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Frequency response of electrochemical sensors in a cone-and-plate modulated flow

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Abstract—In this paper, an analysis of the unsteady laminar flow in a cone-and-plate system where the angular velocity of the cone is modulated sinusoidally with time is performed This is used to test the frequency response of circular or rectangular electrochemical sensors embedded flush with the plate plane By using different viscosities, it is possible to separate experimentally the effect of the hydrodynamic transfer function between the angular velocity and the velocity gradient at the plate from the effect of the frequency response of mass transfer probes between the velocity gradient and the instantaneous limiting current Excellent agreement between theory and experiment is found in the frequency range of interest for both circular and rectangular probes

1. INTRODUCTION

ELECTROCHEMICAL sensors are now widely used in electrochemical engineering processes where an access to wall shear stress or wall velocity gradient in local values is required Recent theoretical developments concerning the methodology of these sensors extend their use to time-dependent flows and provide a new means for spectrum analysis of the velocity field in the wall region Such a procedure, which allows the power spectrum density (psd) of the wall velocity gradient—one-dimensional spectrum—from the experimental psd of the fluctuations of the diffusion current to be deduced, is founded on the knowledge of the dynamic frequency response of these sensors This frequency response is defined for mass transfer probes as the transfer function between the mass flux response and the sine wave modulated wall velocity gradient at a microelectrode on which a fast electrochemical reaction is proceeding in the condition of limiting diffusion current [1, 2].

Theoretical expressions of the transfer function were proposed earlier but improved solutions are now available in a wide frequency range for circular as well as for rectangular probes having their length perpendicular to the mean flow direction [3, 4]

There are only a few experimental confirmations and the first quantitative ones only, were obtained by use of a modulated rotating disk electrode [4] However, with this flow geometry, the instantaneous direction of the velocity vector being not aligned with the time average one except for very low frequencies [5], the comparison between theory and experiment was limited to circular microelectrodes

For extending the validity of the above mentioned theoretical predictions and checking the response of rectangular probes, a similar experimental study with a modulated flow in a cone-and-plate system was carried out. In the absence of secondary flow, this system provides indeed a one-dimensional velocity field in the circumferential direction. In this paper, an analysis of the sinusoidally modulated laminar flow in small oscillations for this system is first reported. The resulting effect on mass transfer is then deduced and the relevant variations with frequency further compared to the experimental data relative to circular or rectangular probes

2. VELOCITY DISTRIBUTION IN MODULATED FLOW

The equations of motion for the cone-and-plate system are adequately expressed in spherical coordinates with the symbols recalled in Fig. 1 In the present case, the cone is rotating at an angular velocity $\Omega(t)$ such that

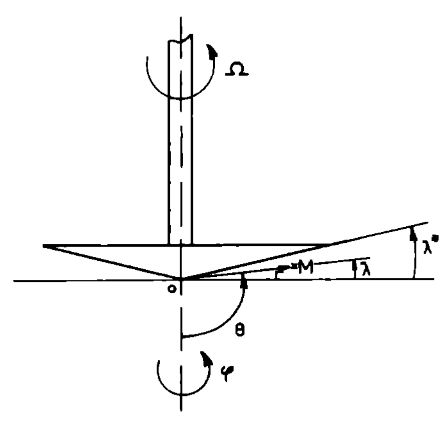

FIG 1 General scheme of the cone-and-plate system a point M (r, θ, φ) between the cone and the plate is at a distance $y = r \sin \lambda$ of the plate and at a distance $r \cos \lambda$ of the axis

NOMENCLATURE

A_1, A_2 integration constants in equation (11)
C concentration of electroactive species [mol cm^{-3}]
D diffusivity [cm^2 s^{-1}]
d diameter of circular probes [cm]
F Faraday number, 96 500 C
f^* reduced frequency of the rotating cone, $1 - j\omega r^2/\nu$
H dimensionless frequency response of mass transfer on a rectangular microelectrode
H_c dimensionless frequency response of mass transfer on a circular microelectrode
I limiting current density [A cm^{-2}]
J limiting diffusion flux [mol cm^{-2} s^{-1}]
j imaginary number, $\sqrt{-1}$
K rate of shear in the r-direction [s^{-1}]
l width of a rectangular microelectrode [cm]
n number of electrons transferred in the redox reaction
p pressure [dyn cm^{-2}]
Re Reynolds number, $\phi^2\Omega\beta/\nu$
Re real component of a complex number
r radial coordinate [cm]
T total torque on the rotating cone [dyn cm]
T_0 torque without secondary flow [dyn cm]
t time [s]
v_r, v_θ, v_φ velocity components in spherical coordinates [cm s^{-1}]
Z experimental mass transfer impedance, $\tilde{I}/\Delta\Omega$
Z_{HD} hydrodynamic transfer function, $\tilde{\alpha}/\Delta\Omega$

