

# The rotating cylinder electrode

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Received 25 July 1977

The transfer of mass onto a rotating cylindrical nickel electrode was investigated at relatively low rates. The simple electrochemical reaction of ferricyanide ion in an alkali medium was applied for this purpose. In the investigations particular attention was paid to the phenomenon of the penetration of eddies into the laminar sublayer. A modification and broadening of the basic Taylor expression, namely Taylor's linear theory, was proposed for the systems with a greater interelectrode distance. The experimental results can be better interpreted with a thus modified expression.

## Symbols

$A$	surface area
$b$	constant
$c_b, c_s$	bulk and surface concentrations
$d_c$	diameter of rotating inner cylinder
$D$	diffusion coefficient
$zF$	Faradaic equivalence
$h$	height
$k_f$	friction factor
$i_l$	limiting current density
$I_l$	limiting current
$j_D = \frac{k_L}{v} (Sc)^{0.644}$	dimensionless number
$k_L$	mass transfer coefficient
$N$	rotation per minute
$r_i, r_o$	radii of inner and outer cylinders
$v = \omega r_i$	peripheral velocity
$x$	distance along the electrode
$y$	distance normal to the electrode
$\delta_N, \delta_{Pr}$	thickness of Nernst diffusion and Prandtl hydrodynamic boundary layers
$\delta_o$	thickness of laminar or viscous sublayer
$\eta$	coefficient of viscosity
$\rho$	density
$\nu$	kinematic viscosity
$\omega$	angular velocity
$(Re)$	Reynolds number, $\omega d_c / \nu$

$(Sc)$	Schmidt number, $\nu/D$
$(Sh)$	Sherwood number, $k_L d_c / D$
$(St)$	Stanton number, $k_L / v$

## 1. Introduction

In industrial and experimental practice, forced convection has an important role in the cases where a reaction is conditioned by the slow rate of mass transfer or by low solubility. Its influence on the structure of the deposit on the electrodes is particularly critical [1-3]. The greatest effect on the mass transfer is obtained at higher rates of streaming, when a turbulence is developed. Consequently, turbulent flow represents a maximization of the mass transfer, and, therefore, the knowledge of the mechanism of the transfer under such conditions becomes significant.

However, in spite of a great number of papers in this field, there is no consensus of opinion which leads to a general solution, due to the complexity of this problem [4-9].

The system with the rotating inner cylinder is an example which demonstrates the complexity of the problem in question, but at the same time it is relatively simple and allows a description of the transport phenomena. As is the case with other systems, this one can be described by usable empiri-

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cal dimensionless relations, although there are no complete fundamental descriptions.

As can be seen from the literature, different values of exponents for ( $Re$ ) and ( $Sc$ ) are obtained for such systems as well as different values of the proportionality constant. The exponent in ( $Re$ ) takes values from  $-0.3$  to  $-0.33$  in the ( $St$ )-correlation [10–12], from  $0.6$ – $0.7$  in the ( $Sh$ )-correlation [10, 11, 13, 14], and the exponent in ( $Sc$ ) from  $-0.59$  to  $-0.66$  [10–12] and from  $0.33$ – $0.356$  [10, 11, 13, 14] in the same correlations. The value of the proportionality constant is  $0.0791$  according to the Chilton–Colburn analogy [10, 12, 13], and from  $0.169$  to  $0.22$  according to the Landau–Levich hypothesis [10, 14]. Divergences may be due to different experimental con-

ditions as well as to different approaches to the problem.

## 2. Experimental

Investigations were performed on a simple rotating cylinder electrode (Fig. 1). A synchronous motor was used, connected to the electrode by means of a friction gear. The rotation rate was measured by the photoelectric method and stroboscopically. The working electrode was a Ni-rod, diameter  $0.4$  cm, whose end was impressed into a plastic cylinder. The working surface ( $A = 1.884$  cm<sup>2</sup>,  $h = 1.5$  cm) was obtained by blocking off part of the cylinder by a thin layer of chemically-resistant resin. The electrical contact was made through mercury

