Application of the electrodiffusion method to measure wall shear stress: integrating theory and practice

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Abstract:

The electrodiffusion method has been used in fluid dynamic research for the past 50 years. It allows to measure wall shear stress, a crucial parameter e.g. for the cleaning of membrane modules used in water filtration. Various authors have published articles dealing with the theory behind this technique. However, there is no document that comprehensively collects all the knowledge that assembled over five decades of application. The objective of the present publication is to provide a comprehensive summary of the theory for steady flow, unsteady flow and transient voltage step experiments. Factors influencing the accuracy of the measurements are discussed. Furthermore, a new approach to calibrate the system from voltage step experiments is introduced and practical issues related to its application in flow measurements are also discussed for an exemplary signal response to a near-wall flow.

Keywords:

Electrochemical methods, shear stress, fluid dynamics

Electrodiffusion method, calibration, frequency response, shear stress

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1 Introduction

The measurement of wall shear stress is of high interest in various fields of process engineering. For example, low shear stress in stirred biological systems will decrease the disintegration of cells or microorganisms, and high shear stress flows in filtration systems or heat exchangers will assist to clean their surfaces. Various techniques have been developed for the measurement of wall shear stress by mechanical, thermal, optical or chemical methods (see Tab. 1). In general, these techniques are non-intrusive on a macro scale and relatively complex data processing is required to obtain shear stress values from the measured parameter (for more information about the different techniques see also [1-3]).

Of the measurement techniques listed in Table 1, the electrodiffusion method (EDM) is of particular interest because of its high sensitivity to near-wall flow fluctuations and its ability to detect local flow phenomena. Extensive literature exists on the EDM technique. However, no single reference document is available that comprehensively summarizes the theory upon which the technique is based as well as applications of the technique to measure wall shear stress. Major Reviews of the techniques focusing on different aspects of the technique have been published [4-7] but none of these comprehensively present the derivations of the underlying theory and the correction necessary for transient flows. To address this gap, the present reference document was developed. The theoretical assumptions and hypotheses used in developing the equations that are used in the post-processing to calculate the shear stress are reviewed in detail. Challenges regarding the calibration of this technique and the care that must be taken before using the technique are also discussed.

2 Electrodiffusion Method: Theory

For measurement of shear stress with the EDM two electrodes and an electrolytic solution are necessary. When a voltage is applied between the cathode and the anode, a heterogeneous reaction takes place at the electrodes. The transfer of the reducing ions to the cathode and the electron exchange leads to charge equalization between anode and cathode which induces a measurable current. The stronger the mass transfers of the ions, the higher the measured value of the current. As the convective part of the mass transfer rate of ions at the cathode is directly related to the hydrodynamic conditions at the proximity of the cathode in the system, the magnitude of current induced at the cathode can be used to measure the magnitude of the shear rate and therefore also the shear stress. It is worth mentioning that this technique based on convective-diffusion controlled mass transfer is in its principles also common in material science investigating e.g. electrodeposition of metals and according literature exists that focuses on this aspect.

2.1 The basic electrical circuit

Reiss and Hanratty [8] presented the basic electrical circuit of an EDM system. The signal is amplified and an ohmic resistance is used in the circuit (about 100 Ω). This should be two orders of magnitude higher than the ohmic resist ance of the electrochemical system so that the latter one does not affect the signal. As measuring electrodes, both circular and rectangular strip cathodes have been used [4, 9]. Platinum or Nickel is often used as anode and cathode material (see e.g. [8] and [10]) but noble metals are preferable. Application of stainless steel as an anode has also been reported [11]. The cathode has to be very small in contrast to the anode which must have a much larger surface area so that the oxidizing reaction is not limiting the process. Common dimensions
for rectangular cathodes are 0.5 mm by 12.5 mm (with the smaller length in flow direction) and 0.5 mm diameter for circular cathodes.

By installing two or more cathodes, each with its own circuit with a very small distance from each other in the flow, it is possible to determine the direction of the flow [1, 12-15]. Having multiple cathodes very close to each other in the flow, the concentration boundary layer of the upstream cathode influences the concentration boundary layer formed on the downstream flow and therefore the signal measured by the downstream cathode is smaller than the signal measured by the upstream cathode. Using a two segmented cathode, which is most common in literature, the direction can only be obtained in a range of 0 to 180° relative to the alignment axis of the cathode. Using a multi-segmented cathode with at least three cathodes both the direction and the shear rate can be determined quantitatively [14].

2.2 The electrolytic solution

There are various combinations of electrolytes mentioned in literature (Tab. 2) but composition and concentrations should be chosen carefully as the choice should integrate thoughts about the whole system including electrode material and flow system size [4]. For most of these solutions, ferri- and ferrocyanide are used as oxidizing and reducing ions. The reaction that takes place at the cathode is:

\[ \text{Fe(CN)}_6^{3-} + e^- \rightarrow \text{Fe(CN)}_6^{4-} \]

Oxygen existing in the system can cause side reactions and influence the induced current. Therefore, oxygen should be purged from the solution.