Greek symbols
α velocity gradient [s^{-1}]
$\beta(\theta, \lambda^*)$ constant in equation (2) tabulated in ref. [6]
θ azimuthal coordinate (spherical system) [rad]
λ $\theta - \pi/2$ [rad]
λ^* angle between cone and plate [rad]
ν kinematic viscosity [cm^2 s^{-1}]
ρ density [g cm^{-3}]
σ dimensionless frequency for a circular microelectrode, $\omega(d^2/\alpha^2 D)^{1/3}$
σ' dimensionless frequency for a rectangular microelectrode, $\omega(l^2/\alpha^2 D)^{1/3}$
ϕ diameter of the cone base [cm]
φ circumferential coordinate (spherical system) [rad]
ω pulsation [rad s^{-1}]
ω^* upper pulsation limit of the quasi steady state domain for Z_{HD}
Ω angular velocity of the cone [rad s^{-1}]
$\Delta\Omega$ amplitude of modulation of the cone angular velocity.

Superscripts
$\bar{}$ time average quantity
$\tilde{}$ Fourier transform of the time-dependent component, i.e $X(t) = \bar{X} + \mathrm{Re}\,(\tilde{X} \exp j\omega t)$

$$\Omega(t) = \bar{\Omega} + \Delta\Omega \,\mathrm{Re}\,\{\exp j\omega t\} \quad (1)$$

The plate is immobile which provides the following set of boundary conditions:

$$\left.\begin{matrix} v_\varphi \\ v_r \\ v_\theta \end{matrix}\right\} = 0 \quad \text{for} \quad \theta = \pi/2$$

$$\left.\begin{matrix} v_\varphi = \Omega r \cos\lambda^* \\ \left.\begin{matrix} v_r \\ v_\theta \end{matrix}\right\} = 0 \end{matrix}\right\} \quad \text{for} \quad \theta = \frac{\pi}{2} + \lambda^*$$

The further analysis will concern the primary flow Walters and Waters [6] established a criterion for the existence of secondary flow based on the deviation of the total torque T with respect to T_0 without secondary flow

$$\frac{T}{T_0} = 1 + \beta(\theta, \lambda^*)\left\{\frac{Re}{\lambda^*}\right\}^2 \quad (2)$$

where β is a constant which has been tabulated for different values of the cone angle and Re is the Reynolds number defined as

$$Re = \frac{\phi^2\Omega\beta}{\nu}$$

where ϕ is the cone diameter.

Considering that secondary flow appears primarily in the outer region and that the region under investigation is located rather closer to the rotation axis, the criterion given by equation (2) is more constraining than required

Therefore, in so far as primary flow is concerned (i.e $v_r = 0$ and $v_\theta = 0$ for any r, θ and φ), for both the steady state and the fluctuating quantities, also all derivatives with respect to φ vanish and the equations of motion are

$$\begin{cases} -\rho \dfrac{v_\varphi^2(t)}{r} = -\dfrac{\partial p(t)}{\partial r} & (3) \\ -\rho \dfrac{v_\varphi^2(t)\cos\theta}{r} = -\dfrac{1}{r}\dfrac{\partial p(t)}{\partial \theta} & (4) \\ \dfrac{\partial v_\varphi(t)}{\partial t} + \dfrac{1}{r^2}\dfrac{\partial}{\partial r}\left\{\dfrac{\partial v_\varphi(t)}{\partial r}\right\} + \dfrac{1}{r^2 \sin\theta}\dfrac{\partial}{\partial \theta} & \\ \quad \times \left\{\sin\theta \dfrac{\partial v_\varphi(t)}{\partial \theta}\right\} - \dfrac{v_\varphi(t)}{r^2 \sin\theta} = 0 & (5) \end{cases}$$

where p is the pressure

When small oscillations are imposed to the mean flow (i e $\Delta\Omega/\bar{\Omega} \ll 1$), linearity is fulfilled and we may write

$$v_\varphi(t) = \bar{v} + \mathrm{Re}\{\tilde{v}_\varphi \exp j\omega t\} \quad (6)$$

Here $\tilde{v}_\varphi$ is a complex quantity.

Steady state solution is readily obtained from equation (5) by assuming small λ values and by setting

$$\bar{v}_\varphi = \bar{K}(\theta)\cdot r. \quad (7)$$

With the previous boundary conditions, one finds

$$\bar{v}_\varphi = \bar{\Omega} r \frac{\sin\lambda}{\tan\lambda^*} \quad (8)$$

where $r \sin\lambda \approx r\lambda$ represents also the normal distance to the wall y, so that the velocity gradient at the wall can be determined

$$\bar{\alpha} = \left.\frac{\partial \bar{v}_\varphi}{\partial y}\right|_0 = \frac{\bar{\Omega}}{\tan\lambda^*} \quad (9)$$

This classical result implies a constant gradient value, whatever the position on the plate