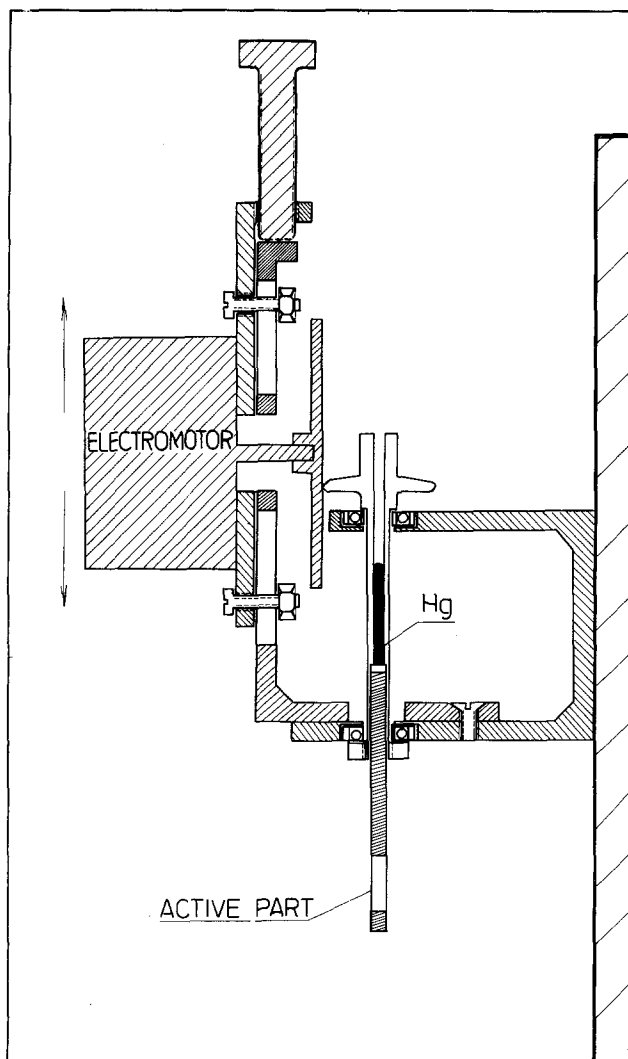


Fig. 1. The rotating cylinder electrode.

placed in the reservoir above the nickel cylinder. Cylindrically bent steel sheet was used as the counterelectrode, and a saturated calomel electrode served as the reference electrode.

Measurements were performed with two solutions of equimolar content of ferri- and ferrocyanide:  $1 \times 10^{-2}$  M and  $2 \times 10^{-2}$  M in 1 N NaOH as supporting electrolyte. Solutions were prepared with p.a. chemicals by dissolving them in redistilled water. Viscosity was determined by means of Höppler's viscometer ( $\eta = 1.198$  cP), and density by the areometer ( $\rho = 1.048$  g cm $^{-3}$ ). All measurements were performed at a constant temperature of 25°C.

Before taking measurements, nitrogen was bubbled through the solution for about one hour, and while the measurements were taken it was introduced only into the space above the solution. Before taking a series of measurements the electrode was washed with detergent, distilled water and alcohol, and then subjected to cathodic activation in the same electrolyte.

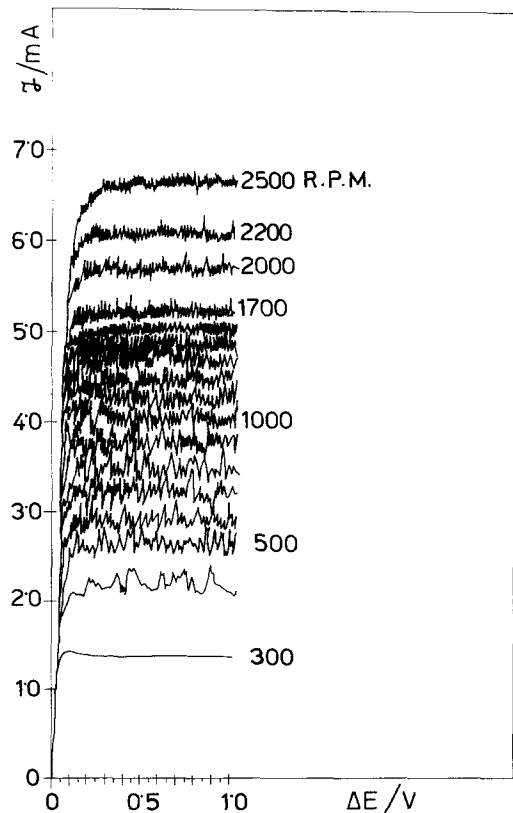


Fig. 2. The voltammetric curves of  $K_3Fe(CN)_6$  reduction. Equimolar solutions of  $1 \times 10^{-2}$  M  $K_3Fe(CN)_6$  and  $K_4Fe(CN)_6$  in 1 M NaOH were used.

