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Scientific Paper

ELECTRODE POTENTIAL IN SUSPENSIONS INTERPRETED AS A MIXED POTENTIAL

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Abstract

A simple experimental method was developed and applied to establish and alter the mixed potential of a measurement electrode in a galvanic cell. The electrode, immersed simultaneously in two different contacting solutions forming a sharp boundary, alters its mixed potential when moved in regard to the boundary, because at the same time inhibition of the electrode reactions changes. Illustrative experiments were made with a Cu electrode in $CuSO_4$ solutions.

Using the same method the electrode potential behaved quite analogously when the electrode was dipped simultaneously in an equilibrium solution and in the sediment of a suspension composing a galvanic cell. This similarity allows interpretation of the potential of the electrode as the mixed potential when it is dipped in a suspension. By bringing the electrode into contact with charged particles, their double layers overlap and form sporadic contact regions, where the electrochemical potential of the potential determining ions is different from that in the surrounding equilibrium solution. Therefore two different electrochemical reactions can take place on the surface of the same electrode, which is the condition for the appearance of the mixed potential.

Keywords: mixed potential, double layer overlapping, suspension galvanic cells, suspension effect of the first kind, method for mixed potential establishment and change

Theoretical Background

A method is presented to visualize the establishment and variation of the *mixed potential* and the accompanying inhibition arising at any electrode This method is important and useful because of its possibility to present the mixed potential of measuring electrodes in potentiometry not only of true solutions but also of aqueous suspensions of charged particles. The mixed potential is also called the *stationary (steady state) potential* or *corrosion potential* in cases of metal corrosion.

The potential of an electrode of a galvanic cell is called the mixed potential when it is established by two simultaneous and electrically coupled electrode reactions and the net Faradaic current of the cell is zero, though these reactions produce and consume ions. The process is not in thermodynamic equilibrium. To illustrate this process experimentally a Cu-electrode was applied, immersed in $CuSO_4$ solutions of different concentrations.

The potential E of a test electrode vs. SHE (standard hydrogen electrode) in a galvanic cell can be calculated from the measured cell voltage V (or V′ for suspensions), when the known potential of the reference electrode used E_{ref} and the diffusion potential E_{dif} (if present and not negligible) are taken into account. This electrode potential can be considered as a result of the mechanisms of partial electrochemical reactions (electronation and deelectronation) at the electrode surface in contact with the solution. Considered as kinetic processes they can be represented by the laws of electrochemical kinetics, in this case by the well-known Butler-Volmer equation.[1,2] This equation correlates the experimental quantities with those significant for the reaction mechanisms.

The diagram in Figure 1 shows schematically the Butler-Volmer equations for the two reactions, (symmetry factor β ~0.5), which occur in the experiment following the presented method at one (Cu) electrode. This is immersed simultaneously in two $CuSO_4$ solutions of different concentration (c_1 and c_2) of the potential determining Cu^{+2} ions, so that each reaction takes place at the separated, visible and variable surface of the same electrode. When the opposite net currents of both reactions are compensated, the mixed potential E_M of the electrode is established. The method can be applied to combinations of different electrodes and solutions.

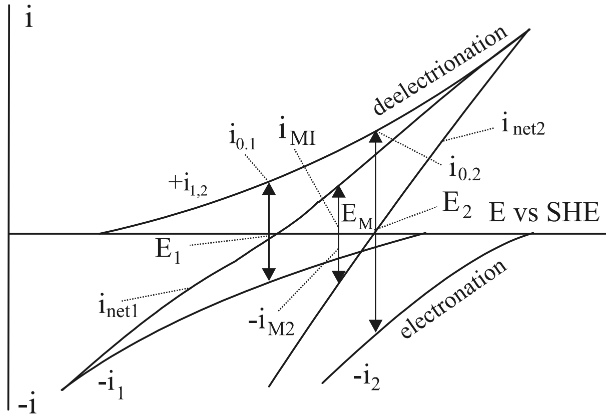


Figure 1. Scheme of a graphical presentation of the Butler–Volmer equations for two reactions occurring at the same electrode, for β ~ 0.5. The equilibrium electrode potentials E^1 and E^2 are evident for each separate reaction, where $i_{net1} = 0$ or $i_{net2} = 0$. Between these potentials the simultaneous immersion of the electrode in both solutions gives rise to the (steady-state) mixed potential E_M of the electrode, when $i_{M1} = | -i_{M2} |$. Index 1 relates to the reaction ′1′ and index 2 to the reaction ′2′. i_0 = exchange current density.

