compensate the pH changes resulting from the enzymatic reaction in the membrane and keep the pH value in the membrane constant. As the ISFET in this application is used in a "static" mode, the sensor is sensitive to long-term drift, but the system is nevertheless superior to the usual open-loop operation of an ENFET.

Although the ISFET-based coulometric sensor-actuator has been successfully used to determine acid or base concentrations [1], to form the heart of a carbon dioxide sensor [3] and a pH-static enzyme sensor [2], less attention has been paid to the theoretical aspects. Recently a theoretical model for this sensor-actuator system has been proposed, which describes the dynamic

behaviour of the system when used in an acid-base titration [4]. The experimental results were found to be in agreement with the theoretical predictions. However, this model considered only the diffusion process and is valid only in the case when a relatively high concentration of supporting electrolyte is added to the solution and for the titration of a weak acid, because the supporting electrolyte increases the conductivity of the solution and decreases the electrical field, so that the migration can be neglected and the mass transport is simplified to free diffusion (convection is assumed to be absent in the stagnant solution). The Sand equation [5] can then be used to predict the concentration profile of the species before it reaches zero concentration at the surface of the generating electrode. In some instances, however, the migration effect cannot be neglected. For example, when a titration is carried out in a fully dissociated acid or base in which the mobility of protons or hydroxyl ions is much higher than that of other ions and the concentration of supporting electrolyte is relatively low, a large error will result from the model if only the diffusion is taken into account. In order to estimate the deviation caused by migration, it is also necessary to specify the limiting value, set for the "excess" concentration of the supporting electrolyte.

Considering both the diffusion and the migration effects, it is first necessary to solve the Nernst-Planck equations. It has been proved to be a non-trivial task to find a rigorous analytical solution [6,7]. Some numerical solutions were proposed in the past [8-10]. One of the earliest efficient numerical solutions for these coupled non-linear differential equations dates back to 1965 [8]. However, Mak and Cheh [11] revealed that only a few studies concentrated on the galvanostatic system, most of the studies being carried out without experimental verification. In this work, the numerical solutions of the Nernst-Planck equations were derived without referring to the Poisson equation and the migration effect occurring at an ISFET-based sensor-actuator coulometric system in the case of acid-base titration was studied. The corresponding experiments were also carried out and the results are compared with those of the numerical solution.

DIFFUSION-MIGRATION MODEL

Theory

The products generated at the surface of the actuator by the hydrolysis of water depend on the direction of the current; the electrode reactions are

The protons or hydroxyl ions generated react with the hydroxyl ions or protons, respectively, in the aqueous solution at the surface of the actuator, causing a decrease in the surface concentration of the reacted ions, which results in a chemical potential gradient. Mass transport then occurs because of this chemical potential gradient.

Mass transport is governed by the Nernst-Planck equations. Here only a one-dimensional model is considered in which the convection is assumed to be absent (stagnant solution). For linear mass transfer the Nernst-Planck equation is presented as follows:

$$J_j = -D_j \frac{\partial C_j(x, t)}{\partial x} - \frac{z_j F}{RT} D_j C_j(x, t) \frac{\partial \phi(x, t)}{\partial x} \quad (1)$$

where J_j and C_j are the flux and concentration, respectively, of species j , D_j and z_j are the diffusion coefficient and the valence of species j , respectively, $\partial\phi/\partial x$ is the electric potential gradient and F , R and T have their usual meanings. Considering the conservation of material, the continuity equation is given by

$$\frac{\partial C_j(x, t)}{\partial t} = - \frac{\partial J_j(x, t)}{\partial x} \quad (2)$$

Substituting Eqn. 1 into Eqn. 2 results in

$$\begin{aligned} \frac{\partial C_j(x, t)}{\partial t} = & D_j \cdot \frac{\partial C_j(x, t)}{\partial x^2} \\ & + \frac{z_j F D_j}{RT} \left[\frac{\partial C_j(x, t)}{\partial x} \cdot \frac{\partial \phi(x, t)}{\partial x} \right. \\ & \left. + C_j(x, t) \cdot \frac{\partial^2 \phi(x, t)}{\partial x^2} \right] \quad (3) \end{aligned}$$

This is the equation describing both the diffusion and the migration processes. The first term on the

right-hand side of Eqn. 3 reflects the diffusion and the second the migration. It is hardly possible to obtain a rigorous analytical solution of this equation, because $\partial\phi/\partial x$ and $\partial^2\phi/\partial x^2$ are caused by the displacement of all ions, so that they are dependent on the concentrations of all ions. This means that all equations which describe the behaviour of ions are interdependent and that a groups of equations should be considered simultaneously. In order to obtain a numerical solution the expression of $\partial\phi/\partial x$ in terms of $C_j(x, t)$ should be found.