Current-potential relations were determined by means of the 'Metaloscan' device, and curves were recorded on a 'Speedomax W' recorder.

Working with a slow sweep rate (0.5 V min $^{-1}$  in most cases) it can be assumed that current-potential relations actually correspond to a steady state.

### 3. Results

Investigations were repeated several times with good reproducibility. Typical current-potential plots are shown in Fig. 2.

Oscillations of current values occur on the current-potential curves when the potential approaches the potential of the limiting current plateau. Therefore, the values of limiting currents were determined as mean values on the plateau.

It was observed that if the polarization is not performed up to the potential of the limiting current plateau and if the resulting current is recorded as a function of time, the current oscillations become weaker as the potential approaches the steady-state potential of the system (Fig. 3).

### 4. Interpretation

First an analysis of experimental results will be made, in which the flux of the substance towards the electrode is expressed as a function of the hydrodynamic parameters, considering particularly the concept of a multilayer structure for the hydrodynamic layer and the penetration of eddies into the laminar sublayer. Finally, the applicability of Taylor's theory will be investigated, and a variant of the  $(Ta)$  expression will be proposed for the characterization of the flow type.

#### 4.1.

The results of steady-state investigations, Fig. 2, show that oscillations occur close to the beginning of the limiting current plateau which are well expressed on the limiting current plateau itself. Only at the lowest rotation rate of 300 rev min $^{-1}$  oscillations do not occur and the curve has a smooth profile. Within the rate range 400–1200 rev min $^{-1}$ , oscillations are very irregular and their amplitude increases. At still higher rates oscillation amplitudes decrease, but their frequency increases. When the

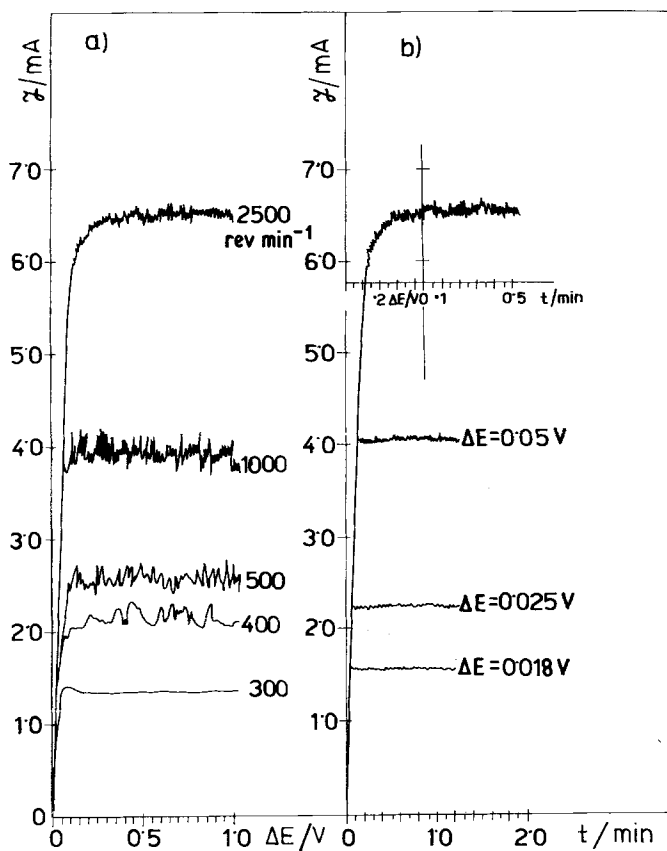


Fig. 3. (a) Representative voltametric curves.  
(b) Current-time curves at different potentials.

polarization is not performed up to the potential of the limiting current plateau, oscillation amplitudes are diminished, this having the greatest effect when the electrode potential is closer to the steady-state potential of the system. Oscillations are diminished not only in comparison with the oscillations at the same rotation rate, but also in comparison with oscillations at currents which have the same values but are the limiting currents for lower rotation rates (Fig. 3).