For modulated flow, both equations (6) and (7) lead to

$$\tilde{v}_\varphi = \tilde{K}(\theta)\cdot r$$

so that equation (5), after removing the steady state solution, becomes

$$\tilde{K}''(\theta) + \tilde{K}(\theta)\left(1 - \frac{j\omega r^2}{\nu}\right) = 0 \quad (10)$$

with the solution

$$\tilde{K}(\theta) = A_1 \exp\{i\theta\sqrt{f^*}\} + A_2 \exp\{i\theta\sqrt{f^*}\} \quad (11)$$

and

$$f^* = 1 - j\frac{\omega r^2}{\nu}.$$

A_1 and A_2 are determined by the same boundary conditions as previously, extended to $\tilde{v}_\varphi$. Therefore

$$\tilde{K}(\theta) = \Delta\Omega \cos\lambda^* \frac{\sin\{\lambda\sqrt{f^*}\}}{\sin\{\lambda^*\sqrt{f^*}\}} \quad (12)$$

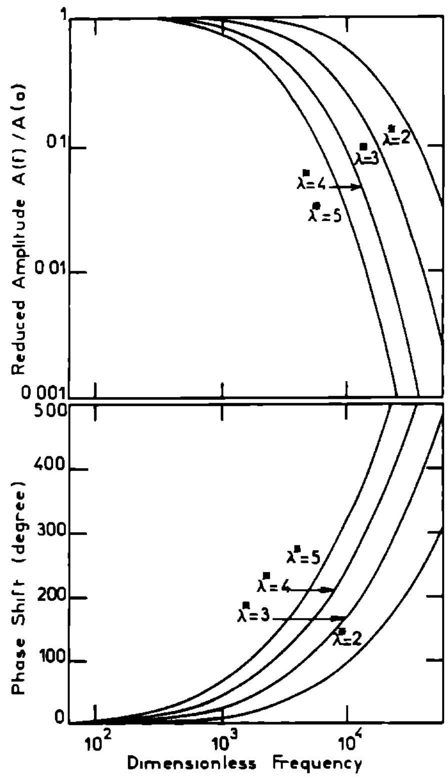

FIG 2. Variation of the transfer function $Z_{HD} = \tilde{\alpha}/\Delta\Omega$ vs the dimensionless frequency $\omega^* = \omega r^2/\nu$ according to expression (13).

The modulated velocity gradient at the wall is given by

$$\tilde{\alpha} = \left.\frac{\partial \tilde{v}_\varphi}{\partial y}\right|_0 = \left.\frac{\partial \tilde{v}_\varphi}{r\partial \lambda}\right|_0 = \frac{\Delta\Omega\sqrt{f^*}\cdot\cos\lambda^*}{\sin\{\lambda^*\sqrt{f^*}\}} \quad (13)$$

The asymptotic behaviour of $\tilde{\alpha}$ when $\omega \to 0$ identifies with the values of $\bar{\alpha}$ (see equation (9)) since $f^* \to 1$

From equation (13), a hydrodynamic transfer function Z_{HD} between the velocity gradient and the angular velocity of the cone, i.e. $\tilde{\alpha}/\Delta\Omega$, can be defined.

Its variations with f^* are presented in amplitude and phase shift for different λ^* values in Fig. 2

3. MODULATED MASS TRANSFER—DISCUSSION

When a fast redox reaction proceeds at a metallic surface in the limiting diffusion current conditions, one species of the couple is consumed infinitely fast so that its wall concentration is $C = 0$. The limiting current is proportional to the diffusion flux J

$$I = nFJ = nFD\left.\frac{\partial C}{\partial y}\right|_0 \quad (14)$$

where n is the number of electrons transferred, F the Faraday number (96 500 C) and D the diffusivity of the consumed species.

The frequency response theoretically predicted in refs [3, 4] corresponded to the quantity $(\partial \tilde{C}/\partial y)/\tilde{\alpha}$ (otherwise referred to as H for a rectangular probe or H_s for a circular one) which is independent of the main flow geometry Equation (14) which expresses the proportionality between the current and the flux, is also true for tilded quantities and therefore, when normalized by its value at zero frequency, the measured impedance $Z = \tilde{I}/\Delta\Omega$ can be written as the product of functions of H by the hydrodynamic transfer function Z_{HD}.

Though the primary aim of this work is to check the validity of theoretical expressions of H or H_s, the function Z_{HD} had also to be confirmed experimentally Indeed in this last case, due to the simple mathematical derivations, it was rather a way to substantiate the existence of the sole primary flow

Functions of H or Z_{HD} are dependent on different dimensionless frequencies which are combinations of different variables characterizing the problem, either geometrical (λ^*, r, d diameter of a circular probe or l width of a rectangular one), or mechanical ($\bar{\Omega}$) or physicochemical (ν, D), each of which can be independently modified (except for ν and D)

Hence, one may ask oneself whether an appropriate choice of those variables allow one to study any of those transfer functions (either H's or Z_{HD}) separately

In other words, we are looking for a set of values for the variables such that one transfer function, H for example, is in quasi-steady state in the frequency range under investigation and the other, in this example Z_{HD}, varies in a large range in amplitude and phase Of course, we are also looking for the opposite situation where Z_{HD} is in quasi-steady state and H varies until its high frequency asymptotic behaviour. Therefore, in each case, the measured impedance Z would be proportional only to H or to Z_{HD}

We will show that from an experimental point of view, it is easy to minimize the effect of Z_{HD}, so that Z basically reflects the variations of H with frequency The opposite situation will be shown to be unrealistic from the experimental point of view

Consider first the additional and permanent constraint stating that the microelectrode must operate in the boundary layer approximation and with no influence of longitudinal diffusion [7] This imposes Ling's condition

$$\frac{\bar{\alpha} l^2}{D} \geqslant 5000$$

(equivalent condition for a circular probe is obtained with $d = l/0.82$ [8]).