In the study of the corrosion processes an Ewans type of diagram[1] is often used (Figure 2). Both diagrams can be applied for interpretations of the measured mixed electrode potentials, irrespective of the electrode type in combination with solutions of one or more electrolytes.

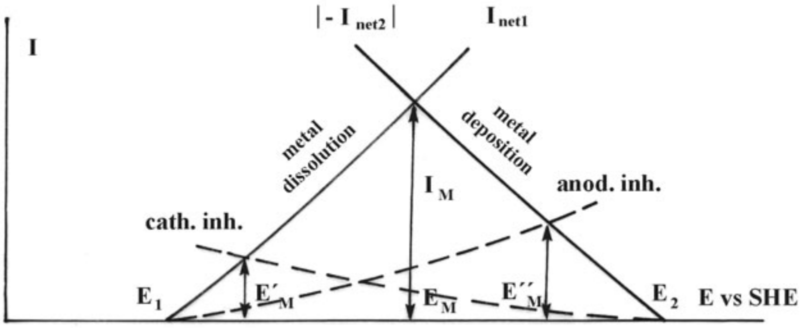


Figure 2. Ewans diagram schematically showing potential–current relations and the influence of inhibition on the cathodic (metal deposition) or anodic (metal dissolution) reaction, due to the change of the proportion of A_1 to A_2.

Experimental

A/ Galvanic cell containing true electrolyte solutions.

For simple and clear experiments a galvanic cell was used (Figure 3) composed of a glass beaker filled some 3 cm high with a dilute $CuSO_4$ solution (e.g. 0.01 mol kg^{-1}, c_1). Under this a 10 or 100 times more concentrated $CuSO_4$ solution (c_2) (greater density!), was slowly poured, also some 3 cm high, by means of a glass capillary so that a very sharp boundary between the two solution was formed.

Due to diffusion the boundary widened with time, but its stability was (mainly) more than sufficient for the planned measurements. A saturated calomel electrode (SCE) or another reference electrode and a ~2 cm long Cu rod-electrode (diameter 2 to 3 mm), connected to an isolated connection wire, controllably movable up or down within a measurable interval, were immersed in the upper solution. Priority was given to the reference electrode, the salt bridge of which was put in the tube T perforated with a small lateral hole to prevent direct outflow from it into the solution (c_1); see Figure 3. The schemes of the proposed galvanic cells using metal electrodes are shown in Figure 4.

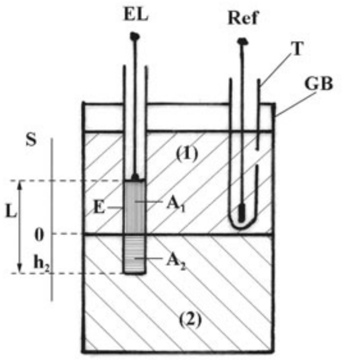
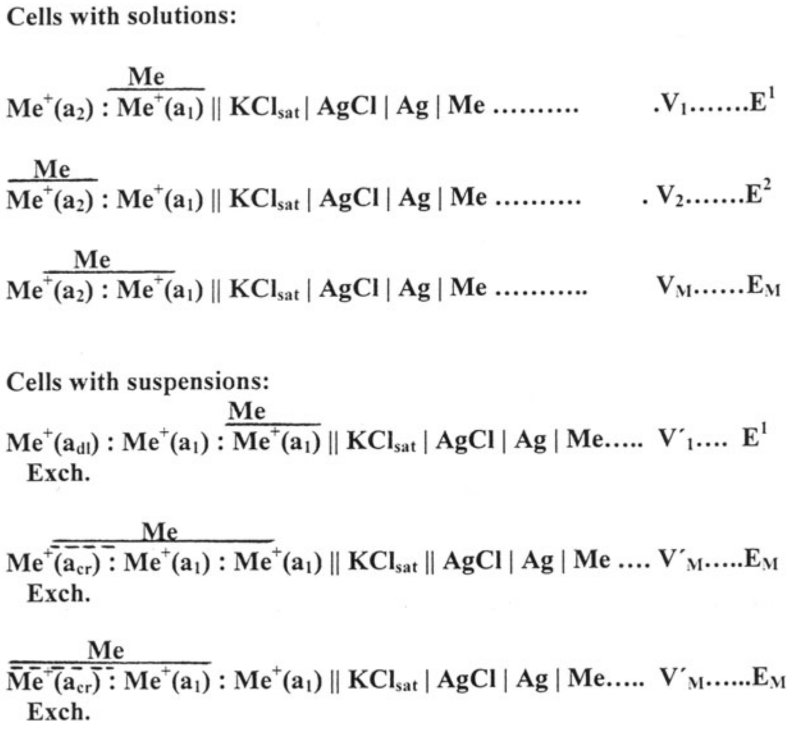