An inert electrolyte needs to be added to the solution to avoid electrical migration. Potassium is commonly used for this purpose. The use of potassium sulphate has the additional beneficial effect that it can also suppress the solubility of oxygen in the solution [16] and therefore it is commonly used in cases of long usage of the solution to ensure, no side reactions with oxygen occurs. It is worth mentioning that this in most cases unwanted side reaction of oxygen has also been used to measure shear stress. Onken and Hainke [17] investigated a multiphase system where the ions from the electrolytes mentioned above lead to an undesired coalescence hindering. Therefore the reduction of oxygen as the governing reaction is used to avoid this influence on the multiphase system.

As the EDM is based on mass transfer, the diffusion coefficient, which is a function of the temperature, is of interest. The Stokes-Einstein relationship (i.e. \( D \mu / T = \text{const.} \)) is valid for solutions with a viscosity similar to that of water [6, 18]. Values of the diffusion coefficient and viscosity of the electrolyte solution at 30°C have been reported to be 8.36*10^{-10} m²/s and 8.33*10^{-4} Pa s, respectively [19, 20]. The viscosity of the electrolyte solution at 20°C is comparable to that of pure water (i.e. \( \mu = 10^{-3} \text{Pa s} \)). Assuming a linear relationship between viscosity and temperature, according to the Stokes-Einstein equation mentioned above, for a temperature of 25°C, the diffusion coefficient is 7.4*10^{-11} m²/s. A different approach for the calculation of the diffusion coefficient has to be used when dealing with high viscosity or non-Newtonian liquids [21] i.e. that for Newtonian fluids with high viscosities (e.g. between 10^{-3} Pas and 1.2 Pas) the diffusion coefficient is proportional to the square root of the viscosity and for the non-Newtonian liquids no clear relation was found.
2.4 Limiting Diffusion Current

For measurements of wall shear stress using the EDM, a threshold for the applied voltage difference exists. The voltage difference controls the reaction rate as it is directly related to the number of electrons available at the cathode. Applying a voltage difference equal or larger than this threshold (not exceeding the upper limit from which on hydrolysis happens) ensures a system that is only limited by the mass transfer and not by the reaction rate. This well-known effect is often described by polarization curves in electrochemistry [1, 5, 22, 23]. The plateau in these curves indicates the limiting current conditions and the current measure is called the limiting diffusion current [8, 9]. This range of limiting current conditions should be obtained for each investigated electrochemical system carefully [77].

2.5 Steady state flow conditions

A well-known theoretical relationship can be derived to calculate the magnitude of wall shear stress from the magnitude of current measured by EDM when the following conditions apply [1], in the following is the x-direction the main flow direction, the y-direction is normal to the electrode, the z-direction is perpendicular to the main flow direction).

- The concentration boundary layer at the cathode is within the region where the velocity gradient is linear.
- No gradients appear in the z-direction.
- The concentration boundary layer thickness at the cathode is thin compared to the width of the electrode.
- Diffusion in the direction of the bulk convective flow in negligible at the cathode.
- Flow normal to the main flow direction is negligible.
- The reacting ion is completely consumed at the cathode.
- No reaction happens in the bulk of the electrolyte solution.
- Steady state conditions prevail.

Due to electrical and chemical driving forces, the Nernst-Planck equation can be used to describe the specific molar flux $\dot{n}$ of ions at the cathode based on diffusion (with the concentration gradient $\nabla c_i$) and convection (with the velocity $v$) on the one hand side and electrical migration (with the electrical mobility $u$ and potential $\phi$) on the other side (eq. (1) and (2)).

$$\dot{n}_i = \dot{n}_{i,\text{diff}} + \dot{n}_{i,\text{migr}} + \dot{n}_{i,\text{conv}}$$  \hspace{1cm} (1)

$$\dot{n}_i = -D_i \nabla c_i + u_i c_i \nabla \phi + c_i \vec{v}$$ \hspace{1cm} (2)

If the conditions listed above are valid and the specific conductivity of the solution is high, the electrical potential gradient is negligible. Assuming no-slip conditions and therefore no velocity at the surface of the cathode, the relationship can be simplified as presented in equation (3) with $y$ as the direction normal to cathode surface.

$$\dot{n}_i = -D_i \left( \frac{dc_i}{dy} \right)_{y=0}$$ \hspace{1cm} (3)

Because the mass flux of ions at the cathode results from reduction, equation (3) can be equated to Faraday’s law, yielding equation (4) (with the current $I$, the number exchanged electrodes $n$, cathode surface area $A$ and
Faraday constant $F$). Assuming limiting current conditions are applied, this is equal to the product of the mass transfer coefficient $k$ and the concentration in the bulk solution.

$$\frac{1}{nAF} = -D_i \left( \frac{dc_i}{dy} \right)_{y=0} = k_mc_b$$  \hspace{1cm} (4)

In equation (4), the concentration gradient as well as the mass transfer coefficient is unknown. To find a describing equation for the concentration gradient, the general mass balance with the conditions described above can be used which yields in equation (5) [9, 13, 24-27].

$$\left( v_x \frac{\partial c}{\partial x} + v_y \frac{\partial c}{\partial y} \right) = D \left( \frac{\partial^2 c_i}{\partial y^2} \right)$$  \hspace{1cm} (5)

Keeping in mind that the actual goal is to determine the wall shear stress, the velocity terms $v_x$ (with $x$ as the main flow direction) and $v_y$ in equation (5) are the relation to Newton’s law for viscosity where the wall shear rate is calculated by multiplying the shear rate $\gamma$ with the dynamic viscosity. For the relatively high Schmidt numbers $Sc$ typically found in aqueous solutions (~1000), as mentioned above the velocity profile can be assumed to have a linear slope in the concentration boundary layer, and therefore can be defined using the shear rate as presented in equation (6). Note that the assumption of linearity is valid regardless of the flow regime for relatively high Schmidt numbers.