Therefore

(i) $\bar{\alpha}$ *must be high* however, too high $\bar{\Omega}$ values are undesirable because of secondary flows Low λ^* values must be selected

(ii) *l or d must be high* a limitation occurs due to the possibility of local evolution of the concentration of active species because consumption of one species and production of the other species of the couple (on the counter electrode) would proceed at high rates in a limited solution volume

(iii) *D must be small* high viscosities must then be used by virtue of the Stokes–Einstein relation

Let us now evaluate the conditions for obtaining significant frequency domains for which in a first situation Z_{HD} can be studied, H being in quasi-steady state and in a second situation H can be studied, Z_{HD} being in quasi-steady state

From ref [3], H is dependent on a reduced frequency

$$\sigma' = \omega \left(\frac{l^2}{\bar{\alpha}^2 D}\right)^{1/3}$$

(slightly different values would be found with H_s and $\sigma = \omega(d^2/\bar{\alpha}^2 D)^{1/3}$) A more convenient form of σ' is

$$\sigma' = (\omega/\bar{\alpha}) \left(\frac{\bar{\alpha} l^2}{D}\right)^{1/3}$$

Quasi-steady state regime for H is realized when $\sigma' < 1$ and high frequency regime where

$$\frac{H(\sigma')}{H(0)} = \frac{3\,72}{i\sigma'} - \frac{4}{(i\sigma')^{1/2}} \tag{15}$$

is realized when $\sigma' > 6$.

Dependence of Z_{HD} with the reduced frequency is not so simple and in particular does not show a power-law behaviour in high frequency. However, from consideration of Fig 2, a reasonable estimate of the upper frequency limit for the quasi-steady state domain is

$$\omega^* = \frac{\omega r^2}{\nu} \approx 10^3 \quad \text{for} \quad \lambda^* = 2$$

Due to the fast variation of Z_{HD} with ω^*, a value of 10^4 can be chosen as the lower frequency for its study (also for $\lambda^* = 2$) This λ^* value was retained for fulfilling both Ling's condition (condition (i)) and that of Walters and Water about the absence of secondary flow

(a) Study of H's, Z_{HD} being in quasi-steady state

From $(\omega/\bar{\alpha})(\bar{\alpha} l^2/D)^{1/3} > 6$ and $\omega r^2/\nu < 10^3$, one obtains

$$\frac{6\bar{\alpha}}{(\bar{\alpha} l^2/D)^{1/3}} < \omega < 10^3 \frac{\nu}{r^2} \tag{16}$$

Typical values of $\bar{\alpha} = 10^2$ and $r = 1$ cm can be assumed in the following A significant ω range in equation (14) is likely to be obtained by use of high viscosity.

As an example, by setting $\nu = 1$ cm^2 s^{-1}, D should be in the range 10^{-7} cm^2 s^{-1} and with $l \approx 3 \times 10^{-2}$ cm, condition (14) becomes

$$6 \leqslant \omega \leqslant 10^3$$

This range of angular velocity modulation can be easily obtained mechanically.

(b) Study of Z_{HD}, H being in quasi-steady state

The condition to be satisfied can be now written as

$$10^4 \frac{\nu}{r^2} \leqslant \omega \quad \text{and} \quad \omega \leqslant \frac{\bar{\alpha}}{(\bar{\alpha}l^2/D)^{1/3}} \qquad (17)$$

Now it is obvious that the only possibility is to decrease the viscosity. A lower reasonable value is $\nu \approx 10^{-2}$ cm^2 s^{-1} with $D \approx 10^{-5}$ cm^2 s^{-1} providing $(\bar{\alpha}l^2/D) \approx 10^4$ which still ensures Ling's condition Finally one finds

$$10^2 \leqslant \omega \quad \text{and} \quad \omega \leqslant 5.$$

Here the measurement is not possible.

Therefore, in a first step a viscous solution will be used to characterize H functions alone A low viscous solution will then allow to check the expression of Z_{HD} while a significant damping by H will be effective.

4. EXPERIMENTAL

To be consistent with the previous section, two cone angles λ^* of 2° or 3° were chosen The cone was rotated at Ω and the plate was immobile Circular or rectangular platinum microelectrodes were embedded flush with the plate plane Both cone and plate were machined from plexiglass A large Pt grid, placed outside the region between the cone and plate, was used as a counter electrode.

