Radial Electrochemical Flow Cell for On-Line Coupling with Mass Spectrometry: Theory and Electrooxidation of Dimethylaminomethyl Ferrocene

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Abstract
A new, radial, miniature, three-electrode flow cell is introduced. The cell’s configuration is most suitable for on-line electrochemistry – mass spectrometry since it is characterized by low resistive losses, high conversion efficiency, and isolation of the counter electrode reaction by-products from the product stream reaching the MS. A mathematical model describing convection diffusion in the radial cell is developed. Cell’s performance can be predicted over a wide parametric range by a simple mathematical expression which converges to the Levich equation under low conversion conditions. The performance of the cell is demonstrated by studies of dimethylaminomethyl ferrocene (DMAMF) oxidation which is a simple single electron charge transfer reaction and allows validation of the mathematical model. The theoretical predictions of the model were in agreement with the results of on-line electrochemistry – mass spectrometry studies of DMAMF.

Keywords: Electrochemistry, Flow cell, Channel electrode, ESI-MS, MS, EC/MS, Dimethylaminomethyl ferrocene, Eigenvalue problem, Boundary value problem

1. Introduction
Electrochemistry coupled by on-line mass spectrometry (EC/MS) is a relatively young experimental technique. It is used for immediate identification of products, by-products and intermediates of electrochemical reactions. The first setup for on-line electrochemistry-mass spectrometry investigations was introduced by Brukenstein and Gadde in 1971 [1] for studies of gaseous products of fuel cells. The difficulty in introducing ionic and polar compounds into the vacuum chamber of the mass spectrometer was resolved with the advent of liquid chromatography-mass spectrometry, which faced a similar challenge. Indeed, thermospray (TSI) [2–13], particle beam (PBI) [14–16], and electrospray interfaces (ESI) [17–29], which were developed primarily for chromatographic applications, were adapted to couple electrochemistry and mass spectrometry. These interfaces enable transfer of the analytes into the gas phase and ionization of nonvolatile solutes. ESI transfers ionic species from the electrolyte into the gas phase without significant fragmentation. Therefore its application seems useful for mechanistic studies of electrochemical processes. ESI involves application of a few kilovolts to the metallic nozzle of the sprayer, which results in a spray current up to few microamperes. Faradaic processes maintain this current [30–32].

A flow through electrochemical cell is a central part of the EC/MS setup. Its quality determines the quality of the liquid sample studied by mass spectrometry. Flow cells of different designs were elaborated for EC/MS studies. A simple two-electrode electrochemical cell was used by Bond and co-workers [33] and Zhou and Van Berkel [34]. The duct from the pump to the ESI/MS included two metal capillaries which were used as the working and counter electrodes. Brajter-Toth and co-workers used a 12 cm² reticulated vitreous carbon working electrode [8–11]. To achieve high conversion efficiency in the cell and high electrolyte flow rate the authors sacrificed separation of counter, working, and quasi reference electrodes and used a porous flow-through electrode which is characterized by complex electrochemistry. A three-electrode flow cell with a graphite working electrode without separation of working and counter electrodes was used in Refs. [13, 14]. Limiting current of ferrocyanide reduction was not achieved in this flow cell [14], apparently due to substantial ohmic losses.

Cole and co-workers placed the electrochemical cell at the very tip of the electrospray nozzle in order to decrease the response time of the EC/ESI-MS [21, 26]. In this configuration the auxiliary electrode of the electrochemical cell functioned also as the high voltage electrode of the sprayer. This design necessarily subjects the electrodes of the electrochemical cell and the potentiostat itself to the high voltage of the sprayer, 2–4 kV. A similar design was used in [35]. The stainless steel needle of the electrospray was at the same time the working electrode of the three electrode cell. A battery was used instead of a potentiostat. Three-electrode thin layer flow cells without separation of working and counter electrode compartments were used by
The ESI decreases when flow rate increases. Close to 100% on the sprayed liquid. The effectiveness of ion emission in chemical processes, however, ESI possesses special constraints. Cation seems useful for studies of mechanisms of electrochemical reactions between the oxidation products and the electrochemical reaction products and reactants of the electrochemical reaction. Voltammograms and the potential dependent abundance of products and reactants of the electrochemical reaction during the potential scan [5, 6].

Since ESI transfers ionic species from the electrolyte into the gas phase without significant fragmentation, its application seems useful for studies of mechanisms of electrochemical processes. However, ESI poses special constraints on the sprayed liquid. The effectiveness of ion emission in the ESI decreases when flow rate increases. Close to 100% efficiency is achieved for 10–100 nL min⁻¹ flow rate [36]. Presence of electrolytes in the liquid suppresses the sensitivity of the ESI/MS measurements [36, 37]. Addition of volatile solvents (methanol, acetonitrile) to aqueous solutions increases the ESI/MS sensitivity [38]. A low concentration of electrolytes in the liquid implies its low conductivity, and thus ohmic drop along the channel electrode can significantly distort the electrochemical response of the thin layer cell [39].

Mechanistic studies of electrochemical processes require transition from qualitative description of the composition of cell effluent to quantitative analysis. The goal of this work is to develop a new electrochemical flow cell, with well characterized flow and predictable conversion that will also be compatible with the specific requirements posed by the downstream electrospay mass spectrometer. Electrochemistry and mass spectrometry provide complementing information. On-line EC/MS should provide means to compare voltammetric and MS responses, thus the EC/MS should provide clear and comprehensible current response and mass spectral data concurrently. The use of channel electrodes raises the problem of ohmic losses within the flow cell. The following additional contradictory requirements should be met in cell design.