$$v_x = \frac{\partial v_x}{\partial y} y = \gamma(x)y$$  \hspace{1cm} (6)

Assuming no dependency on the $z$-direction (i.e. no flow perpendicular to the main flow direction), equation (6) can be substituted into the continuity equation yielding the relationship for $v_y$ presented in equation (7).

$$v_y = - \frac{1}{2} \frac{\partial \gamma(x)}{\partial x} y^2$$  \hspace{1cm} (7)

Substituting equation (6) and (7) in equation (5) and applying the boundary conditions $c=0$ at all $x$ and $y=0$, $c=c_b$ at all $x$ and $y \to \infty$ and $c=c_b$ at $x=0$ and all $y$ based on the boundary layer and film theory [28, 29] yields in equation (8) [13, 24-26] describing the concentration gradient at the surface of the cathode which is a function of $x$.

$$\left( \frac{dc_i}{dy} \right)_{y=0} = \left( \frac{1}{9D} \right)^{1/3} c_b \frac{\gamma(x)}{0.893} \left[ \int_0^x \gamma(x) dx \right]^{1/3}$$  \hspace{1cm} (8)

For a very small cathode, a very thin concentration boundary layer is established on the cathode, making the relationship presented in equation (8) independent of the geometry of the system being investigated and the shear rate independent of the flow direction $x$. The mean mass transfer coefficient over the entire cathode can be described using equation (9) with a definite integral in the limits from zero to the characteristic length of the cathode $L$.

$$k_mc_b = D \frac{1}{L_{char}} \int_0^{L_{char}} \left( \frac{dc_i}{dy} \right)_{y=0} dx$$  \hspace{1cm} (9)

Introducing equation (9) into the relationship for the Sherwood number $Sh$ yields equation (10).
\[
\text{Sh} = \frac{k_m L_{\text{char}}}{D} = \int_0^{L_{\text{char}}} \frac{1}{c_b} \left( \frac{1}{9D} \right)^{1/3} \frac{c_b}{0.893} \left[ \frac{y^{1/2} dx}{x^{1/3}} \right]^{1/3} dx
\]  

(10)

which when solved yields in equation (11).

\[
\text{Sh} = \frac{k_m L_{\text{char}}}{D} = 0.807 \left( \frac{y L_{\text{char}}^2}{D} \right)^{1/3}
\]  

(11)

\[L_{\text{char}}\] for a rectangular cathode is the length of the cathode in the main flow direction. For circular electrodes the characteristic length \[L_{\text{char}}\] is equal to the diameter \[d\] multiplied by a factor of 0.82 [1, 30] as presented in equation (12).

\[
\text{Sh} = \frac{k_m 0.82d}{D} = 0.807 \left( \frac{y(0.82d)^2}{D} \right)^{1/3}
\]  

(12)

Therefore, for a circular cathode, the mass transfer coefficient can be estimated using equation (13).

\[
k_m = 0.862D^{2/3}d^{-1/3}y^{1/3}
\]  

(13)

Combining equations (4) and (13) and rearranging yields equation (14) that describes the relationship between the current and the shear rate for a circular cathode which can be simplified to equation (15) where the Leveque coefficient \(k_{\text{Lev}}\) describes the relationship between the shear rate at the surface of the cathode and current measured through the electrical system.

\[
I = 0.862nAFc_bD^{2/3}d^{-1/3}y^{1/3}
\]  

(14)

\[
I = k_{\text{Lev}}y^{1/3}
\]  

(15)

Because many of the parameters in equation (14) are not accurately known for a given system (e.g. exact cathode surface and diameter) the Leveque coefficient can be estimated by applying a known shear rate at the cathode and measuring the current through the electrochemical system (see e.g. [31]). Although not widely reported in literature, it is worth mentioning that from the author’s experience it is known, that the exponent of the shear rate in equation (15) can be lower for higher Reynolds numbers (usually ranging from 0.3 to 0.33). Tihon et al. [32] mention this effect for a three segmented probe for simultaneous shear rate and flow direction measurements as well, presenting an exponent of 0.32. Therefore, it is recommendable to apply several known shear rates and observe the behaviour of the Leveque coefficient.

### 2.6 Dynamic flow conditions

#### 2.6.1 Voltage step response

The relationship developed for steady state conditions is valid if the concentration boundary layer at the cathode establishes itself simultaneously with the velocity boundary layer [5]. If not, the mass transfer relationship presented in equation (4) must be modified to take into account that the mass transfer is time dependent as presented in equation (16).
The development of the concentration profile as a function of time $t$ and distance from the cathode can be described by Fick’s second law of diffusion [23] presented in equation (17) with $c=c_b$ at $t=0$ and all $y$, $c=0$ at $y=0$ and $t>0$ and $c=c_b$ at $t>0$ and $y\rightarrow\infty$.

\[
\frac{\partial c(y,t)}{\partial t} = D \frac{\partial^2 c(y,t)}{\partial y^2}
\]  