Because the current flow in the solution is carried by all charged species, during the electrolysis the flux J_j is equivalent to the current density carried by species j , which can be separated into diffusion and migration parts. The equation can be written as

$$-J_j = \frac{I_j}{z_j F A} = \frac{I_{d,j}}{z_j F A} + \frac{I_{m,j}}{z_j F A} \quad (4)$$

where A is the electrode area, I_j the current carried by species j and $I_{d,j}$ and $I_{m,j}$ are the corresponding diffusion and migration parts of I_j . Comparing Eqn. 1 with Eqn. 4 results in

$$\frac{I_{d,j}}{z_j F A} = D_j \cdot \frac{\partial C_j(x, t)}{\partial x} \quad (5)$$

$$\frac{I_{m,j}}{z_j F A} = \frac{z_j F D_j}{RT} \cdot C_j(x, t) \cdot \frac{\partial \phi(x, t)}{\partial x} \quad (6)$$

Summing Eqns. 5 and 6 for all n species and rearranging them, the total diffusion and migration currents are obtained:

$$I_d = \sum_n I_{d,j} = F A \sum_n z_j D_j \cdot \frac{\partial C_j(x, t)}{\partial x} \quad (7)$$

$$I_m = \sum_n I_{m,j} = \frac{F^2 A}{RT} \cdot \frac{\partial \phi(x, t)}{\partial x} \sum_n z_j^2 D_j C_j(x, t) \quad (8)$$

Equations 7 and 8 represent the diffusion and migration current resulting from the displacement of all charged species. As the charge must be conserved, the sum of the diffusion and migration currents is equal to the external Faradaic current:

$$I_d + I_m = I \quad (9)$$

Combining Eqns. 7 and 8 with Eqn. 9 yields

$$\frac{\partial \phi(x, t)}{\partial x} = \frac{I/FA}{\sum_n |z_j| u_j C_j(x, t)} - \frac{\sum_n z_j D_j \partial C_j(x, t)/\partial x}{\sum_n |z_j| u_j C_j(x, t)} \quad (10)$$

where $u_j = |z_j| D_j F/RT$ is the mobility of species j .

Equation 10 is the expression of $\partial \phi/\partial x$ for the multi-ion system. The first term on the right-hand side results from the conductance of the solution when current is flowing through it and the second term is caused by the concentration gradient due to the ion transport. Using Eqns. 3 and 10 together with the given boundary and initial conditions, the numerical solution can be derived.

Numerical solution

The finite-difference form of Eqns. 3 and 10 are as follows:

$$\begin{aligned} \frac{C_j(x, t + \Delta t) - C_j(x, t)}{\Delta t} &= D_j \cdot [C_j(x + \Delta x, t) - 2C_j(x, t) \\ &\quad + C_j(x - \Delta x, t)] [(\Delta x)^2]^{-1} \\ &\quad - \frac{z_j F D_j}{RT} \cdot E(x, t) \\ &\quad + \frac{C_j(x + \Delta x, t) - C_j(x - \Delta x, t)}{2\Delta x} \\ &\quad - \frac{z_j F D_j}{RT} \cdot C_j(x, t) \\ &\quad + \frac{E(x + \Delta x, t) - E(x - \Delta x, t)}{2\Delta x} \end{aligned} \quad (11)$$

and

$$\begin{aligned} -E(x, t) &= \frac{I/FA}{\sum_n |z_j| u_j C_j(x, t)} \\ &\quad - \frac{\sum_n z_j D_j [C_j(x + \Delta x, t) - C_j(x - \Delta x, t)]}{2\Delta x \sum_n |z_j| u_j C_j(x, t)} \end{aligned} \quad (12)$$

where $E(x, t) = -\partial \phi(x, t)/\partial x$ is the electrical field.