1) The degree of conversion of the test substance in the cell should be variable within wide limits (preferably from 0 up to 1).

2) The cell should be provided with a qualitative mathematical description of convective diffusion enabling predictions of conversion efficiency of the cell.

3) The cell should be connected to the ESI by a duct enabling fast substance transfer and protection of electrochemical equipment from current leak from the electrostatic sprayer of ESI.

4) Compartments of reference and counter electrodes should be separated from the compartment of the working electrode channel to prevent mixing of products of cathodic and anodic reactions.

5) Operation of the Electrostatic sprayer necessitates passage of Faradaic currents in the test liquid. The interference of these currents on the liquid sample composition should be minimized compared to effect of electrochemical flow cell.

A new flow cell configuration is to meet the special challenges posed by EC/ESI-MS studies. Our first concern was to separate the counter electrode reactions from the flow stream to the mass spectrometer. This was achieved by using a three-compartment cell. Ag/AgCl 1 M KCl counter (CE) and reference (RE) electrodes separated by fine filter membranes were placed upstream of the working electrode (WE). The reason for choosing the upstream configuration will be discussed below. The RE compartment was connected to the chamber which encircled the working electrode (WE). Ag/AgCl 1 M KCl CE was chosen in order to eliminate bubble formation in the CE compartment. The ohmic drop in the electrolyte along the working electrode channel poses a problem which may limit the voltage resolution of the cell, and this was reduced by using a miniature WE.

To decrease ohmic losses along the working channel we used a relatively small disk electrode (d = 1.6 mm) and a high concentration of supporting electrolyte (0.1 M NH₄ Ac). We used a small flowrate in the cell (few µL min⁻¹) in order to obtain high conversion. In order to use a high concentration of aqueous electrolyte in the thin layer flow cell, we diluted the cell effluent by an auxiliary stream of methanol on the way to the mass spectrometer. The auxiliary methanol stream fulfilled several functions: It decreased the liquid conductivity in the transfer line from the flow cell to the ESI, thus uncoupling the high voltage of the ESI sprayer and the working electrode. It substantially decreased the residence time of the analyte in the sprayer line thus reducing unwanted contributions due to Faradaic reactions in the ESI. Dilution of the effluent also quenched chemical reactions between the oxidation products and the reactants, thus reducing compositional changes in the transfer line. Finally, addition of methanol increases the sensitivity of the ESI-MS by enhancing ionization in the spray chamber.

Radial configuration of electrolyte flow in the electrochemical cell was chosen since this design provides low dead volume, relatively small ohmic losses along the surface of the working electrode, high conversion efficiency, and high symmetry of the flow geometry which enables mathematical
description of convection-diffusion in the cell. Radial flow is widely used in amperometric and coulometric channel electrochemical cells [40–44]. However analytical description of convection-diffusion processes in channel electrochemical cells is available only for a few relatively simple cases [45–48] which either assume a frictionless, plug flow configuration or employ Lévêque approximations, i.e., constant velocity gradient perpendicular to the electrode surface and constant concentration in the bulk. Lévêque approximations are inapplicable for EC/ESI-MS cells since conversion in the flow cell should approach unity.

For complex hydrodynamics and for cases where the Lévêque approximations fail it is customary to resort to numerical methods. Numerical algorithms based on finite difference or finite elements also provide unsteady state solutions of the boundary value problem and with small modifications can describe cells involving nonlinear homogeneous kinetics as well [49–55]. The drawback of the numerical methods is the difficulty associated with the generalization of conversion trends and parametric dependencies. Numerical methods have to be applied on a case-by-case basis. We believe that the mathematical approach that is presented here enjoys some of the benefits of analytical methods though it combines a numerical approach.

We demonstrate the main features of the new cell configuration by studying the oxidation of dimethylaminomethyl-ferrocene (DMAMF) to give dimethylaminomethyl-ferroacenium (DMAMF$^+$)

The application of on-line EC/ESI-MS enables direct correlation of the electrochemical voltammetry curve with the simultaneous recording of the potential dependent ion abundances in the cell’s effluent. Electrochemical oxidation of ferrocene was chosen because it is a simple one-electron transfer electrochemical reaction [56] and because it was well documented before. The use of aminomethyl-substituted ferrocene enabled MS detection of both the initial compound and its oxidized form (ferrocenium cation) by EC/MS measurements. The initial compound was detected in its ammonium form, DMAMF$^{+}$. The oxidation product is a singly charged ferrocenium cation, DMAMF$^{+}$.

2. Experimental

Figure 1 shows a schematic of the flow cell. The cell consists of 2 cylindrical Delrin blocks, (1) and (2) separated by a Teflon spacer (3). A miniature Pt, or GC, disk electrode (4) of 1.6 mm in diameter was pressed into a cavity in the lower block. We used PEEK tubes, frits, and fittings, which were all obtained from Upchurch Scientific (Oak Harbor, WA, USA).

A coaxial miniature tube setup (5) and (6) was inserted through the center of the upper Delrin block. The electrolyte containing the test substance was supplied to the working electrode through the narrow annulus between the inner wall of the outer tube (5) (PEEK, nominal OD 1/8", ID 0.062", 0.0025") and the outer face of the inner tube (6) (PEEK, nominal OD 1/16", ID 0.0025"). After assembling all parts within each block its surface was polished using a set of wet emery papers placed on a flat support. A central aperture in the Teflon spacer (3) allowed passage of the electrolyte towards the disk electrode perimeter where it converged towards the opening of the inner tube (6). The blocks were attached by 3 bolts.