Solving equation (17) with the help of a Laplace transformation [33] (analogous to the penetration theory [34, 35]), for a circular cathode, the mass transfer coefficient can be calculated using equation (18).

\[
k_m = \sqrt{\frac{D}{\pi t}}
\]

Combining equations (16) and (18) and rearranging yields equation (19) that describes the relationship between the current and the time for a circular cathode, which can be simplified to equation (20) where the Cottrell coefficient $k_{\text{Cot}}$ describes the relationship between the time and current measured through the electrical system for a short time after a change.

\[
I = nAFc_b \sqrt[\frac{1}{2}]{\frac{1}{2}} \pi^{-\frac{1}{2}} 2^{-\frac{1}{2}} t^{-\frac{1}{2}}
\]

\[
I = k_{\text{Cot}} t^{-\frac{1}{2}}
\]

The Cottrell coefficient can be estimated by applying a voltage step and measuring the current through the electrical system over time [9, 16]. The characteristic time of the system, which is the time it takes for the current from an applied voltage step (equation (20)) to reach steady state conditions (equation (15)), can be estimated by equating equations (15) and (20) yielding equation (21) which describes the characteristic response time of the cathode $t_0$.

\[
t_0 = \frac{k_{\text{Cot}}}{k_{\text{Eff}}} t^{-\frac{2}{3}}
\]

The edge effect, i.e. augmenting the diffusion with additional mass transport from the sides, can also change the behaviour of the cathode under the transient condition [36, 37]. One approach to include the edge effects is to describe this effect with the help of an additional term in eq. (20) where the intercept $I_0$ stands for the correction for edge effects [37] (with the perimeter of the cathode $P$).

\[
I = k_{\text{Cot}} t^{-\frac{1}{2}} + \frac{Dc_bPnF}{2} = k_{\text{Cot}} t^{-\frac{1}{2}} + I_0
\]

To consider the spatial diffusion related to the cathode edge effect, a numerical model for the solution to a 3 dimensional mass transfer model over the surface of the cathode was developed [38]. Based on this model, a correction of $Sh/Sh_{\text{DLA}} = 1 + \psi$ is suggested, where $Sh$ is the actual Sherwood number, $Sh_{\text{DLA}}$ is the Sherwood number for diffusion layer approximation where the effect of streamwise and lateral diffusion is neglected (1 dimensional model) and $\psi$ is the correction factor. For a circular cathode, $\psi$ was estimated for a range of modified Peclet numbers $H$ between 1 and 100. The edge effect can be neglected at high Peclet numbers where
1) the area of the spatial diffusion is very small compared to the total area of the cathode or
2) the velocity and therefore the convection is high so that the spatial diffusion is negligible \([37, 38]\) (see also section 3.3.1).

### 2.6.2 Approximate model of the cathode dynamic response

Knowing the characteristic time of the system, it is possible to correct the wall shear rate measured at conditions when the concentration boundary layer is not able to follow rapid changes in the velocity boundary layer. To consider that the mass transfer is time dependent, equation (6) is modified as presented in equation (23).

\[
v_x = \gamma(x,t)y
\]  

(23)

The mass transfer relationship presented in equation (4) must be modified to take into account that the mass transfer is time dependent, as presented in equation (16). In equation (16), the concentration gradient, as well as the mass transfer coefficient, is unknown. To find a describing equation for the concentration gradient, analogue to the steady state case described above, the general mass balance derived under the conditions described above can be used in combination with equation (23) which yields in equation (24).

\[
\frac{\partial c}{\partial t} + \gamma(x,t)y \frac{\partial c}{\partial x} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right)
\]  

(24)

The concentration profile at the surface of the cathode can be approximated using equation (25) where \(G=f(\zeta)\) is a decreasing function including the concentration boundary layer thickness \(\delta_c\) assuring \(G(0)=1, G(\infty)=0, G'(0)=-1\) (further description of \(G\) can be found in \([39-42]\)).

\[
c(x, y, t) = c_b \left( 1 - G \left( \frac{y}{\delta_c(t)} \left( \frac{L_{char}}{x} \right)^{1/3} \right) \right)
\]  

(25)

By substituting equation (25) into equation (24), assuming axial diffusion is negligible and integrating near the cathode surface in the viscous boundary layer, yields equation (26), which can be used to calculate a transient (i.e. corrected) shear rate \(\gamma_c\) from the shear rate obtained assuming steady state conditions \(\gamma_s\) (equation (15)).

\[
\gamma_c(t) = \gamma_s(t) + \frac{2}{3} \tau_0 \left( \frac{\partial \gamma_s}{\partial t} \right)
\]  

(26)

Substituting equation (15) and (21) into equation (26) yields the relationship presented in equation (22), which is similar to that presented in equation (15), but that can be used for steady and unsteady flow conditions.

\[
\gamma_c(t) = k_{Lev}^{\gamma^3} \left( 1 + 2k_{Col}^2 \frac{\partial \gamma}{\partial t} \right)
\]  

(27)

Note that equation (27) is not valid at conditions with very large or rapid flow fluctuations. Under these conditions, equation (27) provides only rough estimates especially for the peak values, while maxima of the fluctuations are determined more precisely as the probe response is better at high wall shear rates. Similarly, when large wall shear rate fluctuations with dimensionless amplitudes \(\beta=\gamma/\bar{\gamma}\geq1\) lead to the near-wall flow reversal, negative values obtained using equation (27) can be used only as qualitative indicators of potential flow reversal \([43]\).
2.6.3 Other approaches to correct the transient signal

The signal correction with respect to probe dynamic behavior can be obtained either in the time domain (to reconstruct the whole time course of wall shear rate), or in the frequency domain (to provide the correct power spectra of wall shear rate fluctuations).