Figure 3. Scheme of the galvanic cell according to the proposed method. GB – glass beaker containing separated solutions. E-electrode, controllably movable up or down, (connected by isolated wire to junction EL), immersed simultaneously in the solution (1), contacting surface A_1, and in solution (2), contacting surface A_2. Ref – reference electrode (SCE), having a salt bridge in protection tube T, with small side-hole. S – scale of h_2 (mm), the depth of immersion of the electrode E in solution (2). L – length in milimeter of the electrode E.



Cells with solutions:

$$\mathrm{Me^+(a_2) : \overset{Me}{\overline{Me^+(a_1)}} \parallel KCl_{sat} | AgCl | Ag | Me \ldots\ldots\ldots\quad .V_1\ldots\ldots E^1}$$

$$\mathrm{\overset{Me}{\overline{Me^+(a_2)}} : Me^+(a_1) \parallel KCl_{sat} | AgCl | Ag | Me \ldots\ldots\ldots\quad .\ V_2\ldots\ldots E^2}$$

$$\mathrm{Me^{\overset{Me}{\overline{+}(a_2) : Me^+(a_1)}} \parallel KCl_{sat} | AgCl | Ag | Me \ldots\ldots\ldots\quad V_M\ldots\ldots E_M}$$

Cells with suspensions:

$$\mathrm{\underset{Exch.}{Me^+(a_{dl})} : Me^+(a_1) : \overset{Me}{\overline{Me^+(a_1)}} \parallel KCl_{sat} | AgCl | Ag | Me\ldots..\quad V'_1\ldots.\ E^1}$$

$$\mathrm{\underset{Exch.}{Me}\overset{Me}{\overline{\overline{^+(a_{cr})} : Me^+(a_1) : Me^+(a_1)}} \parallel KCl_{sat} \parallel AgCl | Ag | Me \ldots.\quad V'_M\ldots..E_M}$$

$$\mathrm{\overset{Me}{\overline{\overline{\underset{Exch.}{Me^+(a_{cr})}} : Me^+(a_1)}} : Me^+(a_1) \parallel KCl_{sat} | AgCl | Ag | Me\ldots..\quad V'_M\ldots\ldots E_M}$$

Figure 4. Galvanic cell representations corresponding to the proposed method; three cells with two solutions and three with a suspension. The line, double line and dashed line have their common meaning; a single line with parallel dashed line means the electrode in intense contact with particles causing double layer overlapping. The position of the last symbol shows the cell phase in contact with the electrode. Symbol adl means ion activity in particle double layer and acr the activity in the contact region.

Measurement of the cell voltage

The cell voltage V was measured with a high-impedance voltmeter with the aim of hindering the Faraday current from flowing through the cell. When both electrodes are placed as described above, the reversible (equilibrium) potential of the test Cu-electrode E^1 can be obtained from the cell voltage V^1, which may also be calculated by the Nernst equation. Equally E^2 can be obtained from V^2 when both electrodes (or only the Cu-electrode at negligible diffusion potentials between the solutions) are immersed in the solution (c_2).

When the Cu-electrode is lowered down progressively from solution (c_1) to solution (c_2), the ion activities of both solutions are responsible for the Cu electrode potential, called now the mixed potential, E_M. Its values lie between E^1 and E^2, depending on the proportion of both electrode surfaces A_1 and A_2, which are in contact with the solution (c_1) or (c_2), Figure 5.