The working electrode compartment is confined by the parallel planes of the disk electrode (4) and the bottom plane of the inner tube (6). The working disk electrode, the aperture in the Teflon spacer, and the inner (6) and outer tubes were aligned to form a uniaxial system. The thickness of the spacer determines the thickness of the flow cell. In most of the experiments a 50 µm Teflon film spacer was used, though in the experiments for determination of the conversion as a function of cell thickness we used different combination of 25, 50, 75, and 100 µm thick Teflon spacers. With the 50 µm spacer, the volume of the compartment of the working electrode was only 0.1 µL. The length of the PEEK tubing (6) was approximately 10 cm, which gives an additional 0.4 µL volume.

A reference electrode (7) was connected to the flow cell via a horizontal channel and cylindrical vertical chamber (8) drilled in the upper block (2). An auxiliary electrode (9) was
placed upstream of the working electrode. It was connected to the flow channel through a PEEK cross junction (10). The auxiliary and reference electrodes were both Ag/AgCl 1M KCl aqueous electrodes separated from the electrolyte flow by 2 μm PEEK frits (13) and (14). The reference and counter electrodes were made from 0.25 mm diameter silver wire from Aldrich (Milwaukee, WI, USA) which was coated electrochemically with AgCl film. (by 20 minutes anodic polarization in 1 M KCl). The potential of the reference electrode was checked before each test relative to a commercial reference electrode. All the potentials reported below are given relative to the Ag/AgCl 1M KCl reference.

Before introduction into the ESI-MS the effluent stream of the cell was mixed with excess methanol supplied by a syringe pump (YA-12 from Yale Apparatus, Wantagh, NY, USA) through an additional cross junction (not shown in Fig. 1). In most EC/ESI-MS experiments, the flow from the cell was in the range 1–6 μL min⁻¹ and the flow of the auxiliary methanol stream was 50–120 μL min⁻¹. To enhance protonation of uncharged N,N-dimethyl-p-phenylenediamine and its oxidation products, and thus to increase sensitivity of ESI/MS, methanol was acidified by CCl₃COOH.

Computerized PARC 263 potentiostat/galvanostat (Princeton, USA) was used to control the electrochemical cell. Finnigan (San Jose, USA) LCQ ESI mass spectrometer was used for MS data acquisition. Electrochemical and MS data were acquired using two different computers. MS data acquisition was synchronized with electrochemical experiment by simultaneous triggering of the MS data recording and the electrochemical software. Mass spectra were registered continuously at a rate of 1 full spectrum in 2 seconds. Spray voltage was 1 kV. Heated capillary temperature was 120 °C in experiments with (dimethylaminomethyl)-ferrocene and 170 °C in experiments with N,N-dimethyl-p-phenylenediamine. In experiments with N,N-dimethyl-p-phenylenediamine mass spectra were acquired in the m/z range 50–500. In experiments with (dimethylaminomethyl)-ferrocene the MS measurements were performed within the narrow, width 30 m/z units, ion isolation window centered around m/z 243. Heated capillary voltage was 11 V.

(Dimethylaminomethyl)-ferrocene (DMAMF) and N,N-dimethyl-p-phenylenediamine hemioxalate salt (DPD) from Aldrich (St. Louis, MO, USA) were used. CCl₃COOH and NH₄⁺(CH₃COO⁻) were from BDH Chemicals (Poole, England). Solutions were prepared using triply distilled water and methanol HPLC grade (J. T. Baker, Phillipsburg, NJ, USA). Oxidation of DMAMF was studied in methanol-water (50% volume), 0.1 M NH₄Ac electrolyte.

3. Theory: Modeling the Electrochemical Flow Cell

For mathematical simplicity we consider a cylindrical channel electrochemical cell of height H equipped at its bottom with a ring electrode of outer radius r₁ and inner radius r₀ as in Figure 2. This assumption implies that the test compound does not react at the central part of the electrode, r < r₀. Since in our set-up we use a disk electrode this assumption is acceptable only for r₀ << r₁. The electrolyte flow in the cell is assumed to be radial, directed towards the center of the flow cell. We assume fully developed laminar flow throughout the cell. A fully laminar velocity profile develops on a length scale of Δr = 0.04 H Re [57]. Re denotes the Reynolds number based on channel height. In our experiments, the highest flow rate was about 0.2 mL min⁻¹, which corresponds to Re = 1 at the entrance to the flow cell. Thus for 50 micrometer thick cell the laminar flow develops in 2 μm from the entrance to the cell. Convection diffusion in the cell is described by the differential equation

- ∂C/∂r = ∂C/∂z²

in cylindrical coordinates with v being the liquid velocity, which is distributed according to laminar flow:

v = v(r, z) = (3F₀/πH)(z/H - z²/H²)r

Here D stands for the diffusion coefficient, while F₀ is the flow rate in the cell. Equation 1 is subject to the following boundary conditions:

C = C₀ at r = r₁

C = 0 at z = 0

∂C/∂z = 0 at z = H

To analyze Equation 1 with liquid velocity distribution (Eq. 2) and boundary conditions (Eqs. 3–5) we introduce dimensionless variables:

X = C/C₀, ξ = r/r₁, ζ = z/H, β = πD₀ r₁²(F₀/πH).

Equation 2 takes the form:

- 6ζ (1 - ζ) ∂X/∂ξζ = 2β ζ ∂²X/∂ζ²

with the boundary conditions

Fig. 2. Flow configuration in the cylindrical flow cell. Arrows indicate direction of liquid flow. (1) ring electrode; (2) radial flow channel.

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The system is characterized by a single variable $\beta$ which combines the contributions of the diffusion coefficient, flowrate, electrode diameter, and cell height.