The inverse problem of calculating the instantaneous wall shear rate from the measured current signal has to be solved to acquire the near-wall flow variation. Three methods have been developed to cope with this problem:

- numerical computation of the convection–diffusion equation [44].
- application of the combination of signals measured by a double probe [45].
- approximate model [37] (already discussed in the previous section).

The numerical solution of the inverse problem is based on an iteration procedure, in which the initial values of a searched γ(t) function are either assumed in a parametric form [44] or estimated from a quasi-steady interpretation of the measured signal [39]. This numerical approach to the inverse problem solution provides good results, but it is rather tedious and impractical for the processing of experimental data.

The second approach is based on the different dynamic behavior of the front and rear segment of a double probe. Py [45] observed that a certain linear combination of current signals from probe segments provides a better frequency response. Thus the sum of signals (I₁ + I₂) and their difference (I₁ - I₂) is used to obtain the wall shear rate relationship presented in equation (28).

\[ γ = A(I₁ + I₂)^2(I₁ - I₂)^B \]  \hspace{1cm} (28)

The two constants (A, B) appearing in equation (28) are determined by the probe calibration under steady flow conditions. Recently, this correction method was applied also for wall shear stress measurements under flow conditions with Taylor bubbles [46].

The correction in the frequency domain is usually required to obtain proper power spectra from the measurements of near-wall turbulence. Assuming relatively small fluctuations of the wall shear rate, the equation of unsteady mass transport can be solved to provide the transfer function of the probe response [47-49]. The Nakoryakov’s [49] transfer function \( H_{ED} \) calculated for a strip probe is given by equation (29).

\[ H_{ED} = H_0 A_{ED} \exp(-i\phi_{ED}) \]  \hspace{1cm} (29)

This complex function of frequency can be represented with the quasisteady response of the electrodiffusion probe \( H_0 \) and by the pair of real-value functions: the amplitude attenuation \( A_{ED} (\Omega) \) and phase shift \( \phi_{ED} (\Omega) \) of the measured current signal in respect to the imposed wall shear rate variation of a given dimensionless frequency \( \Omega = (f l^2)/(D \gamma^{2/3}) \sim 1/3 t_0 \omega \) as presented in equation (30a) - (31b).

\[ A_{ED} = (1 + 2.21\Omega^2 + 1.96\Omega^4)^{-1/2} \text{ for } \Omega \leq 1 \]  \hspace{1cm} (30a)

\[ A_{ED} = 0.59/\Omega \left( 1 - 0.6\Omega^{-1/2} + 0.21\Omega^{-1} \right)^{-1/2} \text{ for } \Omega > 1 \]  \hspace{1cm} (30b)

\[ \phi_{ED} = \tan^{-1}\left[ 1.7\Omega(1 + 0.79\Omega^2 - 0.41\Omega^4) \right] \text{ for } \Omega \leq 1 \]  \hspace{1cm} (31a)
This prediction of probe dynamics was confirmed by the experiments performed in the modulated flow configuration of a rotating disk [50]. A good agreement between the correction in time and frequency domain has been demonstrated on the experimental data measured for developing annular flows [51]. With increasing computational potential, modelling in this field is still a recent topic and new developments can be expected (see e.g. [16, 38]).

3 Electrodiffusion Method: Application

The theory presented in section 2 was applied to measure the shear rate induced by a gas bubble rising in a vertical flow cell. This application is motivated by the measurement of wall shear stress in membrane systems where aeration is used to detach fouling layers from the membranes. Several groups in this field worked with EDM [52].

The experimental setup, the procedure of data processing and the resulting wall shear rate obtained in this study are discussed in the following sections.

3.1 Experimental setup

The experimental apparatus used consisted of a vertical flow cell, a liquid recirculation system and a gas bubble release mechanism. Details of the system are presented in [31] and summarize as follows. The flow cell consisted of a thin vertical acrylic glass tank (height: 1200mm; width: 160mm; thickness: 7mm). An electrochemical solution as described in [53] was circulated through the flow cell at an average upward velocity of 0.2m/s. Single 3 mm diameter bubbles were introduced into the upflowing liquid at the base of the flow cell.

An array of 8 x 0.5 mm diameter platinum EDM cathodes were installed along the width of the flow cell flush mounted in the wall, perpendicular to the liquid and bubble rise path 800 mm from the base of the flow cell. Data from the EDM cathodes was collected and conditioned using a custom electrical circuit and data collection system. Nitrogen gas was used to generate the bubble and purge oxygen from the electrochemical solution used. Other than the cathode and anode, all system components in contact with the electrochemical solution were non-conductive.

3.2 Practical aspects influencing the measurement

Several factors can influence the calibration of EDM probes. First, the surface area of the cathode may not be perfectly circular. Also, scratches on the surface or cracks in the gluing where the electrolyte solution can infiltrate may exist which increase the overall effective surface. In addition, the build-up of oxidization products on the cathode can affect the effective surface area. The concentration of the reactive species in the electrolyte solution can change due to photocatalytic reactions or reactions with soluble oxygen. A number of parameters are highly sensitive to temperature. Therefore it is important to maintain the temperature at a precise level.