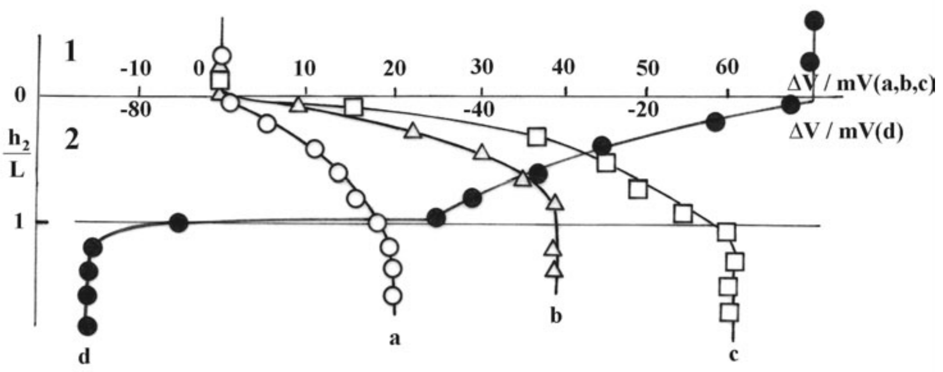


Figure 5. Cell voltage changes ΔV (mV) between E^1 and E^2, due to the mixed potential change of Cu electrode, versus h_2/L. Molalities m (mol kg^{-1}) of $CuSO_4$ solutions for curves a-d: (a1) 0.01/(a2) 0.1— (b1) 0.01/(b2) 1.0 — (c1) 0.001/(c2) 1.0 — (d1) 0.01/(d2) (0.1+0.1EDTA).

A Faradaic current flows through both surfaces and through the electrode, but none between the cell electrodes. Therefore E_M can be regarded as an irreversible *quasi equilibrium potential*. Because the total electrode surface is fixed, alteration of the electrode position up or down causes variation (due to inhibition) of the symmetry factor β and that of the net current densities at the electrode surfaces. This happens first of all when the values of E_M approach the potential E^1 or E^2, as is expected with regard to Figure 2. During the measurement the Cu-electrode was dipped step-by-step and the cell potential read until the electrode was completely immersed in solution (c_2).

B/ Galvanic cells containing suspensions.

Instead of obtaining the mixed potential of a Cu-electrode immersed in two solutions of different Cu-ion activities, enabling the occurrence of two simultaneous reactions indispensable for the appearance of the mixed potential, the same happens when one part of the electrode surface is in the equilibrium solution and the other (or the whole surface) is dipped in the sediment of a suspension forming intense contacts with the charged particles, Figure 6, curves b and d. The scheme of this suspension cell is given in Figure 4.

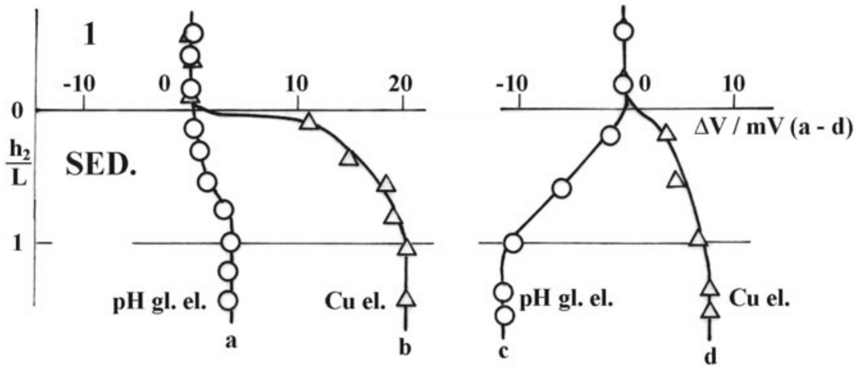


Figure 6. Cell voltage changes ΔV′ (mV), representing E_M changes, as a function of h_2/L, when a Cu- or pH glass- electrode was shifted from equilibrated H_2O into sediments of suspensions, prepared as in text with ion-exchangers in the Cu-form: curves a and b when conditioned in strongly hydrolysed $CuSO_4$ solution, curves c and d, when hydrolysis was reduced.

The potential of the Cu-electrode can be considered as mixed potential by analogy to former experiments, except that the potential of the electrode immersed completely in the sediment represents the maximal possible value of the mixed potential and not a reversible electrode potential as in solutions.