The factor $6\zeta(1-\zeta)$ in the right-hand side of Equation 7 turns zero at the boundaries $\zeta = 1$ and $\zeta = 0$ due to the no-slip conditions at the solid liquid interface. The boundary conditions imply a jump at the point $(\xi, \zeta) = (1,0)$. Under these circumstances, application of finite difference method for computational solution of Equation 7 is cumbersome. On the other hand, Equation 7 allows for separation of variables, and its general solution can be presented in the form:

$$X = \sum C_\lambda \beta(\zeta) B_\lambda(\zeta),$$

or explicitly,

$$X = \sum C_\lambda \exp(\lambda\beta(\zeta^2 - 1)) B_\lambda(\zeta),$$

where $B_\lambda$ is the solution of the generalized eigenvalue problem:

$$d^2B_\lambda/d\zeta^2 = -\lambda 6\zeta(1-\zeta) B_\lambda, \tag{13}$$

$B_\lambda(0) = 0, \tag{14}$

$$dB_\lambda/d\zeta(1) = 0. \tag{15}$$

It is easy to see that solutions of Equations 13–15 corresponding to different $\lambda$s are orthogonal with respect to the scalar product $(f, g) = \int_0^1 6\zeta(1-\zeta)g(\zeta)f(\zeta) d\zeta$, where $f, g$ are any two functions of $\zeta$ fulfilling Equations 12–15. We did not conduct a thorough analysis of the system (Eqs. 12–15) as to the properties of the spectrum $[\lambda]$ and completeness of the system of functions $B_\lambda$. Rather, we approximated differential Equation 13 by a finite-difference one. So we assumed that the functions $[B_\lambda]$ form an orthonormal basis in an appropriate functional space and that that space contains the boundary function $X(\zeta) = 1$. The coefficients $C_\lambda$ are calculated from decomposition of $X(\zeta) = 1$ with respect to the orthonormal basis $[B_\lambda]$, using the scalar products:

$$C_\lambda = (B_\lambda, 1) = \int_0^1 6\zeta(1-\zeta)B_\lambda(\zeta) d\zeta \tag{16}$$

Here we assume that the functions $B_\lambda$ are normalized to unity:

$$(B_\lambda, B_\mu) = \int_0^1 6\zeta(1-\zeta)B_\lambda(\zeta)B_\mu(\zeta) d\zeta \tag{17}$$

To compute the substance flow through the cylinder of dimensionless radius $\xi$ we have to integrate the product $(C \nu)$ over the circumference of radius $\xi$ and by $\xi$ over the interval $[0,1]$. The substance flow will be proportional to the value $j(\xi, \beta)$ defined by Equation 18:

$$j(\xi, \beta) = \sum C_\lambda^2 \exp((\xi^2 - 1)\lambda \beta) \tag{18}$$

Note, that $j(\xi, \beta)$ is the mixed liquid concentration at point $\xi$ since the product in Equation 17 gives different weight for different $\xi$ locations. $j(\xi, \beta)$ is normalized so that $j(1, \beta) = 1$, so that in the following expression we have:

$$j(1, \beta) = \sum C_\lambda^2 = \sum C_\lambda \int_0^1 6\zeta(1-\zeta) B_\lambda(\zeta) d\zeta \tag{19}$$

$$= 6 \int_0^1 \zeta(1-\zeta) \sum C_\lambda B_\lambda(\zeta) d\zeta = 6 \int_0^1 \zeta(1-\zeta) d\zeta = 1$$

Here we used $\alpha_{\lambda} C_\lambda B_\lambda(\zeta) = X(1, \zeta) = 1$, the boundary condition (Eq. 8). Therefore, the difference $1 - j(\xi, \beta)$ has the meaning of conversion efficiency of the test substance in the flow emerging from cylindrical cell with inner radius $r_c$. To determine $C_\lambda$ and $\lambda$ in Expression 18 we solved Equation 13 numerically, using the standard finite difference scheme. Differential Equation 13 is substituted by an algebraic one, and the problem is reduced to the eigenvalue problem for a symmetric operator in a finite dimensional real vector space. We used partition of the $\zeta$-domain $[0,1]$ by 1500 intervals. Taking into account the two boundary conditions, we come to an eigenvalue problem in the 1499-dimensional vector space for an operator with non-zero entries only on the principal diagonal and super- and sub-diagonals. We solved this problem using the MAPLE package. Appendix A shows the first 50 eigenvalues $[\lambda]$ and coefficients $[C_\lambda]$ entering Equation 17. All 1499 pairs of eigenvalues $[\lambda]$ and coefficients $[C_\lambda]$ are available upon request.

Equation 18 for the conversion efficiency in the cell $(1 - j)$ can be rewritten in the following form:

$$(1 - j) = 1 - \sum C_\lambda^2 \exp(-\lambda (t/r_d)). \tag{20}$$

Here $r$ stands for substance residence time in the cell, $r = (1 - \xi^2) \pi r_1^2 H/F_0$ and $r_d$ the characteristic diffusion time in the cell, $r_d = H^2/D$. Despite the fact that we have solved Equations 1 through 5 for a converging radial flow configuration it is possible to show that the generalized solution given in Equation 20 holds for any other laminar flow configuration with constant cell thickness provided that the diffusion in the direction of the flow does not play a significant role, i.e., when the Peclet number, $uL/D \gg 1$, where $u$ is the average velocity (in our case $F_0/(2\pi r_H) L$) is the electrode dimension in the direction of the flow (in our case $(r_1 - r_0)$) and $D$ is the diffusion coefficient of the key reactant. Appendix B delineates the formal derivation of Equation 20 for general flow channel with negligible radial diffusion.
from 21 to 40 contribute only 3 more than 60% (0.042 in absolute value). The terms ranging 0.073, thus changing the approximate conversion by calculated for narrow ring electrode using Equation 20 the contribution of the first exponential term to contribute 5 making the approximate conversion value (1 contribution of the first exponential term is equal to 0.885, the following nineteen terms reduce obtained (1 0.7, the first exponential term only is sufficient to describe conversion in the cell with reasonable accuracy. If \( t/t_d = 0.01 \), contribution of the first exponential term is equal to 0.885, making the approximate conversion value \( (1 - j) = 0.115 \). The following nineteen terms reduce obtained \( (1 - j) \) value by 0.073, thus changing the approximate value of conversion by more than 60% (0.042 in absolute value). The terms ranging from 21 to 40 contribute only 3 \( \times 10^{-16} \) and can be neglected.

3.1. Comparison with Levich Equation

Equations 17, 19 with eigenvalues and coefficients to \( j \) value in Appendix A can be also applied to the disk electrode \( (\xi = 0) \) and narrow strip electrode – narrow ring electrode \( (1 - \xi^2) \) \( \rightarrow 0 \). Figure 3 shows a comparison of the current \( (I) \) calculated for narrow ring electrode using Equation 20 and the Levich equation [48]:

\[
I = 0.925 \frac{F D}{H} \left( \frac{F D^2 F}{0.5 H^3 d} \right)^{1/3} \tag{21}
\]

Here \( F \) stands for Faraday number, \( d = 2 \pi r_1 \) is the length of the electrode strip in direction perpendicular to flow, and \( l \) is the width of the electrode. The channel width was taken to be equal to the electrode length. Current calculations using the proposed model were made by multiplying the conversion by \( (F F_0 C) \). Cell parameters were \( 2 \pi r_1 = 1 \) cm, ring width 0.05 cm, cell height \( H = 0.005 \) cm. The diffusion coefficient of DMAMF in MeOH/H\( _2 \)O was taken as \( 5 \times 10^{-6} \) cm\( ^2 \) s\(^{-1} \). It was evaluated using the ferrocene diffusion coefficient in MeCN (2.3 \( \times 10^{-5} \) cm\( ^2 \) s\(^{-1} \)) [58], accounting for the difference in viscosity between MeCN and the MeOH/H\( _2 \)O mixture by the Stokes equation. Both models should give similar results in the range of applicability of the Levich equation. Indeed, in the range of electrolyte flows corresponding to low conversion \( (1 - j) < 0.2 \), the results of calculations by both models are in very good agreement. At low flowrates, when conversion of the test substance increases to 1, the Levich equation becomes inappropriate, and it shows currents exceeding the material flow.

3.2. Potential Dependent Response

The potential dependent response of the electrochemical cell, i.e. the dependence of the concentration of the reactant (or the product) at the cell outlet on the electrode potential and \( \beta \) can be readily evaluated for the diffusion controlled, Nernstian systems. Under these conditions Equations 7, 8, and 10 still hold, but the boundary condition of Equation 9 is replaced by the heterogeneous boundary condition which reflects Nernstian reactant-product distribution at the electrode surface:

\[
X = X_0 = \left[ 1 + e^{(E - E_0)(RT/nF)} \right]^{-1} \quad \text{at} \quad \xi = 0 \tag{22}
\]

Where \( (E - E_0) \) is the potential measured relative to the formal potential, \( E_0 \).

The solution of the heterogeneous boundary value problem of Equations 7–10 (in terms of \( X \)) by setting \( X = (X - X_0)/(1 - X_0) \) in Equations 7–10.

Thus the solution for the average concentration of the reactant at the cell outlet is given by expression:

\[
\begin{align*}
\dot{j} &= [1 + e^{(E - E_0)/(nF/RT)}]^{-1} + \left[ 1 + e^{(E - E_0)/(nF/RT)} \right]^{-1} \\
&\times \frac{1}{\lambda(t/t_d)}
\end{align*} \tag{23}
\]

Figure 4 delineates several potential dependent conversion curves as a function of \( \beta \). In all cases \( E_{1/2} = E_0 \). Thus the half-wave potential coincides with the formal potential even for incomplete conversion efficiencies in the cell.

3.3. Ohmic Drop Along the Electrode

The resistive effects which arise from difference in IR drops at different points in electrolyte in the channel above the

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Electrooxidation of Dimethylaminomethyl Ferrocene

4. Experimental Results and Discussion

4.1. Response Time of the Flow Cell

To determine the response time of the EC/ESI-MS experimental setup, potential step changes were imposed on a working Pt electrode and the mass spectra were simultaneously recorded. In these studies we used 1 mM DPD working electrodes are considered for an aqueous electrolyte containing 0.1 M 1:1 electrolyte. It should be noted that the ohmic drop in the electrolyte within the channel cannot be compensated. The apparent consequence of the ohmic losses is the distortion of the voltammetry curves. It can cause a confusing effect of current increase in the potential at which the limiting current is not yet reached, and applied potential increase does not change current, while the other site is under a potential at which the residual concentration on high isobestic point is explained in light of the dependence of the residual concentration on high.

