Direct-current polarography dates back 80 years to the discovery by J. Heyrovský that highly reproducible current-potential curves could be obtained using a dropping mercury electrode [1-3]. Faradaic and non-faradaic processes at this electrode have become soon an attractive field of research for many chemists, physicists, biologists, physicians, and environmental scientists. Nowadays, polarographic method and theory are being applied to approach a number of challenging physico-chemical and analytical problems such as electrochemical oscillations, two-dimensional phase transitions, ion or electron transfer across an interface between two immiscible electrolyte solutions, and the DNA damage analysis. Progress in this area has been based mainly on the extensive experimental research worldwide. Indeed, Heyrovský had always stimulated his colleagues and students to look first of all for an unknown experimental effect. Nevertheless, the theory of the polarographic current formulated by his student Ilkovič has turned to be one of the most remarkable achievements reached in the Heyrovsky's laboratory.

D. Ilkovič (1907-1980) was born in Slovak Republic. In 1926, he enrolled at the Faculty of Chemical Technology of the Czech Technical University in Prague. Since he wished to study also mathematics and physics in addition to chemistry, he changed to Faculty of Science of Charles University in Prague, where he could read all three subjects simultaneously. With this background it was quite natural that he became interested in physical chemistry and, in 1930, he started to work in the Heyrovský's laboratory as a graduate student. His main contribution to polarography has been the derivation of the equation for the limiting mean diffusion current $i_d$ at the dropping mercury electrode [4],

$$ i_d = 0.627nFc^0D^{1/2}m^{2/3}t_1^{1/6} $$  \hspace{1cm} (1)
where \( n \) is the number of electrons exchanged in the electrode reaction, \( F \) is the Faraday's constant, \( c^0 \) is the bulk concentration of the electroactive substance (mol cm\(^{-3}\)), \( D \) is the diffusion coefficient (cm\(^2\) s\(^{-1}\)), \( m \) is the mercury flow rate (g s\(^{-1}\)) and
\( t_1 \) is the drop time (s).

The Ilkovič equation has a rather curious history. In 1934, W. Kemula, a former Heyrovský’s student, visited the Heyrovský’s laboratory to hold a seminar on his new results illustrating the strong effect of the internal diameter and length of the polarographic capillary on the limiting diffusion current. After the lecture, Heyrovský turned on Ilkovič and said: "This would be something for you!" Ilkovič cleared off and returned to the laboratory only after two weeks with the problem solved. However, in the original paper that he published soon after [4] the derivation of Eq. (1) is lacking. In 1937, Mac Gillavry and Rideal [5] solved the same problem taking into account the effect of the spherical diffusion and, upon some simplifications; they actually re-derived Eq. (1). This work prompted Ilkovič to publish a simplified derivation of his equation in 1938 [6]. The derivation neglects the contribution of the spherical diffusion and assumes that the thickness of the diffusion layer is much less than the radius of the mercury drop. The key argument was that a liquid is incompressible and, consequently, the product of the electrode area \( A \) and the distance \( x \ll \sqrt{A} \) from the electrode surface should be constant,

\[
Ax = \text{const} \quad (2)
\]

Due to the increasing area, the convection rate \( \frac{dx}{dt} = -(2x/3t) \) is negative\(^1\), i.e. the convection and diffusion contributions to the material flux have the same sign.

For almost two decade’s, the Ilkovič equation was considered as being rather accurate. Nevertheless, the role of the spherical diffusion has puzzled many polarographists. In 1950, Lingane and Loveridge [7] combined the equation for the at a spherical electrode, and they obtained the equation

\[
\bar{i_d} = 0.627nFv^0D^{1/2}m^{2/3}t_1^{1/6} (1 + S \frac{D^{1/2}t_1^{1/6}}{m^{1/3}}) \quad (3)
\]

where \( S \) is a numerical coefficient. A rigorous derivation of the diffusion current

\(^1\) Although the argument behind this derivation appears to be straightforward, a typical answer to the question about the direction of the convection that one can hear from an undergraduate student is just opposite.

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equation with the correction for the spherical diffusion was given by Koutecký [8],

$$
\overline{I_d} = 0.627nFc^0D^{1/2}m^{2/3}t_1^{1/6} \left[ 1 + 3.4 \frac{D^{1/2}t_1^{1/6}}{m^{1/3}} + \left( \frac{D^{1/2}t_1^{1/6}}{m^{1/3}} \right)^2 \right]
$$

According to this equation, the diffusion currents for normal capillaries should exceed those calculated from Eq. (1) by about 10%. However, a number of authors demonstrated that the mean diffusion current measured agrees rather well with that calculated from the Ilkovič equation. This discrepancy was clarified by Hans and Henne [9], who studied the current-time curves on the first mercury drop, i.e. on the drop that is formed in a solution unaffected by the previous polarization. This and subsequent studies have shown that the solution is depleted in the immediate vicinity of the capillary by the previous electrolysis, which leads to a decrease in the measured current. The effect of the depletion can be largely suppressed using the Smoler's capillary [10]. Thus, the apparent precise validity of the Ilkovič equation appears to be mainly a consequence of the mutual compensation of the effects of the spherical diffusion and the so-called transfer of the concentration polarisation. In physical sciences, such compensations are not rare.

D. Ilkovič stayed in Prague until 1940, then he returned to Slovakia to become professor of physics at Slovak Technical University in Bratislava. He lost interest in polarography and devoted himself entirely to physics.

References