Ion exchanger particles (Dowex 50 W of different size and others) in contact with their equilibrium water (for greater cell voltage differences ΔV′!) or the corresponding solution were used in the illustration experiments. The boundary between the equilibrium solution and the sediment is equivalent to the boundary of solutions in the former cases. In the whole equilibrated suspension an equal electrochemical potential of Cu ions exists and therefore the same Cu-electrode potential is expected. Nevertheless, when the electrode was dipped step-by-step from the equilibrium solution into the sediment, the potential of the Cu-electrode changed in the same way as in experiments using only solutions. In this case the initially equilibrated system was no longer in equilibrium, as it will be interpreted below.

C/ Secondary processes occurring in the experiments in galvanic cells.

A simple Cu electrode was used because of its easy preparation, but it involves some dificulties. $CuSO_4$ solutions are highly hydrolysed and contain different amounts of hydrogen ions (H^+). Therefore also a H^+ -sensitive glass electrode was used to show the mixed potential, when it replaced the Cu-electrode in the experiments with $CuSO_4$ solutions (Figure 7, curve a and b), and also when it was in contact with two acidic e.g. HCl, solutions of different concentration (Figure 8, curve b).

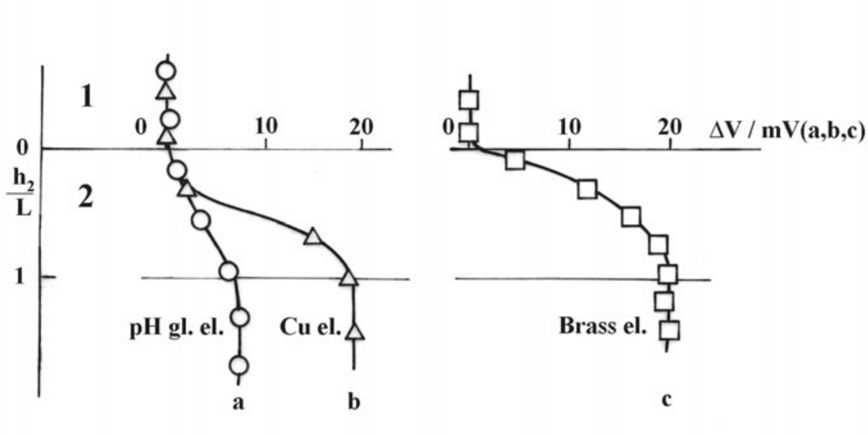


Figure 7. ΔV (mV) changes, dependent on h_2/L when pH glass electrode (curve a) or Cu electrode (curve b) are dipped from the same $CuSO_4$ (0.01 mol kg^{-1}) solution (c_1) into the solution (c_2) (0.1 mol kg^{-1}). The equilibrium electrode potential E^1 in solution (1) passes over to mixed potential E_M, when the electrode contacts solution (2), and to E^2 when it is wholly dipped into solution (2). Curve c: change of the mixed potential E_{M1} of a brass electrode into E_{M2} as a function of h_2/L in the same solutions as curves a or b.

The same happens *in suspension systems*, where a Cu-metal electrode and the sediment of ion exchanger (in Cu-form) in combination with $CuSO_4$ equilibrium solutions or water are applied. The measured mixed potential depends on the proportion of Cu^{2+}/H^+-counterions belonging to the beads of the ion-exchanger in the Cu-H-form, obtained by conditioning hydrolysed $CuSO_4$ solutions (Figure 6). It must be emphasized that different H^+-sensitive electrodes (e.g. Sb/Sb_2O_3, OH′- and Bi/Bi_2O_3, OH′- rod-electrodes (of the second kind!) give different changes of mixed potential in comparison with the glass (membrane!) electrode when the experiments are performed in the identical sediment and equilibrated solution (Figure 9), which is of interest for the theoretical treatment of the phenomenon.