The ohmic drop along the radial channel electrode was calculated for two cases: The first case corresponds to a situation where the counter electrode is located upstream of the working electrode compartment (as in our system), and the second one corresponds to downstream location of the counter electrode. In the latter case, ohmic drop is greater since the same current originates from the localized vicinity of the opening of the narrow inner tube. In the limiting case of very narrow inner channel, we come to infinite growth of ohmic losses at point contact. We took into account only radial current in the electrolyte. It was assumed independent of height within the gap. We assumed that ohmic losses do not affect current distribution over the working electrode of the cell. For upstream position of the counter electrode, the ohmic drop between points in electrolyte located at the entrance to the channel \( r_0 \) and the point within the channel with radial coordinate \( r_i \) is given by the expression

\[
\Delta V = \int^{r_i}_{r_0} \frac{FF_0 \rho}{2\pi H} \left( 1 - \frac{j}{j_f} \right) d\xi
\]

or

\[
\Delta V = \int^{r_i}_{r_0} \frac{FF_0 \rho}{2\pi H} \left( 1 - \frac{j}{j_f} \right) d\xi
\]

\[
\Delta V = \int^{r_i}_{r_0} \frac{FF_0 \rho}{2\pi H} \left( 1 - \frac{j}{j_f} \right) d\xi
\]

where \( \rho \) is the electrolyte specific resistance and \( \xi_i = r_d/r_j; j_f \) is \( j \) at \( \xi_i \). The ohmic drop for a channel that is located upstream to the counter electrode is given by

\[
\Delta V = \int^{r_i}_{r_0} \frac{FF_0 \rho}{2\pi H} \left( 1 - \frac{j}{j_f} \right) d\xi
\]

or explicitly,

\[
\Delta V = \int^{r_i}_{r_0} \frac{FF_0 \rho}{2\pi H} \left( 1 - \frac{j}{j_f} \right) d\xi
\]

The dependence of the ohmic drop on \( \beta \) (actually of \( D \) and \( r_j \), while \( H \) and \( F_0 \) should be kept constant) is depicted in Figure 5 for the following cell parameters: \( \rho = 1 \Omega \cdot \text{m} \) (corresponding to 0.1 M supporting electrolyte [59]); \( H = 50 \mu \text{m}; F_0 = 4 \mu \text{L} \cdot \text{min}^{-1}; \xi_f = 0.1; \) and \( C_0 = 1 \text{mM} \), one-electron reaction. Figure 5 underscores several important practical facts: 1) Upstream location of the counter electrode is always preferable since the current flows through the outer section of the cell rather than through the inner radius of the radial cell. Thus, the average current pathlength is smaller, since current generation is higher near the inlet to the cell and additionally the cross section of the cell, in converging radial flow cell, is larger near the cell inlet. 2) For the upstream position of the counter electrode (Eq. 24) under the conditions which were used in our tests the ohmic drop is smaller than 2.5 mV. 3) The dependence of the ohmic drop on \( \beta \) is non-monotonic. The reason for the decrease of the ohmic losses for low \( \beta \) is obvious. The increase of \( \Delta V \) for high \( \beta \) is explained in light of the dependence of the residual concentration on \( \beta \) that is also shown in Figure 5. At high \( \beta \), after nearly full conversion is attained, the current remains constant but it is generated at a ring that becomes closer to the inlet outskirt of the cell. Thus the reaction layer and the characteristic length which contribute to the ohmic drop shrink as \( \beta \) is further increased.

Fig. 4. Calculated residual concentration \( (C/C_0) \) of the mixed outflow from the cell as a function of applied potential. \( E_0 = 450 \text{mV} \); outlet radius \( r_0 = 0 \); curves correspond to \( \beta = 3 \), 1.5, 0.6, 0.3, 0.15, 0.06, 0.03, and 0.015, where higher \( \beta \) corresponds to higher conversion.
4.2. Conversion Efficiency

Conversion efficiency of the cell was determined by measurements of the limiting current of oxidation of DMAMF in 0.25 M NH₄Ac, MeOH/H₂O = 1 at variable flowrate. Oxidation of DMAMF is a one-electron electro-chemical reaction. Figure 7 shows the dependence of the oxidation efficiency of the cell on electrolyte flowrate. The frames present results obtained with the cell of different channel thickness: 25 μm, 50 μm, 75 μm, 100 μm, 125 μm, 175 μm, 200 μm, and 250 μm. Each point represents steady state current at the specified flowrate. Oxidation efficiency was calculated as the ratio between the observed limiting current and the theoretical current that is required for complete electro-consumption of the DMAMF feed. For the 50 μm thick channel, conversion of DMAMF above 80% was observed for flowrates below 2 μL min⁻¹. The lines drawn on the diagrams of Figure 7 were calculated using 5 exponential terms in Equation 20, though only the first one or at most the first two terms were sufficient for accurate calculation of the conversion. The agreement between theory and experiment was very good for flowrates down to 1 μL min⁻¹. The discrepancy between the experimental observations and the theoretical curves at very low flowrates are attributed to pulsation of the flow due to presence of small bubbles in the liquid duct. Another source of inconsistency can be mechanical inaccuracy in the alignment of the cell parts, which arises from the elasticity of the cell spacers and cell blocks.

