A MIXED ELECTRIC DOUBLE LAYER MODEL AT THE SOLID (LIQUID) / ELECTROLYTE INTERFACE

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abstract. The tension surface defined by Gibbs in treating the interface area is structurally specified by a transition layer made up by the inner Helmholtz plane and the one containing the surface of active centres. In the double mixed electrode model, considered to be one step taken towards the microscopic-level understanding of the electrolyte interface phenomena, the electrochemical sensors operations, as well as the electric phenomena at the membrane level are explained in a simple manner, and the cyclic polarization diagrams can be more simply interpreted.

Introduction

More than four ten-year period, the working mechanism of the electrochemical sensors (SE), based on the ionic exchange equilibrium, between *membrane* containing the ion *i* and the ions *i* from the studied solution, was unanimously acknowledged and accepted by the specialists in field [1-6].

Beginning with 1974, as alternative, it was advanced a general model (based on charge transfer phenomena-CT), which admitted that the working mechanism of SE, rely on equilibria CT between the superficial active centres of the surface and the ions from the analysed solution [7-10].

From this point of view, by means of the new concept of the *mixed-selectivity*, a new classification of SE, in anion-, cation- and mixed selective-electrodes, was made.

By way of consequence, arised the idea, suggesting a microscopic treatment of the solide-, liquide- electrolyte interface processes and the structure's specification of Gibbs' tension surface [11-12], considered until then a *black box* from microscopic point of view (Fig. 1 a). Therefore, we advanced, for the solid (liquid) / electrolyte interface, *a mixed electrode double layer model,* which accounted for much better the interfacial phenomena from the interface metal-oxide / electrolyte.

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The main features of the new model are [13]:

-The interface with the electrolyte is *heterogeneous* (it contains, associated to the oxide MO, both *active centres* with *donor character* ($O^{\delta-}$) and *active centres* with *acceptor character* ($M^{\delta+}$));

-The direct adsorption (chemosorption) leads to a total alteration of the structure's surface and, simultaneous, to a modification of its selectivity (in fact, another interface), no matter how it is produced: spontaneously (chemical), or artificially (electrochemical);

-The inner Helmholtz plane (IHP) (the plane of the contact-adsorbed ions from the electric double layer classical models) is, in this way, shifted with a molecule of solvent towards the inner of the electrolyte.

Consequently, the Gibbs' tension surface is structurally specified (Fig. 1 b) and corresponds to the *transition layer*, composed from the new IHP and the active centres of the surface [6-13].

The equilibria CT between the ions from the solution (on a level with the new IHP) and surface's active centres are, therefore, mediated by a molecule of solvent, strongly polarized.

Analysing *the fund noise* from current-time registerings on condition that the over potentials applied to be small [14], experimental arguments, in this respect, have been produced.

Such a picture on the interface solid / electrolyte, has been the basis of the new concepts, such as the mobile interface and the organization of the interelectrodic space (the structural interelectrodic arrangement), as well as the basis of the several reconsiderations in the electro-chemistry, bioelectrochemistry, corrosion of metals, polarography, etc.

It was possible, in this way, the promotion of the new concepts, such as *mixed chemical bound*, *hard intermolecular forces*, *electronic conductivity through the electrolyte solutions* (under the electrolysis threshold), as well as an *electronic model* for bioreception, transmission, processing and depositing of the information on a brain level, in which *the ionic pumps* are a simple effect and not the cause of the transmission of the nervous impulse [14].

In a shocking work [15], E. Pungor called attention about a remarkable fact that the ionic exchange mechanism, used till now to account for the working of SE, must be thoroughly reanalysed. He suggests that the adsorption phenomenon is, most likely, the first step in the mechanism of the electrode response.

It was thus considered opportune, from the theoretical and practical point of view, an attempt to systematize a large quantity of experimental data obtained in the last 30 years [14]. At first, one brings arguments in favour of the CT mechanism of SE. That presumes the structural specification of the Gibbs' tension surface (Fig. 1a and 1b) and, implicitly, the building of *the mixed electrode double layer model*, with a partial presentation of the implications following from this.

Experimental results

The classical approach of the electrode-electrolyte interface supposes a thermodynamically description of this, through observations (measurements of current, electric charge and potential) concerning the effect of the disturbances of the equilibrium state.