The electrochemical reaction used was the reduction step of a very rapid redox system—potassium ferri-ferrocyanide 10^{-2} M—with KCl (0.7 M) as supporting electrolyte This solution was used either as prepared for low viscosity measurements or with an admixture of glycerol (50 or 70%) so as to increase viscosity

Viscosity was measured with a Couette viscometer (CONTRAVES) and diffusivity determined by measuring the Schmidt number with a modulated rotating disk electrode by using the EHD impedance technique [9]

A similar experimental set-up to that already devised for measuring the EHD impedance was used, the functional scheme of which is displayed in Fig. 3.

The sine wave modulation of the angular velocity is obtained by superimposing a sine wave voltage of low amplitude to the constant voltage used as reference for defining the average angular velocity of the d c. motor. Due to inertia limitations, the upper frequency limit is $\omega/2\pi \approx 100$ Hz.

The experimental transfer function $\tilde{I}/\Delta\Omega$ is measured by means of a two channel transfer function analyser (TFA SOLARTRON 1250) which delivers the potential signal for flow modulation two responses are sent to the channels of the TFA, one from the optical encoder yields a voltage signal proportional to the instantaneous angular velocity and the other from the electrochemical interface a voltage signal proportional to the instantaneous current Correlation performed by the TFA removes the time average value

5. EXPERIMENTAL RESULTS

5.1 *Circular probe*

5 1 1 *High viscosity solution H_ν measurement.* The experimental data for a (70–30) glycerol–water mixture are reported in Fig 4 The values of parameters ($r = 1$ 14 cm, $\nu = 0$ 2 cm^2 s^{-1}, $D = 4 \times 10^{-7}$ cm^2 s^{-1}, $d = 0$ 032 cm, $\bar{\Omega} = 50$ rpm) are in the ranges of those used for the condition of the H_ν study, Z_{HD} being in quasi-steady state As it can be seen in Fig. 4, the relative positions of theoretical curves for Z_{HD} and H_ν verify this assumption. The overall impedance data $(\tilde{I}/\Delta\Omega)$ which corresponds to open circles, corrected from the effect of Z_{HD}, provide the solid circles which show a very fair agreement with the curve in full line representative of the theoretical prediction of H_ν given in ref [3]

$$\begin{cases} \left|\dfrac{H_\nu(\sigma)}{H_\nu(0)}\right| = (1+0\,049\sigma^2+0\,0006\sigma^4)^{-1/2} \\ \arg H_\nu = -\arctan[0.242\sigma \\ \qquad \times (1+0\,0124\sigma^2-0.00015\sigma^4)] \end{cases}$$

for $\sigma \leqslant 6$ and

$$\frac{H_\nu(\sigma)}{H_\nu(0)} = \frac{4\,416}{i\sigma} - \frac{5.3}{(i\sigma)^{3/2}} \qquad (18)$$

for $\sigma \geqslant 6$

In particular, the high frequency behaviour of the amplitude as a power law ω^{-1} is observed over more than one decade, a result which is very important for psd analysis.

This very close agreement confirms also another point about the hypothesis put forward in the calculation of H_ν [4] in particular in the absence of influence of the transverse diffusion term By comparing our previous results obtained with a rotating disk system to this one, it is very likely that the deviation observed at that time between the data (especially the phase shift) and theoretical expression (equation (18)) were actually explained by the existence of a fluctuating component of the modulated velocity vector interacting with a defect of circular symmetry of the probe This explanation is now confirmed

5 1 2 *Low viscosity solutions. Influence of Z_{HD}* When the aqueous solution without glycerol is used, the following set of parameters is involved ($\nu = 0.0085$ cm^2 s^{-1}, $D = 0.7 \times 10^{-5}$ cm^2 s^{-1}, $\lambda^* = 3°$, other parameters being identical to Section 5 1 1) These values are compatible with Ling's condition The corresponding experimental data have been reported in Figs. 5(a) and (b) for two different values of $\bar{\Omega}$ because Z_{HD} is not an explicit function of σ In both cases, H_ν has been assumed as correctly representing the experimental variations of $\tilde{I}/\tilde{\alpha}$, and the theoretical