The electrical field gradient $\partial^2 \phi/\partial x^2$ and concentration gradient $\partial C_j/\partial x$ are expressed as

$$\begin{aligned} \frac{\partial^2 \phi(x, t)}{\partial x^2} &= -\frac{\Delta E(x, t)}{\Delta x} \\ &= -\frac{E(x + \Delta x, t) - E(x - \Delta x, t)}{2\Delta x} \end{aligned}$$

and

$$\frac{\partial C_j(x, t)}{\partial x} = \frac{C_j(x + \Delta x) - C_j(x - \Delta x)}{2\Delta x}$$

When $x = x_k = k \Delta x$ ($k = 1, 2, \dots$), the prime (') denotes the time level t_{i+1} , and $C_j(k)$ is the concentration value of species j at $x = x_k$, then the numerical equations for Eqns. 11 and 12 become

$$\begin{aligned} C_j(k)' &= C_j(k) + W_j [C_j(k+1) - 2C_j(k) \\ &\quad + C_j(k-1)] \\ &\quad + \lambda_j E(k) [C_j(k+1) - C_j(k-1)] \\ &\quad + \lambda_j C_j(k) [E(k+1) - E(k-1)] \end{aligned} \quad (13)$$

and

$$\begin{aligned} -E(k) &= \frac{I/FA}{\sum_n |z_j| u_j C_j(k)} \\ &\quad - \frac{\sum_n z_j D_j [C_j(k+1) - C_j(k-1)]}{2\Delta x \sum_n |z_j| u_j C_j(k)} \end{aligned} \quad (14)$$

where

$$W_j = \frac{D_j \Delta t}{(\Delta x)^2} \quad \text{and} \quad \lambda_j = -\frac{z_j F D_j \Delta t}{2RT \Delta x}$$

At this point the initial and boundary conditions have to be considered. Before electrolysis, the solutes are homogeneously distributed. The concentrations at the electrode surface equal the bulk concentrations, so the initial equation is

$$C_j(x, t)|_{t=0} = C_{j,\text{bulk}} \quad (15)$$

As the flux is equivalent to the current density at the electrode, the boundary equation is obtained from Eqn. 1:

$$J_j|_{x=0} = -D_j \cdot \frac{\partial C_j(x, t)}{\partial x} \Big|_{x=0} - \frac{z_j F}{RT} \cdot D_j C_j(x, t) \cdot \frac{\partial \phi(x, t)}{\partial x} \Big|_{x=0} = -\frac{S_j I}{FA} \quad (16)$$

where S_j is the stoichiometric coefficient with respect to the chemical reaction. For the cathodic electrolysis of water at a noble metal electrode, $S_{OH} = 1$ and for other ions $S_j = 0$.

For the sake of accuracy, an image point is introduced at the $x = 0$ point, where the respective concentration is $C(-1)$. The corresponding numerical form of the boundary equation is

$$C_j'(-1) = C_j(1) - \frac{2S_j I \Delta x}{FD_j} + \frac{2z_j F \Delta x}{RT} \cdot C_j(0) E(0) \quad (17)$$

where

$$-E(0) = \frac{I/FA}{\sum_n |z_j| u_j C_j(0)} - \frac{\sum_n z_j D_j [C_j(1) - C_j(-1)]}{2\Delta x \sum_n |z_j| u_j C_j(0)}$$

As the reaction of protons and hydroxyl ions occurs simultaneously during the diffusion and migration processes, after each iteration step the equilibrium has to be re-established. The equation is

$$\left. \begin{aligned} C_H^{\text{eq}}(k) C_{OH}^{\text{eq}}(k) &= K_w \\ C_H^{\text{eq}}(k) - C_{OH}^{\text{eq}}(k) &= C_H(k) - C_{OH}(k) \end{aligned} \right\} \quad (18)$$

where C_H^{eq} and C_{OH}^{eq} are the concentrations of protons and hydroxyl ions after equilibrium is established. Solving this equation yields

$$\left. \begin{aligned} C_H^{\text{eq}}(k) &= 0.5 \left\{ C_H(k) - C_{OH}(k) \right. \\ &\quad \left. + \sqrt{[C_H(k) - C_{OH}(k)]^2 + 4K_w} \right\} \\ C_{OH}^{\text{eq}}(k) &= C_H^{\text{eq}}(k) / K_w \end{aligned} \right\} \quad (19)$$

Using Eqns. 13, 14, the initial eqn. 15 and the boundary eqn. 17, together with equilibrium Eqn. 19, the simulation can be realized. Either the concentration profiles of all ions at any given time or the concentration changes at any given distance from the actuator electrode can be determined. The corresponding pH change and the titration time t_{eq} to reach the equivalence point can also be calculated. As the equivalence point is detected by the ISFET, the gate of which is ca. 20 μm away from the actuator electrode, the concentration and pH changes of interest will be focused on the gate surface of the ISFET in the simulation. For a titration of the fully dissociated acid, when the calculated pH at the gate surface of the ISFET reaches 7, t_{eq} is determined.

