Electrolysis at the Interface of Two Immiscible Electrolyte Solutions: Determination of Ionophores*

Jiři Koryta1,*** and Vladimír Mareček2

1 Institute of Physiology, Czechoslovak Academy of Sciences, Vídeňská 1083, CS-14220 Prague 4, Czechoslovakia
2 J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, CS-18223 Prague 8, Czechoslovakia

Abstract. The principles of electrolysis and facilitated ion transfer at the interface of two immiscible electrolyte solutions are outlined. The method of determination of ionophores is exemplified by assay of monensin in cultures of Streptomyces cinnamomeus.

Key words: electrolysis at ITIES, ionophore, monensin.

In the study of uncoupling of oxidative phosphorylation in mitochondria a number of substances were found which had the following properties:

(1) They form stable complexes with alkali-metal and alkaline-earth metal ions.
(2) They facilitate transfer of these ions across biological membranes, bilayer lipid membranes (BLM) and thick organic-solvent membranes.
(3) They induce characteristic membrane potentials at BLM and thick membranes.
(4) They uncouple oxidative phosphorylation in mitochondria.
(5) Their actions are ion-selective.
(6) Most of them function as antibiotics.

Pressman [1] termed these substances ionophores (ion-carriers). For a review see [2].

A wide field of application of ionophores was opened by Štefanac and Simon in the field of ion-selective electrodes [3]. The valinomycin K+-selective electrode [4] is a favourite tool for potassium determination. Other natural substances, such as the nonactin group antibiotics and monensin, as well as many synthetic ionophores, are also used as the active substances in ion-selective electrodes (for a review see e.g. [5]).

* Dedicated to Professor W. Simon on the occasion of his 60th birthday
** To whom correspondence should be addressed
Monensin

Though many of the ion-carriers mentioned above are too toxic to be used in human or veterinary medicine, monensin (Fig. 1), produced in cultures of *Streptomyces cinnamonensis*, is widely used as a coccidiostat in poultry breeding and cattle veterinary medicine [6, 7]. Biological assay is mainly used for its determination, and the spectrophotometric method [8] is not specific. The determinations by mass spectrometry [9, 10] and thin-layer chromatography with microbial detection [11] require a rather lengthy separation. In the present paper a rapid and accurate method of monensin determination based on voltammetry at the interface of two immiscible electrolyte solutions (ITIES) is described as an example of ionophore determination by means of this method.

Principles of Electrolysis at the ITIES

Search for various models of biological membranes had already started at the end of the last century. In the context, Nernst [12, 13] suggested the interface of two immiscible solutions as the simplest model of a membrane surface, and introduced the concept of the Nernst potential between two liquid electrolyte solutions in order to support his approach to bioelectrical phenomena,

\[
\Delta_0^r \phi = \phi(w) - \phi(o) = \mu^0_i(o) - \mu^0_i(w)/z_i F + RT/(z_i F) \ln a_i(o)/a_i(w)
\]

\[
= \Delta G^w_{r,i} - \mu^0_i(z_i F) + RT/(z_i F) \ln [a_i(o)/a_i(w)]
\]

\[
= \Delta_0^w \phi^0_i + RT/(z_i F) \ln [a_i(o)/a_i(w)],
\]

where \(w\) and \(o\) denote the aqueous and the organic phase, respectively, \(\phi\) is the inner electric potential, \(\mu^0_i\) the standard chemical potential of ion \(i\) with charge number \(z_i\), \(\Delta G^w_{r,i} \phi^0\) the standard Gibbs energy of transfer of the species \(i\) from water to oil, \(a_i\) the activity of ion \(i\) and \(\Delta_0^w \phi^0\) the standard potential difference of transfer of the ion \(i\).

As shown by Gavach and Henry [14] and by Koryta et al. [15], the ITIES exhibits similar properties to those of a polarizable electrode. Thus after polarization of the ITIES from an external source, in the presence of ions of appropriate potential difference \(\Delta_0^w \phi^0\), voltammograms are obtained that are identical in shape to those