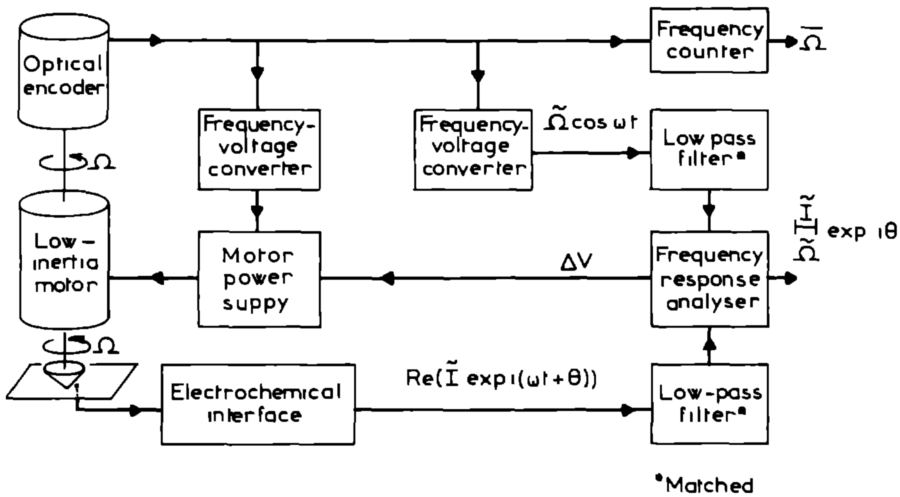

FIG 3 Block diagram of circuit used for measurements

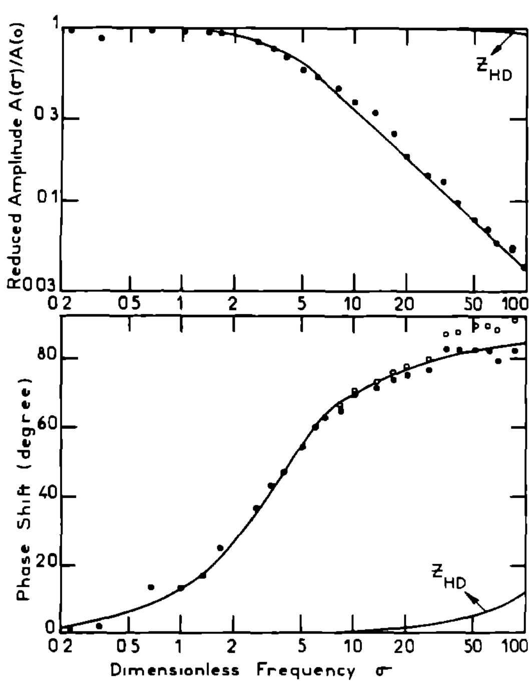

FIG 4 Theoretical transfer function H_x for a circular microelectrode plotted vs the dimensionless frequency according to the expressions given in ref [3] The theoretical hydrodynamical transfer function Z_{HD} is also plotted in these coordinates with $r = 1\ 14$ cm, $\nu = 0\ 2\ cm^2\ s^{-1}$, $d = 0\ 032$ cm, $D = 4 \times 10^{-7}\ cm^2\ s^{-1}$, $\lambda^* = 2^{\circ}$, $\Omega = 50$ rpm The experimental points (○) are corrected by Z_{HD} in order to get the experimental H_x (●)

variations of Z_{HD} were reported by a solid line Reconstructed values of $Z = Z_{HD} \cdot H_x$ by dashed lines show also a very good agreement with the experimental ones (open circles). This fact provides a confirmation of the calculated expression of Z_{HD} and indirectly substantiates the primary flow assumption

The same procedure was used for an intermediate situation where a (50–50) water–glycerol mixture was used with ($\nu = 7 \times 10^{-2}\ cm^2\ s^{-1}$, $D = 1\ 25 \times 10^{-6}\ cm^2\ s^{-1}$ and $r = 1\ 8$ cm). The relevant data shown in Fig 6 exhibit again a very good agreement between the theoretical H_x curve and the reconstructed values (solid circles) from the experimental one (open circles) by use of $H_x = Z/Z_{HD}$

5.2 *Rectangular probe*

So far, no experimental verification of the validity of the theoretical expression of function H in the case of a rectangular electrode has been successfully performed Two guard electrodes of the same width as the working one were placed at each side of it The impedance data are displayed in Fig. 7 with the same set of parameters as in Fig 4. Due to the rather large value of the microelectrode length ($\Delta r \approx 0\ 26$ cm) the correction effected by Z_{HD} required an integration

$$H = \frac{Z \cdot \Delta r}{\int_r^{r+\Delta r} Z_{HD}\, dr}$$

Here again, the agreement between the corrected data (solid symbols) and the theoretical curve (solid line) is excellent According to refs. [3, 4], this expression is

$$\begin{cases} \left|\dfrac{H_x(\sigma')}{H_x(0)}\right| = (1+0\ 056\sigma'^2+0.00126\sigma'^4)^{1\ 2} \\ \arg H = -\arctan\,[0.276\sigma' \\ \qquad \times (1+0\ 02\sigma'^2-0\ 00026\sigma'^4)] \end{cases}$$

for $\sigma' \leqslant 6$ and

$$\frac{H(\sigma')}{H_x(0)} = \frac{3.72}{i\sigma'} - \frac{4}{(i\sigma')^{3/2}} \qquad (19)$$

for $\sigma' \geqslant 6$.