4.2.1. EC/MS Studies of the Electrochemical Oxidation of DMAMF

Figure 8 shows the results of EC/MS studies of electro-chemical oxidation of DMAMF in the flow cell at the GC electrode. Mass spectra were recorded along with a hydrodynamic voltammetry curve which is shown in Diagram (A). The voltammetry curve is in agreement with reported results for the oxidation of amine-substituted ferrocene in water containing electrolytes [60, 61]. EC/MS measurements were staged by imposing a potential ramp from 0.1 V to 0.65 V and back at a rate of 1 mV s⁻¹. The electrolyte flowrate was 2 μL min⁻¹. On the exit from the cell, the effluent was diluted by a 50 μL min⁻¹ auxiliary stream of methanol. Diagrams (B) and (C) show the potential dependence of the relative abundance of ions m/z 244, and m/z 243, respectively. Potential readings on Diagrams (B) and (C) were reproduced using a 0.2 min delay time of MS response to potential change in the cell. Diagrams (D) and (E) show portions of the mass spectra recorded at E = 0.1 V and E = 0.65 V, respectively. The peak at m/z 244 corresponds to the protonated cation of DMAMF-(DMAMF₂H⁺). DMAMF (N,N-dimethyl-p-phenylenediamine) in 0.1 M CCl₃COOH. E = 0.8 V establishes diffusion limited oxidation of DPD, while no oxidation occurs at E = 0.1 V. Thus we set the step changes between these two potential values. The electrolyte flow through the cell was 3 μL min⁻¹. Figure 6 shows the change in relative abundance of MS peak m/z 137 with the potential step changes. The m/z 137 MS peak corresponds to the protonated molecule, DPDH⁺. Changes of potential are followed by rather steep changes of abundance of the DPDH⁺ species with a delay time of about 0.2 min. This delay time corresponds to time lag caused by liquid transport through the cell (cell volume 0.1 mL) and through the central capillary (volume 0.4 μL) and the transfer line to the mass spectrometer.
(M = 243) itself is uncharged and for this reason cannot be detected by MS measurements. The relatively small peak at m/z 245, shown in Diagram (D), corresponds to the heavy isotope of (DMAMFH⁻), which constitutes 17% of the main isotope m/z 244. The peak with m/z 244, shown in Diagram (E) comprises both, 17% of the heavy isotope of ferricinium cation (m/z 243) and the protonated form of the reduced ferrocene (DMAMFH⁺). According to Diagram (B) the concentration of (DMAMFH⁻) starts to decrease at E = 0.35 V in agreement with the voltammogram shown in Diagram (A). The decrease of the peak corresponding to (DMAMFH⁻) is accompanied by a simultaneous build-up of the peak around m/z 243, Diagram (C). The voltammogram and potential dependences of the abundances of (DMAMFH⁻) and the ferricinium cation are consistent and symmetrical relative to the turn around point E = 0.65 V. However, the dip in the potential dependence of MS peak m/z 244 at E = 0.65 V is not as deep as could be expected based on the conversion efficiency of the cell. According to the data shown in Figure 7, the conversion of DMAMF in the 50 μm thick cell at 2 µL min⁻¹ flow rate is about 80%. In

Electroanalysis 2004, 16, No. 5

Fig. 7. Dependence of oxidation efficiency of the flow cell with spacers of different thickness on electrolyte flow rate. Efficiency was tested by measurements of the limiting current in 1 mM DMAMF, 0.25 M NH₄Ac, MeOH/H₂O = 1. Lines on the diagrams were drawn using Equation 20. Cell channel thickness is indicated in the diagrams.

Fig. 8. EC/MS study of electrochemical oxidation of DMAMF in 0.1 M NH₄Ac, pH 10, MeOH/water = 1 at GC electrode. Potential scan rate was 1 mV s⁻¹. Effluent of the flow cell was diluted by 50 µL min⁻¹ flow of MeOH. Curves shown in Diagrams (A), (B), and (C) were recorded in the same experiment. Electrolyte flow rate was 2 µL min⁻¹. Spray voltage was 1 kV, spray current was below 1 µA, heated capillary temperature was 120 °C. Numbers at diagrams (B) and (C) give integration limits used for peak area detection. Potential scale in Diagrams (B) and (C) was calculated from time trace using delay time 20 s. Diagram A: hydrodynamic voltammetry. Diagram B: potential dependence of the relative abundance of ion m/z 244, which corresponds to protonated molecule of DMAMF-DMAMF + H⁺. Diagram C: potential dependence of relative abundance of ion m/z 243, which corresponds to oxidized form of DMAMF-ferrocinium cation. Diagram D: portion of mass spectrum measured at E = 0.1 V. Diagram E: portion of mass spectrum measured at E = 0.65 V.

Diagram (B) the peak height of the ion with m/z 244 falls down to about 33% of the initial value. However, the contribution of the ferricinium cation isotopomer at m/z 244 is 14% of the intensity of the isotopomer at m/z 243 what accounts for about 40% of total height of the peak at m/z 244 at E = 0.65 V.

A comparison of the calculated and experimental residual concentration of DMAMF during slow scan (1 mV/s)
hydrodynamic voltammetry is presented in Figure 9. Calculation was based on Equation 22. While the residual concentration at high overpotential agreed very well with the theory, some deviation from the theoretical curve took place at intermediate potentials. We attribute these deviations to some dead volume in the transfer line to the mass spectrometer. This small dead volume is also responsible for the slight deviation from the ideal step change of the MS response to the potential step change in Figure 6. The effect of the dead volume is more significant at high conversions but it has no effect on the steady state conversion as is clearly shown in Figure 7.

5. Conclusions

A radial thin layer electrochemical cell which is characterized by low resistive voltage losses and high efficiency (up to 99%) of conversion of test compounds is developed. The cell can be operated at a rather high concentration of supporting electrolyte retaining its compatibility with ESI-MS requirements.

A mathematical model describing diffusion convection in the cell is developed. The model describes convection diffusion currents in thin layer radial cells with disk and ring electrodes at high, up to 100%, and low, down to few % conversion of the test substance. Theoretical results were found in agreement with the cell calibration experiments and with the Levich equation for a low degree of conversion at a narrow ring electrode.