From the diffusion model proposed [4], it is found that $t_{\text{eq}}^{1/2}$ can be expressed as an approximately linear function of the concentration of the species to be titrated. Consequently, the same expression will be adopted in this paper.

EXPERIMENTAL

Device

The construction of the sensor-actuator device has been described previously [12]. The ISFET was fabricated using a standard NMOS technique [13] with a tantalum pentoxide film as a sensing layer. A 0.3- μm platinum film was deposited on top of the ISFET chip around the gate area as a planar generating electrode (actuator). Between the tantalum pentoxide and the platinum there is a thin layer of titanium to improve the adhesion. Polyimide was used as a passivation layer to protect the device and leave a photolithographically defined 1-mm² window to expose the sensor to the solution, determining the desired active area of the generating electrode. The device is shown schematically in Fig. 1.

Two sensor-actuator devices were glued on a single printed circuit board and encapsulated with epoxy resin. On the reverse side of the board there is a copper strip with a deposited gold film on the surface, serving as the counter electrode.

Fig. 2. Measurement set-up for coulometric titration.

Measurement set-up

The measurement set-up is shown in Fig. 2. The measurements were carried out in a differential mode. One of the advantages of this operating mode is that it is possible to use a simple platinum wire as a pseudo-reference electrode instead of a normal liquid-filled reference electrode. In this specific case the actuator electrode of the second (reference) device serves as the pseudo-reference electrode. In this way, the influence of salt leakage from the liquid-filled reference electrode, which might change the concentration of the supporting

electrolyte during the measurement, is also avoided. The differential output of the amplifier was sampled by a computer and displayed on a cathode-ray tube. The equivalence point was easily detected from the first derivative of the output by calculating the time needed to reach the maximum. A typical recording of a coulometric titration is shown in Fig. 3.

Nitric acid was titrated in a 25-ml vessel with potassium nitrate as the supporting electrolyte. A constant current density of $20 \mu\text{A mm}^{-2}$ was used through all the experiments if not specified otherwise. After each measurement a reversed current was sent through the electrode and the solution was stirred to let it become homogeneous in the proximity of the electrode surface. After stirring there was a 1-min pause before the next measurement started in order to eliminate the effect of convection. It was found that the time needed to reach the equivalence point was reproducible within the experimental accuracy for a fixed acid concentration after a pause of > 30 s.

Fig. 3. Typical registration of the coulometric titration curve (solid line) and the first derivative (dashed line). $[\text{HNO}_3] = 3$ mM; $[\text{KNO}_3] = 100$ mM; titration time = 1.98 s.

Simulation

The simulation was realized with a personal computer using PASCAL. The actual distance of ca. $20 \mu\text{m}$ between the gate of the ISFET and the actuator electrode was accepted in the simulation. The current density was set at the same value as used in the experiments, normally $20 \mu\text{A mm}^{-2}$.

RESULTS AND DISCUSSION

The typical titration times required to reach the equivalence point t_{eq} were found to be 0.5–10 s, the corresponding titrated nitric acid concentrations being 0.5×10^{-3} – 6.5×10^{-3} mol l^{-1} with high concentrations of supporting electrolyte. If the titration is performed at a relatively low concentration of the supporting electrolyte, the electrical field caused by both the flow of the current and the concentration gradient of ions will enhance the transport of the H^+ ions from the bulk solution towards the actuator electrode. Hence, when the migration effect is taken into account, the titration time t_{eq} should be longer than the time found if only diffusion is considered.

Figure 4 shows $t_{eq}^{1/2}$ as a function of titrated acid in different concentrations of supporting electrolyte from both the simulation and the experimental results. As expected, the titration time increases when the concentration of supporting electrolyte decreases. Also, the curves gradually bend upwards and depart from the linear relationship for the pure diffusion at lower concentrations of supporting electrolyte; both the simulation and the experimental results show the same trend. The curvature is more pronounced at the intermediate concentration of supporting electrolyte (curve 2),

Fig. 4. Square root of titration time as a function of nitric acid concentration from the simulations (lines) and experiments (symbols). Line 1 and Δ , $[KNO_3] = 1$ mM; line 2 and $\blacksquare$, $[KNO_3] = 10$ mM; line 3 and $\bullet$, $[KNO_3] = 100$ mM; line 4, diffusion only.