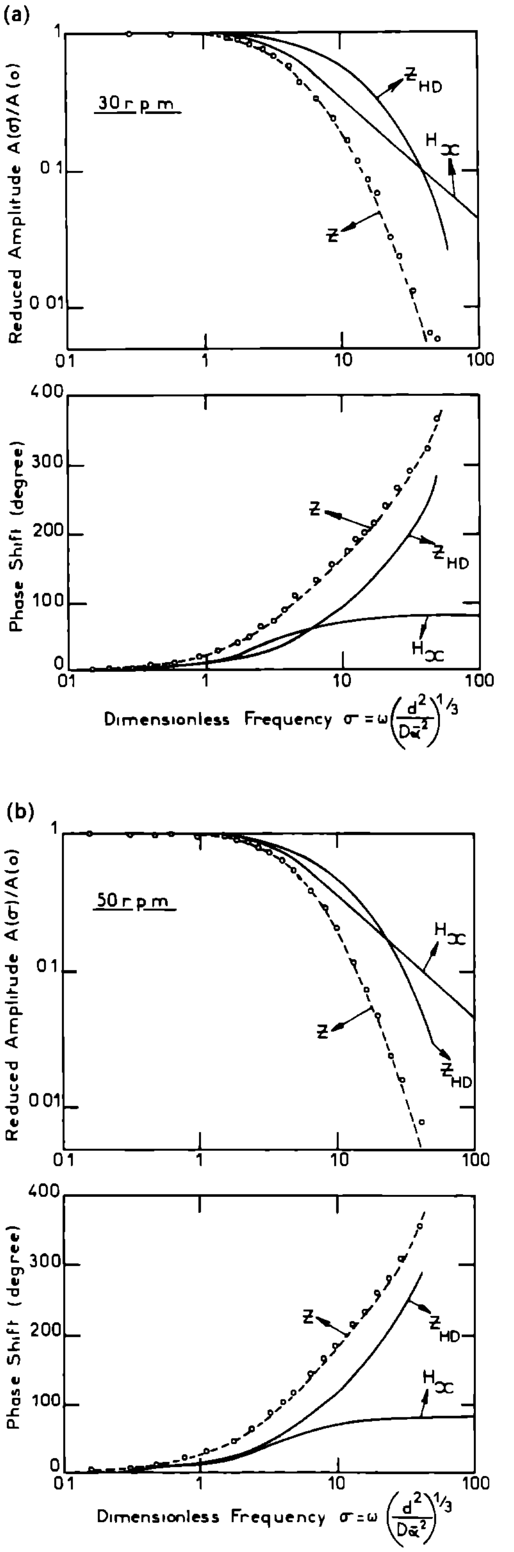

FIG 5 Theoretical transfer function H_x for a circular microelectrode plotted vs the dimensionless frequency according to the expressions given in ref [3] The theoretical hydrodynamical transfer function Z_{HD} is also plotted in these coordinates with $r = 1.14$ cm, $\nu = 0.0085$ cm^2 s^{-1}, $d = 0.032$ cm, $D = 0.7\times10^{-5}$ cm^2 s^{-1}, $\lambda^* = 3$ The deduced theoretical transfer function $Z = Z_{HD}H_x$ is plotted as a dashed line, the experimental points are represented by open circles (a) $\Omega = 30$ rpm, (b) $\Omega = 50$ rpm

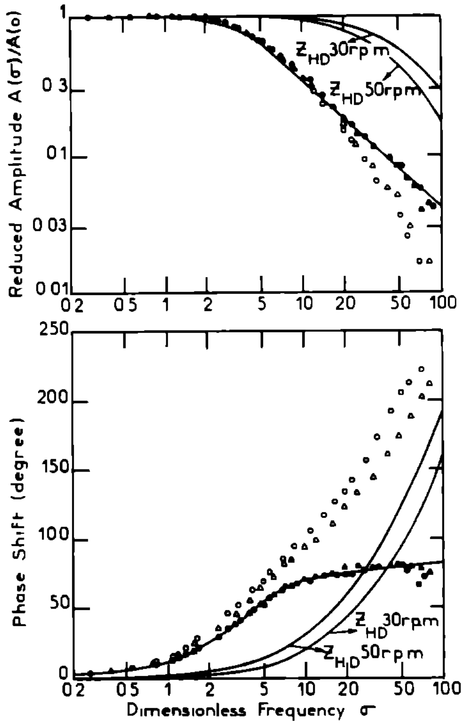

FIG 6 Same conditions as in Fig 5 with a 50–50 water–glycerol mixture $\nu = 7\times10^{-2}$ cm^2 s^{-1} and $D = 1.25\times10^{-6}$ cm^2 s^{-1} $\Omega = 50$ rpm (○, ●), 30 rpm (△, ▲)