Quantitative agreement between MS and electrochemical data on DMAMF oxidation was observed.

6. Appendix A

List of the first fifty eigenvalues (λ) and coefficients (C_i).

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7. Appendix B

7.1. Conversion vs. Retention Time

In this appendix we derive Equation 20 and in a following example we show that Equation 18 is a particular case of Equation 20.

Consider the solution of the general Equation 1.

\[ - \partial C / \partial r = D \partial ^2 C / \partial z^2 \]  

(B1)
We assume that the velocity, \( v \) in an electrochemical cell of an unspecified configuration can be expressed as a product of velocity dependence in two coordinates \( v_{avg}v_z \). Here \( v_{avg} \) is the dimensional average velocity at the entrance to the cell. \( v_z \) and \( v_r \) are dimensionless variables expressing the dependence of \( v \) on the \( z \) and \( r \) coordinates. (e.g., for radial flow, \( v_{avg} = F_0/(2\pi r_1 H) \), \( v_z = 6[2z/H(1 - z/H)]; v_r = r_1/r \). Using this velocity field, Equation B1 is transformed to

\[
\frac{H^2}{D} \frac{d(v_{avg}v_z)}{dz} = - \frac{r_1 d^2 X}{v_{avg}dz^2} \quad (B2)
\]

\( v_z = v_z; v_r = v_r \) and \( \xi = r/r_1 \). \( r_1 \) is the electrode characteristic length perpendicular to the direction of the flow (e.g., \( r_1 \) = outer radius of a ring electrode in a radial flow cell). \( \xi, \xi, X \) are defined by Equation 6 in the article as the dimensionless concentration, and \( x \) and \( z \) are coordinates.

Assuming \( X \) is a separable variable that can be expressed by the product \( \rho(\xi, \lambda) \cdot B(\xi, \lambda) \) then Equation B2 is transformed to the corresponding eigenvalue problem:

\[
\left( -\frac{1}{v_z B_\xi} \right) \frac{d^2 B}{dz^2} = \lambda \quad (B3)
\]

Note that Equation B3 subject to the boundary conditions given by Equations 14 and 15 is identical for different types of flow configurations including straight channel electrodes, converging radial flow or even diverging radial flow configuration (where the flow is opposite to the one described in Fig. 2). Thus, the eigenvalues and eigenfunctions of Appendix A fit equally well all these problems provided that \( X = 1 \) at the entrance to the flow cell.

Equation B4 can be transformed into a more general form by denoting \( \tau_D = H^2/D; y = v_z \rho \) and \( dr = - (1/v_{avg}v_z)(r_1)dz \) or \( \tau = \int^1_0 r_1 \frac{dz}{v_z v_z} \) where \( \tau_D \) and \( \tau \) are the diffusion and hydraulic retention times.

\[
\frac{dy}{y} = -\frac{\lambda}{\tau_D} \frac{dr}{z} \quad (B5)
\]

Equation B5 is subject to the initial conditions \( \rho_\xi = v_z = y = 1 \) at \( \tau = 0 \) (or \( x = 1 \)). The solution of Equation B5 is a simple exponential term which can be readily converted to Equation B6 by introducing \( y = v_z \rho \).

\[
\rho_\xi = \frac{1}{v_z} e^{-\lambda\tau_D} \quad (B6)
\]

\[
j_\xi = \sum C_i^2 \rho_\xi(\xi) \quad (B7)
\]

8.2. Example A: Laminar Converging Flow

\[
v_z = 6(z(1 - z); \quad v_r = 1/x; \quad v_{avg} = F_0/(2\pi r_1 H) \quad (B8)
\]

\[
\tau = \int^\xi_0 \frac{2ar_1^2 H(1 - \xi^2)}{F_0} \frac{dz}{\xi} = \frac{\pi r_1^2 H(1 - \xi^2)}{F_0} \quad (B9)
\]

Thus, introducing from B8 and B9 in B6 and B7 one gets the solution B10–B12

\[
\rho_\xi = \xi e^{-\frac{\xi^2(1 - \xi^2)}{\tau_D}} \quad (B10)
\]

\[
X = \sum C_i^2 \xi e^{-\frac{\xi^2(1 - \xi^2)}{\tau_D}} B_i(\xi) \quad (B11)
\]

\[
j_\xi(\xi, \beta) = \sum C_i^2 \xi e^{-\frac{\xi^2(1 - \xi^2)}{\tau_D}} \quad (B12)
\]

8.3. Example B: Linear, Straight Channel Flow Cell With Laminar Flow

In this case the fluid velocity is given by Equation B13

\[
v_z = 6\xi(1 - \xi); \quad v_r = 1; \quad v_{avg} = F_0/(HL) \quad (B13)
\]

where \( L \) is the electrode width (perpendicular to the flow) and thus \( \tau \) is given by B14

\[
\tau = \int^\xi_0 \frac{\xi L r_1/f_0}{L H r_1/f_0(1 - \xi)} \frac{dz}{\xi} \quad (B14)
\]

Introducing from B13 and B14 in B6 and B7 gives the solution B15–B17:

\[
\rho_\xi = e^{-\frac{\xi^2(1 - \xi^2)}{\tau_D}} \quad (B15)
\]

\[
X = \sum C_i^2 e^{-\frac{\xi^2(1 - \xi^2)}{\tau_D}} \quad (B16)
\]

\[
j_\xi(\xi, \beta) = \sum C_i^2 e^{-\xi^2(1 - \xi^2)} \quad (B17)
\]

8. Acknowledgement

We gratefully acknowledge the financial aid of the ISF, Israel Science Foundation.
9. References