A number of operational conditions can also affect the measurement collected using EDM. Electromagnetic fields generated from surrounding devices such as computers, phones, chargers etc. can contribute to background noise. Therefore such devices should be turned off or shielded. The pumping of the electrolyte solution itself can also generate electromagnetic fields. Therefore the path length over which the liquid is pumped should be

$$\phi_{ED} = \tan^{-1}\left[3.31\Omega^{-1/2} - 1\right] \quad \text{for } \Omega > 1$$
minimized. Formations of galvanic cells within the system can also contribute to the magnitude of the signal. All surfaces should be non-conductive or coated with non-conductive material. Furthermore, as mentioned in section 2.3, a negligible electrical migration is necessary. This depends on the conductivity of the electrolyte solution which needs to be high and the distance between the cathode and anode which should be minimal. Usually it is sufficient if one of the two conditions is fulfilled. A limitation of reacting ions at the cathode would also affect the current. Two things are affecting this point. First of all a sufficient concentration of the reactants should be in the liquid and second of all, the effect can be avoided by having a much larger sized anode and therefore a large area for the counter-reaction. Regarding the electrical equipment, the amplifier, Ohmic resistances in the system and the grounding affect the signal. It should be also kept in mind that besides the forced convection, at low Reynolds numbers the free convection can influence the measurements [78]. Chan [11] gives a sensitivity study of the signal to selected parameters from the list above. The highest sensitivities were found for the parameters probe diameter and ion concentration. The list does not claim completeness as there are always factors specific to the used setup and its surroundings.

3.3 Data conditioning

Data conditioning consisted of first establishing a relationship between the measured current and the imposed wall shear rate (i.e. calibration), and then correcting the acquired wall shear rate signal in respect to the unsteady near-wall flow conditions observed during the bubble rise.

3.3.1 Calibration

Both direct and indirect calibration is possible. For direct calibration, a known shear rate is applied at the surface of the cathode and a resulting current through the EDM system is measured. Equation (15) is then applied to determine the relationship between the measured current and the imposed wall shear rate. Ideally, direct calibration is done in-situ. However, for some more complex flow systems where it is not possible to achieve well defined flow conditions in-situ, the calibration should be performed ex-situ. In this case, a versatile removable probe is temporarily moved from the system of interest into a separate ex-situ calibration system where the Leveque coefficient is determined. Care must be taken to ensure that the temperature and composition of the electrolyte solution in the ex-situ calibration system are the same as those in the system of interest. For indirect calibration, a voltage step approach described in section 2.6.1 is used not only to determine the Cottrell coefficient but also to estimate the Leveque coefficient (see [9]). A typical result obtained from such voltage step experiments for our cathodes is presented in Figure 1. The Cottrell coefficient is estimated from the shape of the log-log plot of the current measured over time during the transient period of the voltage step. As the current at the beginning and end of the transient process is influenced by a number of parameters (such as cathode surface roughness or gradual approaching the magnitude of steady current), only the middle linear part of the transient response is considered for data regression. Our experience indicates that such a relevant time interval ranges from 0.01 s to 0.5t₀. As the characteristic response time t₀ is not known beforehand, the authors suggest an iterative determination procedure schematically illustrated in Figure 2. For the regression, a polynomial of first order (I=kₜ₀*x+I₀) according to eq.(22) with x=t^{1/2}) is chosen where the I-intercept I₀ takes into account potential edge effects as described in section 2.6.1. Here the t₀ value is determined by the interception between the transient and steady state asymptotes. For the data presented in Figure 1, this procedure provides for the Cottrell coefficient a value of kₜ₀=1.13*10⁻⁶ As¹/₂. The theoretical relationship for the Cottrell
coefficient (compare equations (19) and (20)) then can be used to obtain an estimate of the diffusion coefficient \( D \) (equation (32)).

\[
k_{\text{Cot}} = nAFc_bD^{1/2}\pi^{-1/2}
\]

(32)

For the known parameters of applied electrochemical system \( (n=1, \, F=96485 \text{ C/mol}, \, c_b=3 \text{ mol/m}^3) \) and circular probes \( (d=0.00055 \text{ m}, \text{ thus } A=\pi d^2/4=0.238 \text{ mm}^2) \); due to the manufacturing procedure the real diameter of the sensor is slightly larger than the nominal diameter of the used platinum wire), it provides a value of \( 8.48 \times 10^{-10} \text{ m}^2/\text{s} \). This value is in good agreement with those measured in previous experiments (see chapter 2.3) and therefore it can also be applied to indirectly determine the Leveque coefficient, using the theoretical relationship (compare equations (14) and (15)) as presented in equation (33), which for the data presented is \( k_{\text{Lev}}=6.48 \times 10^{-7} \text{ As}^{1/3} \).

\[
k_{\text{Lev}} = 0.862nAFc_bD^{2/3}d^{-1/3}
\]

(33)

For comparison, the Leveque coefficient obtained by direct calibration done in our experimental set-up under known conditions of the single-phase channel flow has a similar value of \( 6.3 \times 10^{-7} \text{ As}^{1/3} \).