Systems with forced convection can be described by a relation of the general form

$$I_1 = k v^n \quad (1)$$

where it is possible to determine the value of the exponent  $n$  and thus get information on the type of flow which is developed in the system [6]. Checking our results in this way, the following expression was obtained:

$$I_1 = 0.63 \times 10^{-3} v^{0.6} \quad (2)$$

According to the obtained value  $n = 0.6$  and

according to literature data [6], it can be assumed that our investigations were performed in the transitional flow region. This aspect will be examined in more detail later. On the basis of Wranglen and Nilsson [15] as well as on the basis of the theory of the laminar sublayer, Arvia *et al.* [14] have proposed that systems with a rotating cylinder should be checked by means of the relation

$$(Sh) = k(Re)^{3/5}(Sc)^{1/3} \quad (3)$$

If our results are represented in this way, the following relation is obtained (Fig. 4)

$$(Sh) = 0.22(Re)^{3/5}(Sc)^{1/3} \quad (4)$$

which is in excellent agreement with the result achieved by Arvia *et al.* [14]. In this treatment we accept the value of the exponent of  $(Sc)$  of  $1/3$ , with respect to the results of others [6, 14], whereas the values of  $(Re)$  and  $(Sh)$  were calculated for the cylinder diameter.

The value for  $D_{Fe(CN)_6^{3-}}$  in 1M KOH =  $0.677 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  was taken from literature [16].

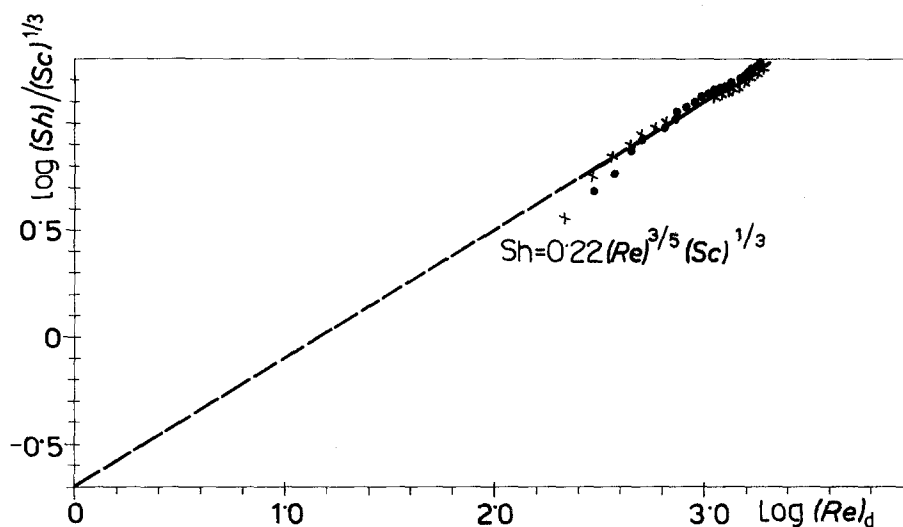


Fig. 4. Plot of Equation 3 for the two concentrations applied.

According to Arvia [13] the obtained value of 0.6 for the exponent of  $(Re)$  corresponds to the developed turbulent regime of flow in the system. For the sake of further explanation of this point, the analysis will be made with the assumption of a more complex situation in the boundary hydrodynamic layer next to the electrode. A different explanation of the flow type on the basis of the exponent value is not due to the difference between Equations 2 and 4, which are equivalent.

Actually, all our results cannot be described by these relations, this dependence only being obtained for rates over  $600 \text{ rev min}^{-1}$ . However, oscillations were also observed on the limiting current plateaux at lower rates. These oscillations indicate that even in this region the flow is not of a purely laminar type, but that the formation and penetration of eddies takes place, as typical characteristics of the transition flow region. On the basis of the corresponding interpretation of Levich [6], a four-layer structure was assumed in the turbulent flow regime, according to which the diffusion layer occupies only a small part of the laminar sublayer. The laminar sublayer performs, therefore, the role of a buffer which diminishes the turbulence effect, i.e. damps eddies which penetrate through it towards the electrode. The latter statement is supported also by our work, if current oscillations represent just the penetration of eddies. Namely, by polarization of the

electrode in the system a concentration gradient was formed in a way conditioned by the established hydrodynamic conditions. If the diffusion layer is formed within the laminar sublayer,  $\delta_0$ , the penetration of eddies into the laminar sublayer will also influence the structure of the diffusion layer. A picturesque example of the influence of turbulence, which enables an easier understanding of the above explanation, was given by Eckert [4] (p. 323). The penetration of eddies results finally in a changed current value, i.e. its oscillations. Similar oscillations have also been observed by some other authors [15, 17, 18].