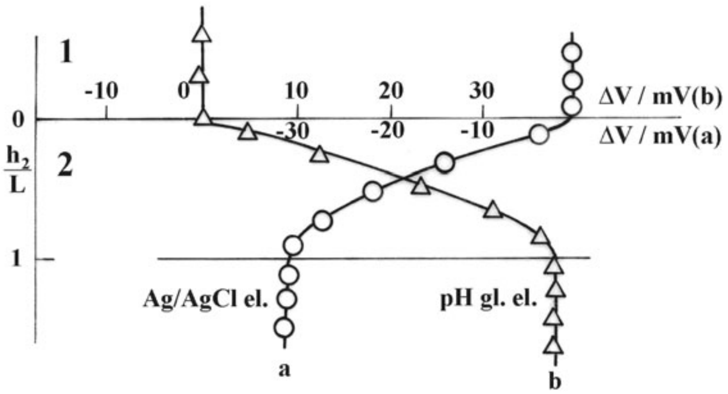


Figure 8. Cell voltage changes ΔV (mV) representing the mixed potential E_M changes between E^1 and E^2 as a function of h_2/L: curve a— for Ag/AgCl electrode (of the second kind!) in NaCl solutions, $c_1 = 0.005$, $c_2 = 0.05$ (mol kg^{-1}); curve b— for pH glass (membrane!) electrode in HCl solutions $c_1=0.001$, $c_2=0.01$ (mol kg^{-1}).

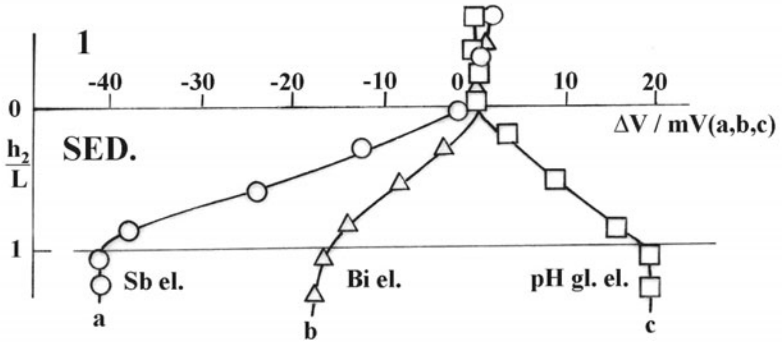


Figure 9. Cell voltage changes ΔV′(mV) representing different mixed potential E_M changes of three pH sensitive electrodes as a function of h_2/L, when dipped from equilibrated H_2O, (where they show reversible E^1 values), into the sediment of the equal ion exchanger in H-form.

To emphasize the versatility of the method presented, its applications using an Ag/AgCl,Cl′ electrode (of the second kind!) (Figure 8, curve a) and a (heterogeneous!) brass rod-electrode is presented, Figure 7, curve c. The first electrode is sensitive to (chloride) anions (in contrast to other electrodes, sensitive to cations) and the second takes up a mixed potential in both $CuSO_4$ solutions of the galvanic cell. The mixed potential of the brass electrode can be changed but cannot take up any equilibrium potential.

D/ Modified galvanic cells containing true solutions.

The widening of the boundary between the solutions due to ion diffusion (Figure 3) results in a not exactly defined contact region with the electrode. In addition, the thin film of solution adsorbed on the electrode surface needs some time to be replaced by the new solution after each electrode transfer step. To eliminate these deficiencies modified galvanic cells of classical design can be applied, shown in Figure 10.

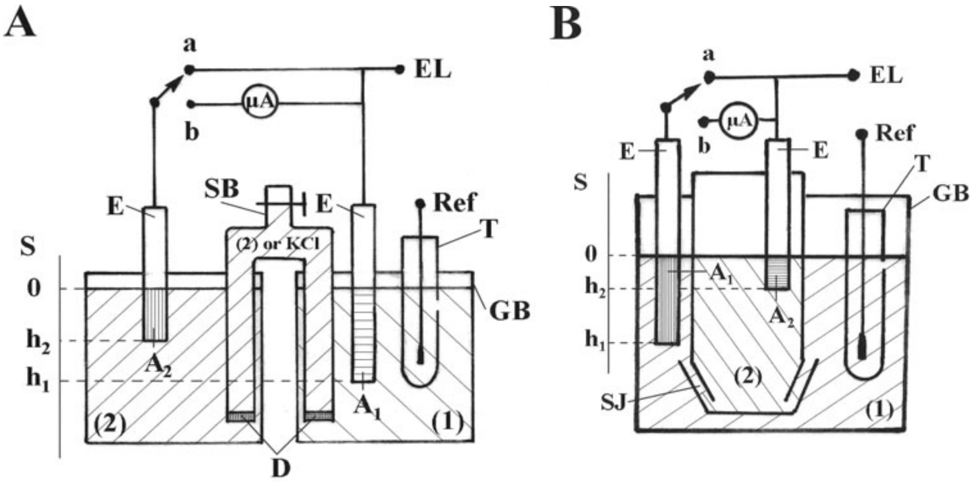


Figure 10. A/ Design of a classical cell, equivalent to the proposed cell. The meaning of the legend as in Figure 3, in addition: SB – salt bridge, D – diaphragm, μA – microamperemeter, switched on by contact b, contact a – switch for electrode short-circuit. B/ Cell with a glass sleeve junction (SJ) of solutions, the boundary of which does not contact the electrode. Remaining legend as in Figures 3 and 10 A.