Considering the influence of edge effects as discussed in section 2.6.1, the Peclet number calculated for typical wall shear rate in our experimental set-up \( (\gamma=100 \text{ s}^{-1}) \) has a value of \( \text{Pe} = \gamma d^2/D = 31000 \). The modified Peclet number \( H= 52 \) then provides a small edge-effect correction factor of \( \psi = 0.02 \) (see [37] for details), which means that a correction factor of 2% would be needed to find the actual Sherwood number considering the edge effects.

### 3.3.2 Signal acquisition and pre-processing

The accuracy of the correction for dynamic flow conditions can be affected by the signal sampling rate. If the sampling frequency is too small, peaks (i.e. maxima and minima) in the signal can be damped, whereas background noise in the measured signal can be amplified if the sampling rate is too large. In general, the sampling frequency should be at least twice that of the frequency of expected flow fluctuations in the system \([54]\). For the investigated flow system, this frequency can be estimated from the time necessary for a bubble to pass the sensor (bubble size/bubble velocity). Considering 3 mm bubbles rising in co-current liquid flow of 0.2 m/s, the minimal sampling frequency is estimated to be 200 Hz. To obtain wall shear rate response to a rising bubble in more detail, sampling frequencies ranging from 500 to 750 Hz have been used \([31]\). The advantage of using higher frequencies is that a moving average can be used to remove background noise without substantially dampening the peaks in the signal. Figure 3a presents typical results for a signal sampling frequency of 500 Hz, with and without averaging. As presented, averaging approximately over 8 measurements significantly reduces the background noise of the signal (Figure 3b, showing the standard deviation at steady flow conditions for different averaging ranges) without significantly affecting the overall profile of the signal (Figure 3a). Taking into account the characteristic response time of the sensor (estimated to be in the order of 0.1 s), signal pre-processing is also necessary for the correct calculation of time derivatives needed for the signal correction.

### 3.4 Wall shear rate calculation and correction

With the Leveque and Cottrell coefficient determined from direct or indirect calibration, the properly measured current signal through the electrochemical system can be converted to a wall shear rate course. When time variations of the current are slow (i.e. \( \partial I/\partial t \) values become negligibly small), the quasi-steady equation (15) can
be applied to calculate the actual wall shear rates. As a general rule of thumb based on experience, a criterion for such quasi-steady measurement conditions can be assumed as long $2k_{c2} \frac{\partial I}{\partial t} < 0.05I$ is valid. This means, that if this criterion is fulfilled, in equation (27) the unsteady correction part is small in comparison to the result of the quasi-steady equation (15). Under unsteady flow conditions, as in the case of near-wall flow induced by rising bubbles, this condition is not fulfilled, the frequency response of electrodiffusion sensors should be taken into account, and equation (27) has to be used for wall shear rate calculations.

Typical results from wall shear rate measurements characterizing the near-wall flow response to a rising bubble are presented in Figure 4. Raw (open symbols) and averaged (line) current data are presented in Fig. 4a. The signal noise observed in raw data is reduced by a moving average procedure applied over 9 measurements, which does not significantly affect the signal peak value. The smoothed current data are then linearized, to obtain local values of time derivatives of the averaged measurements (shown in Fig. 4a by solid symbols). Fig. 4b presents the wall shear rate response corresponding to the measured averaged measurements. It compares the quasi-steady data interpretation (calculation of wall shear rate according to equation (15); open symbols) with the results obtained by applying the approximate method of signal correction (calculation according to equation (27); line). It is clearly visible that the signal correction in respect to probe dynamic behavior is necessary for the conditions investigated, e.g. the peak value obtained by quasi-steady calculation is highly underestimated (by about 60%).

4 Summary and Conclusions

The purpose of this article is to summarize the theoretical background necessary to interpret the data provided by the EDM in practical applications. First, complete derivations of the steady flow equations that govern the mass transfer induced by the electrochemical reaction in the system are gathered from the available EDM literature. Then, the methods used for unsteady data processing and the approximate method of signal correction recommended for the measurement in unsteady flow systems are discussed. Finally, some practical aspects of the direct, indirect in-situ and ex-situ calibrations are discussed together with a comprehensive list of factors potentially influencing the electrodiffusion experiments. Special attention is drawn to those factors that should be obviated in the experimental preparation.

The EDM is then applied to a system where a single bubble rises in a vertical, narrow rectangular channel with a co-current flow of the electrolyte solution. The data collected is presented as an example to demonstrate the practical aspects of the data interpretation. A new mathematical approach is suggested to evaluate transient calibration data where the Cottrell calibration factor is determined iteratively.

The approximate method of signal correction then demands the precise calculation of time derivatives. This is achieved by using appropriate methods of signal smoothing and linearization. For the system considered, signal correction is necessary to obtain accurate measurements of the wall shear rate.

In conclusion, it can be stated that the EDM is a very sensitive wall shear stress measurement technique. However, the measurements and data treatment should be done carefully and the obtained results critically scrutinized.
Acknowledgments

This work is part of the Collaborative Research Centre "Integrated Chemical Processes in Liquid Multiphase Systems" coordinated by the Technische Universität Berlin. Financial support by the Deutsche Forschungsgemeinschaft (DFG, SFB/TR 63 and KR 1639/18-1) and the Deutsche Akademische Austauschdienst (DAAD, D/10/46059) is gratefully acknowledged. Partial support of Grant Agency of the Czech Republic under the project P101/12/0585 is also appreciated.