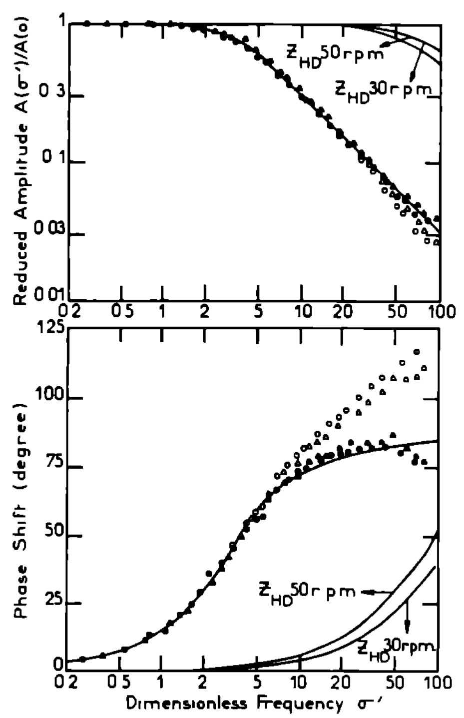

FIG 7 Theoretical transfer function H for a rectangular microelectrode plotted vs the dimensionless frequency σ' ($\sigma' = \omega(l^2/D\Omega)^{1/3}$) according to the expressions given in ref [3] The theoretical hydrodynamical transfer functions Z_{HD} are plotted in these coordinates for each rotation speed with $r = 1.04$ cm, $\nu = 0.2$ cm^2 s^{-1}, $l = 0.026$ cm, $D = 4\times10^{-7}$ cm^2 s^{-1}, $\lambda^* = 2$. The experimental points (open circle for $\Omega = 50$ rpm and open triangle for $\Omega = 30$ rpm) are corrected by Z_{HD} in order to get the experimental H_x (black points)

6 CONCLUSION

It has been shown that the cone-and-plate system in modulated conditions is appropriate for testing the frequency response of electrochemical sensors as mass transfer probes As a matter of fact, it provides a one-dimensional velocity field for which the time average and instantaneous vectors are aligned at any frequency This results in a greater simplicity for both the mathematical treatment and the experimental set-up

The obtained experimental data of the mass transfer functions H_x and H confirmed the recent theoretical expressions predicting a dependence of the amplitude on the reciprocal frequency (f^{-1}) in high frequency instead of $f^{-3/2}$ in earlier studies Incidentally, the electrochemical reaction used was proved to be rapid in the whole frequency range investigated

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REPONSE EN FREQUENCE DE CAPTEURS ELECTROCHIMIQUES EN ECOULEMENT CONE-PLAN MODULE

Résumé—Dans ce travail, on analyse l'écoulement laminaire non-stationnaire dans un système cône-plan dont la vitesse angulaire du cône est modulée avec le temps, de façon sinusoidale Ce système a été utilisé pour tester la réponse en fréquence de capteurs électrochimiques rectangulaires ou circulaires affleurant la paroi du plan en regard du cône On a pu séparer expérimentalement, par variation de la viscosité, l'effet de la fonction de transfert hydrodynamique entre la vitesse angulaire et le gradient de vitesse, de l'effet de la réponse en fréquence entre le courant limite instantané sur ces capteurs et le gradient de vitesse On a obtenu un excellent accord entre la théorie et l'experience dans le domaine de frequences étudié, à las fois pour des capteurs circulaires et rectangulaires

FREQUENZVERHALTEN EINES ELEKTROCHEMISCHEN SENSORS IN EINER MODULIERTEN STRÖMUNG EINES KEGEL-PLATTE-SYSTEMS

Zusammenfassung—Es wird die instationare laminare Stromung in einem Kegel-Platte-System analysiert Dabei wird die Winkelgeschwindigkeit des Kegels sinusformig mit der Zeit moduliert Es wird das Frequenzverhalten von kreisformigen oder rechteckigen elektrochemischen Sensoren untersucht, die bündig in der Plattenebene eingebaut sind Durch Verwendung verschiedener Viskositäten ist es moglich, den Einfluß der hydrodynamischen Übertragungsfunktion zwischen Winkelgeschwindigkeit und Geschwindigkeitsgradient an der Platte vom Einfluß des Frequenzverhaltens der Stoffübergangssensoren zwischen Geschwindigkeitsgradient und dem gleichzeitig begrenzenden Strom experimentell zu trennen Im interessierenden Frequenzbereich wird fur kreisförmige und rechteckige Sensoren eine hervorragende Übereinstimmung zwischen Theorie und Experiment festgestellt

ЧАСТОТНЫЕ ХАРАКТЕРИСТИКИ ЭЛЕКТРОХИМИЧЕСКИХ ДАТЧИКОВ В МОДУЛИРОВАННОМ ПОТОКЕ В СИСТЕМЕ КОНУС–ПЛОСКОСТЬ

Аннотация—Анализируется нестационарное ламинарное течение в системе конус–плоскость, в которой угловая скорость конуса гармонически меняется со временем. Целью анализа является проверка частотного отклика круглых или прямоугольных электрохимических датчиков, установленных заподлицо с плоскостью пластины. Использование жидкостей с различной вязкостью позволило экспериментально отделить эффект гидродинамической функции обмена между угловой скоростью и градиентом скоростей на поверхности пластины от эффекта частотного отклика датчиков массообмена между градиентом скоростей и мгновенным предельным током В рассматриваемом диапазоне частот найдено хорошее соответствие между теорией и экспериментом как для круглых, так и для прямоугольных датчиков.