The schemes represent cells where the solution boundaries are not in contact with the electrodes. The cell electrodes are connected and the electrical contact of the solutions is realized by a salt bridge (10A) or by a glass sleeve junction (10B). In addition to the concentration cells used above classical chemical cells can also be used, where the two solutions are separated by a salt bridge, filled with KCl_{sat}, diminishing the diffusion potential. In order to obtain results comparable to those obtained by the method presented above, in all modified galvanic cells the surfaces A_1 and A_2 in contact with the solutions, must fulfil the condition A_1+A_2 = constant, when different proportions of A_1 and A_2 are set up. The modified cells can also be used - cum grano salis- as suspension galvanic cells.

With a microampermeter interpolated between the two parts of the Cu-electrode, the Faradaic corrosion current I_{corr} can be estimated. Beside the electrode polarization, this is also dependent on the electrical resistance of the cell and on the outer current circuit, including the resistance of the ammeter.

Results

The cell voltage differences ΔV (or $\Delta V'$ in suspensions) in figures 5 to 9 represent the changes of the mixed potential values of the measuring electrode, as a function of the parameter h_2/L, where h_2 is the depth (in millimetres) of the electrode from the solution boundary into the solution (c_2) and L the length (in millimetres) of the measuring electrode. Because all the electrodes have cylindrical form of constant diameter, the value h_2/L represents the part of the electrode surface dipped in solution (c_2), $A_2/(A_1+A_2)$. For each series of measurements the parameters of the cell components are given in the figures. The voltages were read at room temperature (20 °C to 25 °C) after they attained a practically constant value.

Discussion

A/ The method presented renders it possible to distinguish visibly two separated surfaces of a single electrode, where two different electrochemical reactions take place, which is the essential condition for calling the electrode potential the “mixed potential”. The total electrode surface (A_1+A_2) is constant, while the proportion of A_1 and A_2 changed visibly during the measurements, resulting in change in the mixed potential values and affecting the inhibition of the electronation or deelectronation reactions. This can be observed from the shape of the curves in figures 5 to 9, from which the relative values of the (corrosion) currents can also be estimated as a function of h_2/L or of the mixed potential, as Figure 11 shows. Theoretical treatments of the above illustrative experiments can be found in the electrochemical literature as long as true solutions are used in the galvanic cells.[1,2,3]

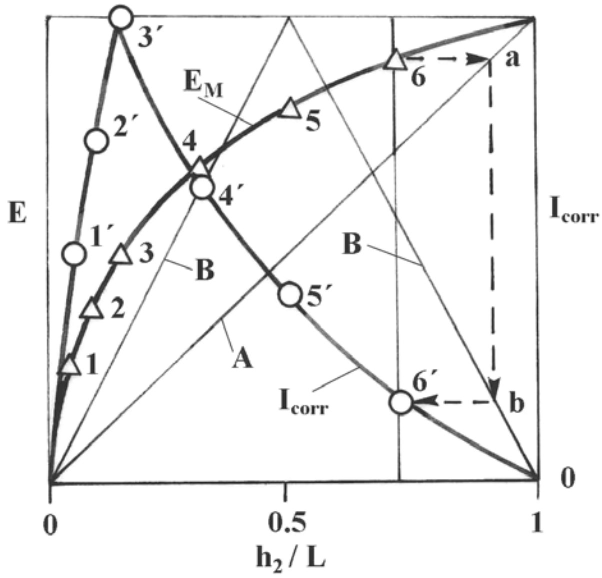


Figure 11. Schematic diagram for graphic estimation of the relative corrosion current I_{corr} as a function of h_2/L, with the aid of the measured E_M and the ideal mixed potential values (curve A), when the hypothetical theoretical current I_{rel} (curve B) is taken for comparison. The points 1 to 6 on the E_M curve correspond to the points 1′to 6′ on the I_{corrr} curve. Their method of derivation, e.g. 6′ from 6, is shown in the diagram: 6→a→b→6′ as an example.