In the theoretical thermodynamics tackled by Gibbs, for the study of the interface, it supposes, mainly, that all the properties of the transition layer are determined by the area and the curvature of an ideal geometric surface, so-called *tension surface* (Fig 1a).
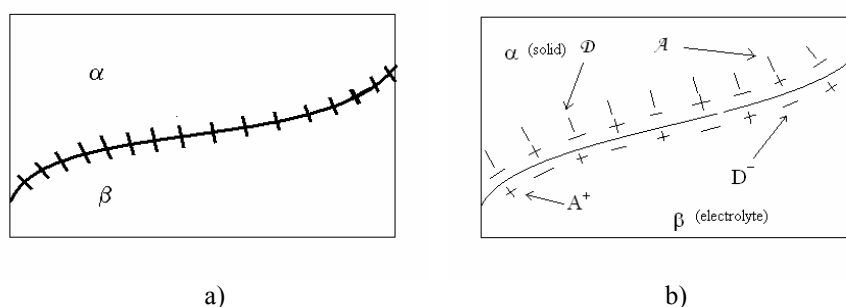

a)   b)

Fig. 1 *Interface aria: a) Gibbs tension surface, b) Structure's specification of Gibbs tension surface*

The Gibbs' model has the advantage to lead at results with a wide domain of practice, without being necessary to take into account the detailed structure of the transition layer. However, such treatment does not permit the understanding in detail of the interfacial phenomena like those from the electrode / electrolyte interface. Deciphering of the working mechanism of SE, impose a structural specification of Gibbs' tension surface and a microscopic approach of the phenomena.

The working mechanism of the electrochemical sensors that is based on the ionic exchange equilibrium between membrane and the studied solution is, sometimes, in contradiction with the experimental data [6-10]. An interesting reason, which is in the detriment of this mechanism, can be expressed by a simple and reproducible experiment. One produces three liquid electrochemical sensors: the first is of the type R^+X^- and contains alchil dimetil benzil ammonium iodide as active substance, the second is of the type R^-Y^+ and contains potassium dodecyl-sulphonate and the third is of the type R^+R^- with alchil dimetil benzil ammonium dodecyl-sulphonate.

All three sensors were previously tested in corresponding aqueous solutions containing the ions of the active substances with which they were filled.

Using a milli-voltmeter with very high impedance, we obtained the results shown in Figures 2a, 2b, 2c, 2d, 2e, which represent the response of the electrodes according to Nernst's relation:

$$E = E^0 \pm \frac{RT}{zF} \, ln \, a_i \, ,$$ where a_i is the activity of the i-ion in solution.
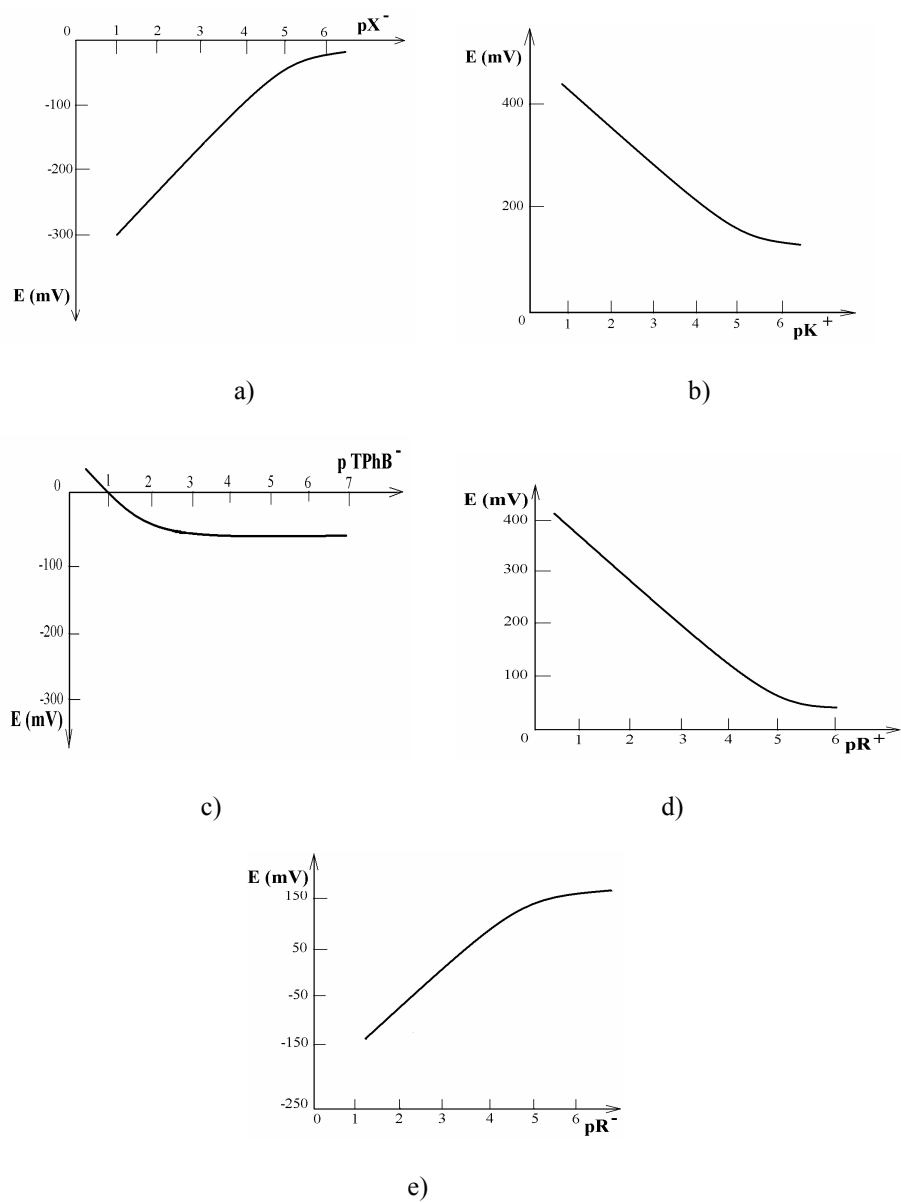
Fig. 2. *Calibration diagrams of the electrochemical sensors: a) electrode R^+X^- for the anion ClO_4^-; b) electrode R^-Y^+ for the cation K^+; c) electrode R^-Y^+ for the anion dodecyl sulphonate; d) electrode R^+R^- for the cation alchil dimetil benzil ammonium; e) electrode R^+R^- for the anion dodecyl sulphonate*

The dependence from Figure 2a presents a response of Nernst type that shows the decreasing of the potential once with the increasing of the anion ClO_4^- activity in the analyzed solution.

In Figure 2b, we have a linear dependence of the potential as a function of the variation of the cation activity K^+ from the tested solution. The potential decreases once with the decreasing of the cation K^+ activity in the analysed solution.

Until now, one can consider that the principle of the ionic exchange equilibrium is valid. Thus, these two electrochemical sensors present reversibility for the macro-cations R^+ (alchil dimethil-benzil ammonium), in the first case, and for the macro-anions R^- (dodecyl-sulphonate), in the second case.

The Figure 2c shows the response of the electrode for the dodecyl-sulphonate macro-anion for the second electrochemical sensor. It is observed that, instead of an anionic response, increasing towards values of the negative potential concomitantly with the increase of the activity of the dodecyl-sulphonate macro-anion, the response is slowly cationic, especially for the high concentrations of the potassium dodecyl-sulphonate (in accordance with the selectivity constant of the selective electrode for K^+ in the presence of sodium ions).

We obtained the similar results in the case of a sensor with alchil dimetil benzil ammonium perchlorate, tested in alchil dimetil benzil ammonium chloride solutions.

The behaviour of such ion-selective electrodes would be justified either by the too small mobility of these macro-ions, or by the fact that such macro-ions suffer a process of fast extraction from the aqueous solution to the extracting solvent of the membrane.

These speculative reasons can be easily removed by using the third electrochemical sensor, with alchil dimetil benzil ammonium dodecyl-sulphonate (R^+R^-). This sensor has reversibility relative to the dodecyl-sulphonate (R^-) and alchil dimethil benzil ammonium macro-cation (R^+) too. The cationic and anionic nernstian responses of this sensor are shown in Figure 2d and Figure 2e, respectively. These are linear functions and are not disturbed neither by the very slow mobility of the macro-ions in the studied solution, nor their extraction in the organic phase. Finally, we ask ourselves, why the supposed macro-ionic exchange equilibria are possible only in the case of the membranes made up of R^+R^- and they are not possible in the case of those made up of R^+X^- or R^-Y^+ ?