The fact that oscillations are considerably less well expressed at currents which are not limiting currents also supports the penetration of eddies model (Fig. 3). The fact that these oscillations are smaller than both those at the same rotation rate and those at currents of the same value (but which are limiting currents for lower rotation rates) is easily explained by considering that at potentials lower than the ones corresponding to the limiting current plateau, the concentration gradient has a correspondingly lower value. Thus any penetration of eddies will cause a relatively smaller change of concentration, i.e. current oscillation.

It should be noticed that oscillations become more frequent with increase of rotation rate, but their amplitude diminishes. This is explained by the fact that the turbulent flow does not represent

a uniform compressive effect. However, it approaches such an effect when eddies are very frequent, this being realized at higher rotation rates.

Studies of the rotating cylinder which connect the roughness of the cylinder with turbulence [11, 19], give rise to the observation that in our system oscillations occur at  $(Re) > 200$ , which would correspond to the established limits for the transition into the turbulent regime of  $(Re) = 50-200$ , with respect to  $(Re)_{crit} = 200$  for the smooth cylinder. The transition region of the flow, characterized by the laminar flow with the occurrence of eddies, could, in this case, be the region in which the experimental values do not lie on a straight line (Fig. 4).

Summarizing, the obtained results are in good agreement with literature data, if the explanation is based on the theory of the gradual damping of eddies in the laminar region rather than on the theory of the complete damping of turbulence before the laminar sublayer is reached. A part of the laminar layer is occupied by the diffusion layer which is also (with the measurement techniques employed\*) disturbed by the penetration of eddies into the laminar sublayer.

#### 4.2.

For the flow between two coaxial cylinders due to the rotation of the inner cylinder, an instability of the flow occurs and the liquid is divided into layers.

Taylor investigated the stability of the flow between cylinders for viscous liquids. Investigations have shown that eddies appear in the system, filling the total space between the cylinders, and three flow regimes have been observed. For the characterization of the flow type, Schlichting proposed the modified Taylor number:

$$(Ta) = \frac{v(r_o - r_i)}{\nu} \left( \frac{r_o - r_i}{r_o} \right)^{1/2}. \quad (5)$$

\* We must take into consideration that the zone of the spreading of the diffusion layer under conditions of applied potential is defined by the hydrodynamics of the system, and that there is no possibility of its change by altering the electrode potential. However, the galvanostatic pulse method applied to this system enables the probing of the space next to the electrode [20-24] as deep as one wishes, and the results of such investigations support the explanation above [20].

According to the given criterion, the critical values of  $(Ta)$  were determined, at which a change of the flow type occurs:

- $(Ta) < 41.3$  – laminar Couette flow
- $400 > (Ta) \geq 41.3$  – laminar flow with the occurrence of Taylor's eddies
- $(Ta) > 400$  – turbulent flow

Turbulent flow is established only when a mutual mixing of the liquid layers takes place. Then a three-dimensional flow of the liquid is established which has a considerable influence on the mass transfer towards the electrode. According to literature data [10, 11] the usage of the  $(Ta)$ -criterion is limited to a system where

$$(r_o - r_i) \ll 1/2 (r_o + r_i) \quad (6)$$

This implies almost directly that the rate gradient is formed from one wall to the other of the system. As our system does not correspond to this condition ( $r_o - r_i = 1 - 0.2 = 0.8$  cm), and it is doubtful whether it is possible to use this criterion for less suitable ratio conditions, we come to the key point of the forced limitation of the validity of this criterion.

We have assumed that the fundamental picture of the flow in the system with a rotating cylinder electrode is still valid, but that the flow practically dies away at a certain distance which is not that of the other wall. Thus it is necessary to modify the  $(Ta)$  expression.