Fig. 5. Influence of the supporting electrolyte. Results from simulations (lines; dashed lines indicate pure diffusion) and experiments (symbols). Line 1 and $\bullet$, $[HNO_3] = 1$ mM; line 2 and $\blacksquare$, $[HNO_3] = 2$ mM; line 3 and $\blacktriangle$, $[HNO_3] = 3$ mM; line 4 and $+$, $[HNO_3] = 4$ mM.

which corresponds to comparable concentrations of supporting electrolyte and electroactive species. This implies that the approximately linear relationship between $t_{eq}^{1/2}$ and the concentration of the species can be found if either the diffusion or the migration dominates the mass transport.

As noted, there is a slight difference between the simulation and experimental results, the experimental plot being more curved than that of the simulation. The explanation for this difference is possibly that edge effects contribute to the experimental deviation, because the gate of the ISFET is located near the edge of the electrode, where the current density is inhomogeneously distributed. Nevertheless, the experimental results are still in fairly good agreement with the theoretical predictions.

If the concentration of the electroactive species is fixed and that of the supporting electrolyte is changed as a variable, the migration effects can be seen more clearly. Figure 5 shows the simulation and experimental results, illustrating the influence of the supporting electrolyte. The experiment is also in good agreement with the simulation. It can be seen from both the simulation and the experiment that if the concentration of supporting electrolyte is decreased to approximate that of the

electro-active species, the titration time to reach the equivalence point, t_{eq} , is substantially increased, which means that not only the diffusion but also the migration contribute to the mass transport of ions. Obviously, it would cause a large deviation if only the diffusion process were considered in this instance.

From the above results it can be concluded that if the concentration of the supporting electrolyte is sufficiently high, the migration contributes only slightly to the mass transport of ions and can be neglected. The minimum concentration of the supporting electrolyte required to eliminate the migration effects is determined by the required accuracy. When the deviation of $t_{eq}^{1/2}$ between the pure diffusion process and both the diffusion and the migration process is calculated from the simulation results, it is found that if the concentration of the supporting electrolyte is ≥ 20 times higher than that of the electroactive species, the mass transport can be regarded as a pure diffusion; the deviation caused by migration is less than 5%, as can be deduced from curve 2 in Fig. 6, which shows the simulated deviation for different concentration ratios. This is considered to be acceptable, because it was found from the experiments

that a deviation of $\leq 5\%$ is within the experimental error. The deviation, Dev., from simulation results is calculated as follows:

$$\text{Dev.} = \frac{|t_d^{1/2} - t_m^{1/2}|}{t_d^{1/2}} \cdot 100\% \quad (20)$$

where t_d is the titration time to reach the equivalence point if only the diffusion is considered and t_m reflects the case when both diffusion and migration are considered.

It has been noted that the deviation caused by migration is dependent not only on the concentration ratio of the supporting electrolyte to the electroactive species, but also on the time needed to reach the equivalence point, which is determined by the acid-base concentration and the generating current density, because the accumulation of the deviation caused by migration becomes larger for a longer titration time. From the calculated deviation shown in Fig. 6, it is found that t_{eq} increases with increasing concentration of the electroactive species.

It should also be noted that in most of the literature, it was only indicated that the transference number could not be directly used to estimate the migration effect while diffusion occurs [11,14]. There was no proper parameter given to estimate quantitatively the deviation caused by migration. The extent of the migration effect was often shown in the form of the initial migration flux calculated from the transference number at the beginning of the electrolysis [5,11]. The reason is that at the beginning of the electrolysis there is no concentration gradient, whereas the migration flux is at its maximum value, and can thus easily be calculated via the transference number. However, with the initial flux deviation, the final deviation caused by migration still cannot be predicted. Although the migration flux in the following transport process continuously decreases and is smaller than the initial value, as the titration time increases, the small deviation will accumulate in a large difference. Figure 6 shows an increase in the deviation with increasing species concentration. Hence, the time needed to reach the equivalence point, determined by the acid or base concentration and the generating current density, must also

Fig. 6. Deviation of the square root of the titration time between the pure diffusion and diffusion-migration model vs. concentration of nitric acid, as obtained from the simulation. Concentration ratios of KNO_3 to HNO_3 are (1) 30:1, (2) 20:1 and (3) 10:1.