Notation

A [-] constant in equation (28)
A [m²] electrode area
A_{ED} [-] amplitude attenuation of the current signal fluctuations
B [-] constant in equation (28)
c_o [mol/ m³] concentration of the oxidizing ion in the bulk
∇c_i [mol/m³] concentration gradient of the oxidizing ion
c_i [mol/m³] concentration of the oxidizing ion
d [m] diameter of the electrode
D, D_i [m²/s] diffusion coefficient
f [1/s] frequency
F [(A s)/mol] Faraday constant
G [-] function used in eq.(25)
H [-] modified Peclet number as described in [38]
H_{ED} [-] transfer function between the probe current response to the wall shear between the probe current response to the wall shear
H_0 [A s] quasisteady response of the electrodiffusion probe = I/(3γ)
i [-] complex number
I [A] current
I_0 [A] current correction for edge effects
I_{steady} [A] current when EDM signal is steady
k_{Cott} [A S^{1/2}] Cottrell coefficient
k_{Lev} [A S^{1/2}] Leveque coefficient
k_m [m/s] mass transfer coefficient
l [m] length of the strip probe in the mean flow direction
L_{char} [m] characteristic length of the cathode
n [-] number of electrons transferred during the reaction
\dot{n_i} [mol/(s m²)] molar flux
\dot{n_{i,conv}} [mol/(s m²)] molar flux due to convection
\dot{n_{i,migr}} [mol/(s m²)] molar flux due to migration
\dot{n_{i,diff}} [mol/(s m²)] molar flux due to diffusion
**P** [m]  perimeter of the circular electrode

**Pe** [-]  Peclet number \( \text{Pe}=\frac{\gamma d^2}{D} \)

**Sc** [-]  Schmidt number \( \text{Sc}=\frac{\mu}{(\rho D)} \)

**Sh** [-]  Sherwood number

**Sh\_DLA** [-]  Sherwood number for diffusion layer approximation

**t** [s]  time

**t\_0** [s]  characteristic time

**T** [K]  temperature

**u_i** [m²/(V s)]  electrical mobility

**v** [m/s]  velocity

**v_x** [m/s]  velocity component in x direction

**v_y** [m/s]  velocity component in y direction

**x** [m]  x-coordinate, main flow direction

**y** [m]  y-coordinate, normal to the probe surface

**z** [m]  z-coordinate, perpendicular to the main flow direction

**Greek Letters**

**\( \beta \)** [-]  relative wall shear rate fluctuation amplitude

**\( \gamma \)** [1/s]  wall shear rate

**\( \gamma_c \)** [1/s]  transient corrected wall shear rate

**\( \gamma_s \)** [1/s]  wall shear rate at steady state

**\( \bar{\gamma} \)** [1/s]  the amplitude of wall shear rate fluctuations

**\( \bar{\gamma} \)** [1/s]  the mean value of wall shear rate

**\( \delta_c \)** [m]  concentration boundary layer thickness

**\( \zeta \)** [-]  variable for the edge effect correction function

**\( \mu \)** [Pa s]  dynamic viscosity

**\( \rho \)** [kg/m³]  density

**\( \nabla \Phi \)** [V/m]  electrical potential gradient

**\( \Phi_{ED} \)** [-]  phase shift of the current signal in respect to the wall shear rate

**\( \Psi \)** [-]  correction function for edge effects as described in [38]

**\( \Omega \)** [-]  dimensionless frequency = \( (f l^{2/3})/(D \gamma^{2/3}) \)

**References**


Short text for the Table of Contents

The electrodiffusion method allows to measure wall shear stress. Various authors have published articles dealing with the theory; however there is no document that comprehensively collects all the knowledge that assembled over five decades of application. The present publication provides a comprehensive summary of the theory for steady flow, unsteady flow and transient voltage step experiments.

Figure for the ToC
Table 1: Shear stress measurement techniques sorted by their measurement principle

Table 2: Substances used for preparation of the electrolytic solution

Figure 1: Voltage step data and the different regression lines from each iteration step

Figure 2: Structured flow chart for the iteration process to determine $k_{\text{Cut}}$

Figure 3: Current response generated by a rising bubble: noise reduction by moving averages (a) and standard deviations of the signal for different averaging ranges (at steady flow conditions) (b)

Figure 4: Typical experimental results for the current measurements with raw and averaged data (over 9 measurements) and time derivative (a) and the corresponding averaged and transient corrected shear rate (b)
Table 1: Shear stress measurement techniques sorted by their measurement principle

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<th>Principle</th>
<th>Measured Parameter</th>
<th>Example Publications</th>
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<td>shear stress / temperature / particle movement</td>
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<td>pressure</td>
<td>[56]</td>
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<td>pressure</td>
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Voltage step data and the different regression lines from each iteration step.
Structured flow chart for the iteration process to determine $k_{Cot}$

97x111mm (300 x 300 DPI)
Current response generated by a rising bubble: noise reduction by moving averages (a) and standard deviations of the signal for different averaging ranges (at steady flow conditions) (b)
Typical experimental results for the current measurements with raw and averaged data (over 9 measurements) and time derivative (a) and the corresponding averaged and transient corrected shear rate (b)

160x219mm (300 x 300 DPI)