The performed modification comprises the following:

- (a) the calculation of  $(Re)$  on the basis of the electrode diameter [13], and not on the basis of the interelectrode distance [5],
- (b) the introduction of a new value for the magnitude  $(r_o - r_i)$  in the second member of the  $(Ta)$  expression. It seems logical for our system that instead of  $(r_o - r_i)$  under the square root, a linear dimension is used which defines the region round the electrode in which the rate gradient is developed. If one accepts that

$$\delta_N = \delta_{Pr} (Sc)^{-1/3} \quad (7)$$

is a kind of empirical relation ([6] p. 151), it is easy to calculate  $\delta_{Pr}$  from experimental results and introduce it into the second member.

Now the value of the second member is not a constant of the system any more as it is dependent

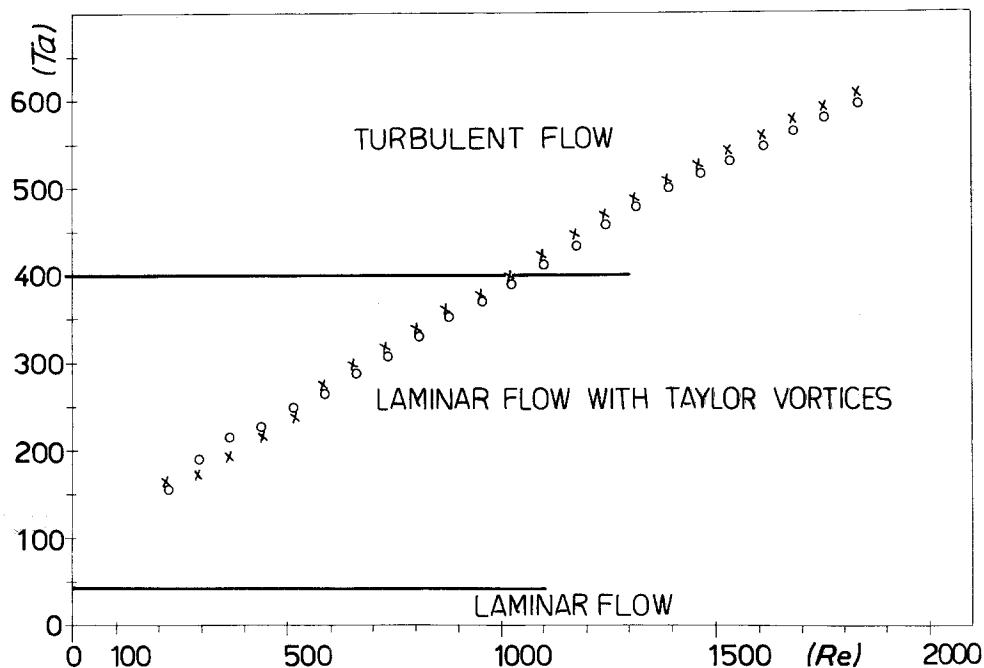


Fig. 5. Dependence of the Taylor number on the Reynolds number for the two concentrations applied.

on the rotation rate. The dependence on the diffusion coefficient is also introduced into the expression. By this adaptation the following expression is obtained:

$$(Ta) = (Re) \sqrt{\left(\frac{\delta_{Pr}}{r_i}\right)} \quad (8)$$

according to which the values of  $(Ta)$  were calculated (Fig. 5). It is interesting to discuss the obtained values with respect to the  $(Ta)$ -criterion. If the original  $(Ta)$  expression is used for the investigated system (Equation 5) all the measurements would be under the conditions of developed turbulence [ $(Ta) = 700-6000$ ], this being contrary to the observation and the above discussion. Using the modified expression, it can be seen that only the occurrence and influence of eddies should be present at lower rotation rates. A developed turbulence should only take place at higher rotation rates. This is in fairly good agreement with the above quoted result with respect to Equation 4. Previously we assumed that in the transition flow region the experimental points did not lie on the straight line. However, the transition region is well within the drawn line, so it does not delineate

a sharp limit for the change of the flow type. By amplifying the measurements the curve, which is obtained by connecting experimental points, shows also a break at the place corresponding, according to the modified  $(Ta)$ -criterion, to the value of  $(Ta) = 400$ ,  $(Re) = 1000$ , corresponding to  $N = 1400 \text{ rev min}^{-1}$ .

It seems, accordingly, that the modification of the linear Taylor theory is in accordance with the previous analysis on the basis of Levich's theory, which could be expected as the modification comprised also a part of Levich's approach.

By a combined approach which includes both above quoted aspects it is possible to expect, from the engineering point of view, reasonable success. This would contribute to the adoption and construction of these types of electrochemical systems.

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