          a)   b)   c)   d)
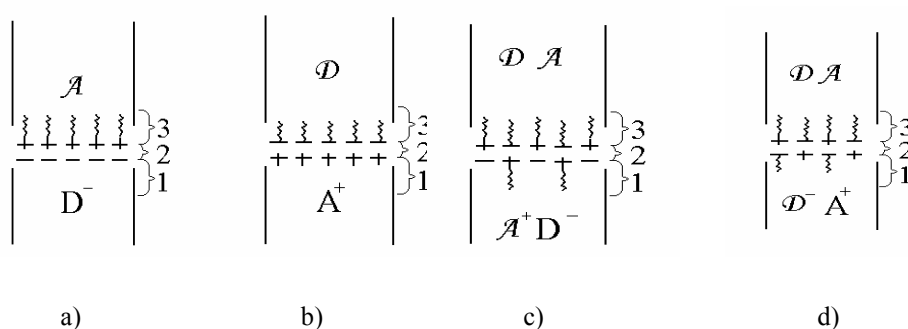
Fig. 3 *Structure of the interface in four cases: a) ideal anion-selective electrode, b) ideal cation-selective electrode, c) mixed-selective electrode for macro-cation R^+, d) mixed-selective electrode for macro-anion R^-.*

The answer can be only one, namely that the processes which determine the variation of the electrode potential versus the activity of the ion in solution are not based on the ionic exchange equilibria, but on the electronic transfer equilibria. The letter occurs between the ions in solution and the active superficial centres (counter-ions) of the selective membrane, which have a donor or acceptor character. Thus, the ion-selective interfaces, whose response are shown in Figures 2a, 2b, 2d and 2e can be simply represented in the Figures 3a, 3b, 3c and respectively 3d. As a support of this idea, we also obtained other experimental results.

Discussions

For the understanding of the phenomena, which take place at solid / electrolyte or liquid / electrolyte interface, it is necessary to take into account a double mixed electrode layer model [16, 17]. In the *mixed electrode double layer* model, the origin of the potential of electrode is sought at the level of some interfacial charge transfer equilibria, but one cannot exclude the existence of the equilibrium of ions change with their implications. The two phenomena can superpose more or less. In case of the electrochemical sensors, the ionic change between membrane and the studied solution can lead to instability of the electrode potential. With this model, one can be made some remarks about some electrochemical domains of general interest.

Conclusions

On the base of the donor-acceptor character of the active superficial centres ($\mathcal{A}$ and $\mathcal{D}$), one can give the following scheme and a general electrochemical system for the electrochemical sensors.

The aqueous solution of ions for analysis	The interphasic transition layer formed in the superficial actived positions donor ($\mathcal{D}$) and/or acceptor ($\mathcal{A}$) with a fixed concentration and the ions from solution.	The conductive inert support
PHASE I	PHASE II	PHASE III

The reply time of the electrochemical sensors is determined by the transport stage of the ions from the electrolyte to the zone IHP of the electrode. This stage is caused by the diffusion and not by the migration of the ions through membrane. The selectivity of the electrochemical sensors is associated with the chemical affinity of the ions in electrolyte for the counter-ionic active positions at the level of transition layer (A^+ and D^-), and not with their chemical affinity for the *membranar phase* in its ensemble [7-10].

Depending on the structure of the interface at the level of mixed electrode double layer, one can make a general classification of the electrochemical sensors in anion- (Figure 3a), cation- (Figure 3b), and mixed-selectives (Figures 3c and 3d).

On the basis of this model, the construction of the i-selective electrochemical sensors does not imply the presence of the ion i in the two phases lain in contact, which is necessary for the achievement of the equilibrium of ionic change, but that implies the presence of the superficial active donor positions $\mathcal{D}$ and/or acceptor $\mathcal{A}$, with a counter sign that of the ion i, implied in equilibrium of electrons change [7-10].

The extent of the detection limit of the mixed-selective electrochemical sensors, in the characteristic area of the potential jump from the anionic reply to that cationic or inverse is an error. It consists of the trend of over-appreciation of the electrodes performance (10^{-14} ion g I^{-1} H^+ for glass electrode or less than 10^{-20} ion g I^{-1} S^{2-}-for those ones of Ag_2S). In fact, the pH-selective glass electrode is a mixed-selective electrode with sensitivities approximately equal for H^+ and OH^-.

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