B/ The establishement of a mixed potential in galvanic cells, which contain suspended charged particles needs additional interpretation not found in the literature, except partly in our earlier publications on the suspension effect.[4] To assure a defined and reproducible experimental state of a suspension, its sediment together with the equilibrated supernatant must be used. This represents a system in equilibrium, throughout which the electrochemical potential of ionic species (e.g. Cu^{2+} or H^+) must be equal and consequently should also be equal the electrode potential, in this case that of the Cu- or pH glass- electrode. Almost all investigators of the suspension effect were convinced that a pH glass electrode immersed in sediment or in its equilibrium supernatant behaves in this manner. But our study of the suspension effect, focused on the experimental findings,[5] showed that the pH electrode may change its potential when it is displaced from the equilibrium solution into the sediment and forms intensive contacts with the particles. The same happened with a Cu-electrode dipped from the equilibrium solution into the sediment of an ion-exchanger in Cu-form. We suppose this happens as the consequence of double-layer overlapping, according to the forecasts of this possibility in publications on double-layer interactions.[6] Many papers dealing with the forces between interacting surfaces as a consequence of double layer overlapping are cited in the literature, but others are disregarded, e.g. such as those treating the change of electrode potential as a consequence of the double layer interaction.

In sporadic contact regions so formed at the electrode surface, the activities of the electrode potential determining ions are present, which are different from the ion activities in the equilibrium solution. The electrode surface is subject to two different ion activities, making possible two different electrochemical reactions, and the mixed potential appears as a consequence on the electrode. The similarity of the experimental manipulation as far as the origin and behaviour of the mixed potential in both types of cells is obvious. The mixed potential depends on the size and charge of the particles, on the type and the ionic strength of the solution, and on the surface structure and electrical charge of the electrode. The phenomenon must also be taken into account in ion activity measurements, when the electrode contacts a charged surface in a non-controllable way, e.g. in ion activity measurements in vivo.

A nonequilibrated system has the tendency to restore its equilbrium, but this could occur very slowly and usually needs much more time (lasting even months) than is needed for a common ion activity determination, e.g. in pH measurement. The fact that the mixed potential is apparently, though only temporarily constant, is the reason for considering it erroneously as a reversible one.

A treatment of the relations between the ranges of the mixed potential or their changes, and the corresponding reasons will be given in a paper which is in preparation.

Conclusions

A procedural method to establish and vary the mixed potential of an electrode dipped simultaneously in two solutions of different ion activities in a galvanic cell is presented. The measured electrode potentials are in accordance with the known laws of electrochemistry. The corresponding results of analogous measurements in suspensions, where the electrode is dipped simultaneously in the equilibrium solution and into contiguous sediment of charged particles, suggests that also in suspensions mixed potentials are established at the electrode under certain conditions. Mixed potentials, identical with the “suspension effect of the first kind” in pIon (e.g. pH) measurements, and essential in the study of corrosion, are simple to reproduce with the method presented.

Acknowledgments

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Povzetek

Razvita in uporabljena je bila enostavna eksperimentalna metoda za vzpostavitev in spreminjanje mešanega potenciala merilne elektrode v galvanskem členu. Elektroda, potopljena istočasno v dve različni, dotikajoči se raztopini, ki tvorita ostro mejo, spremeni mešani potencial, kadar se premakne glede na mejo, ker se istočasno spremeni inhibicija elektrodnih reakcij. Za ilustracijo so bili izvedeni eksperimenti z bakreno elektrodo v $CuSO_4$ raztopinah. Pri uporabi iste metode se ponaša elektrodni potencial popolnoma analogno, če je elektroda potopljena istočasno v sediment in pripadajočo ravnotežno raztopino, ki sestavljata galvanski člen. Ta podobnost dovoljuje, da se tolmači elektrodni potencial kot mešani potencial, kadar je elektroda potopljena v suspenzijo. Ko pride elektroda v stik z nabitimi delci, se njihove dvoplasti prekrijejo in tvorijo sporadično porazdeljena stična področja, kjer je elektrokemijski potencial ionov, ki določajo elektrodni potencial, različen od potenciala v obdajajoči ravnotežni raztopini. Zato tečeta dve različni elektrokemijski reakciji na površini iste elektrode, kar je pogoj za pojav mešanega potenciala.