Fig. 7. Relationship between the square root of the titration time and the inverse of the current density. Results obtained from simulations (lines) and experiments (symbols). $[\text{HNO}_3] = 2 \text{ mM}$. Line 1 and Δ , $[\text{KNO}_3] = 1 \text{ mM}$; line 2 and $\blacksquare$, $[\text{KNO}_3] = 10 \text{ mM}$; line 3 and $\bullet$, $[\text{KNO}_3] = 100 \text{ mM}$; line 4, diffusion only.

be considered when estimating the deviation caused by migration.

The relationship between $t_{eq}^{1/2}$ and the inverse of the generating current density was found to be linear even considering the migration effect. The results obtained from the simulation and experiment are shown in Fig. 7. It has been reported [11] that, based on the theoretical analysis, a similar linear relationship exists between the transition time and the current density in galvanostatic chronopotential analysis with migration included. Our simulation, supported by the experimental results (Fig. 7), shows that this linear relationship can still be found when the position where the equivalence point is reached is even several tens of μm away from the actuator electrode within the diffusion layer.

During the electrolysis the hydroxyl ions are generated continuously from the surface of the cathodic electrode and react with the protons, eventually resulting in exhaustion of the protons. The established electrical field causes the potassium ions to migrate towards the actuator (cathode) and the nitrate to the counter electrode (anode). As they are chemically inactive species, their diffusion, due to the concentration gradient caused by migration, are in opposite directions to

Fig. 8. Surface ion concentrations and pH changes at the gate surface of an ISFET during the titration, as obtained from the simulation. Titration time = 3.19 s.

their migration. Therefore, the concentrations of both the electroactive species and the supporting electrolyte near the electrode change during the electrolysis. The changes in the ion concentrations and variation of the pH at the gate surface of ISFET obtained from the simulation are plotted in Fig. 8. Compared with the registration of the ISFET output shown in Fig. 3, the curve of the pH change was found to resemble the experimental observation.

Fig. 9. Ion concentration profiles when the equivalence point is reached. Results obtained from the simulation. Concentration of the supporting electrolyte = 100 mM; bulk concentration of nitric acid = 1 mM; titration time = 0.37 s.

Fig. 10. Ion concentration profiles when the equivalence point is reached. Results obtained from the simulation. Concentration of the supporting electrolyte = 1 mM; bulk concentration of nitric acid = 1 mM; titration time = 0.85 s.

The simulated concentration profiles and the electrical potential profiles at the time t_{eq} in an acid–base titration containing different concentrations of supporting electrolyte are plotted in Figs. 9 and 10 and Fig. 11, respectively. From the concentration profiles it can be seen that all the ions participate in the mass transport and contribute to the establishment of the electrical field. Because of the migration effect, the concentration of potassium ions near the cathodic actuator electrode increases and that of nitrate decreases (Figs.

9 and 10). However, with a high concentration of supporting electrolyte (Fig. 9), only very small relative changes are observed. In the proximity of the electrode, the electrical potential curve (Fig. 11) bends upwards from linearity (illustrated with a dashed line in Fig. 11); the higher the concentration of the supporting electrolyte, the more the electrical potential will curve. This means that more species arrive at the electrode by diffusion in the vicinity of the electrode with a higher concentration of the supporting electrolyte than with a lower concentration of the supporting electrolyte, resulting in a decreased potential gradient. With a very low concentration of the supporting electrolyte the electrical potential curve is almost a straight line (curve 2 in Fig. 11). In this instance, the electrical potential gradient near the electrode is approximately the same as that in the bulk solution where only migration exists and dominates the mass transport.

In conclusion, both the simulation and experiment show that, for the ISFET-based coulometric sensor–actuator system, with a relatively low concentration of supporting electrolyte, both the diffusion and migration will contribute to the mass transport of the ions and should be taken into account. The diffusion–migration model based on the numerical solution of Nernst–Planck equations as described here can be used to predict the dynamic behaviour of the system.

Fig. 11. Electrical potential profile when the equivalence point is reached at the gate of ISFET. Results obtained from the simulation. Bulk concentration of nitric acid = 1 mM. Line 1, $[KNO_3] = 100$ mM; line 2, $[KNO_3] = 1$ mM.

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