

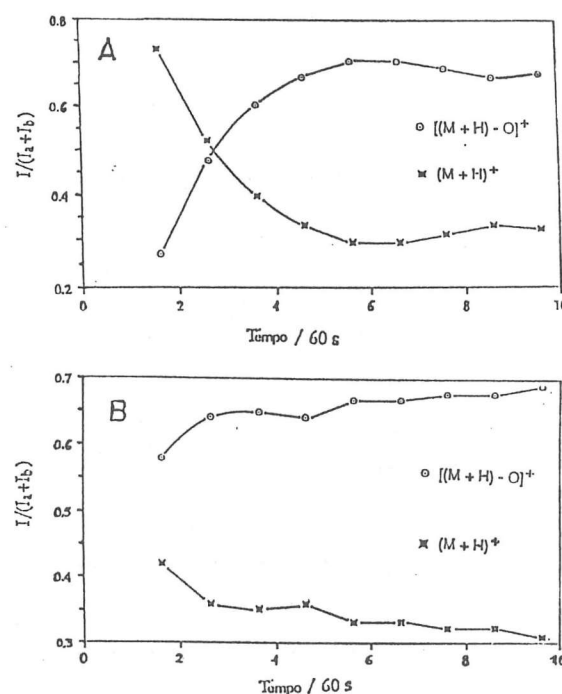


Figure 4 Time dependent plots of $[M+H]^+ / ([M+H]^+ + [(M+H)-O]^+)$ and $[(M+H)-O]^+ / ([M+H]^+ + [(M+H)-O]^+)$
 A - in the absence of surfactant
 B - in the presence of surfactant

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ADSORPTION AND ELECTROCHEMICAL ACTIVITY OF IMIDAZOLE DERIVATIVES ON Pt/Pt, Au AND Hg ELECTRODES.

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ABSTRACT.

Adsorption of 1-hydroxy-2,4,5-trimethylimidazole-3-oxide (HOTMI) on Pt/Pt, Au and Hg electrodes was studied using the methods potentiodynamic and differential charge capacity. It is shown that adsorption depends on the medium nature and on the ionic state of the compound in solution. Electrooxidation products were characterized by HPLC, IR spectroscopy, NMR and H-MS.

EXPERIMENTAL.

Synthesis of HOTMI was carried out by the method (1). Dichloromethane was purified according to (2). Quaternary salts were Merck spectral grade as were the inorganic salts.

The measurements of the differential capacity of the polycrystalline gold electrode and of the mercury electrode were carried out using an automatic equipment (3). Adsorption measurements and potentiodynamic curves on Pt/Pt were performed with a P-5827 potentiostat.

Oxidation of HOTMI was performed in CH_2Cl_2 (E vs Ag/Ag) and in aqueous media (E vs SCE) under potentiostatic conditions on Au and Pt electrodes at different potentials (0,6-0,95 V).

RESULTS AND DISCUSSION.

When the Pt/Pt was immersed in a 0,024 M HOTMI aqueous in 1 N H_2SO_4 solution at open circuit, a shift of the preestablished potential was observed with time indicating the adsorption of HOTMI on Pt/Pt. By choosing the E_p values in the capacitive and of hydrogen adsorption regions, the potential was shifted in the

cathodic region from 500 mV to 320 mV and from 60 mV to 300 mV in the anodic region. Nearly with the same speed the potential was shifted in the case of 0,024 M imidazol (IMD) from 500 mV to 200mV anodically under the same conditions. After being in contact with the HOTMI solution the Pt/Pt electrode was washed several times with supporting electrolyte. The chemisorbed substance was responsible for the decrease of hydrogen adsorption and the oxidation at anodic potential (Fig.1). A similar behaviour was observed for adsorbed IMD (Fig.2).

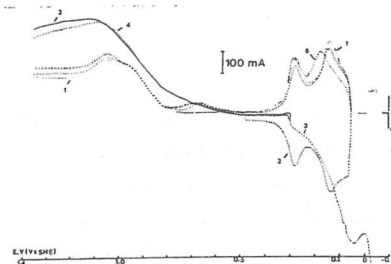


Fig.1. Potentiodynamic curves of Pt/Pt in 1 N H_2SO_4 (1,2) and in 0.024 M HOTMI solution after adsorption at different potential values: $E_a=500$ mV (3); $E_a=60$ mV (4); $E_a=-20$ mV during 30 min (5). All curves were obtained after washing the electrode with supporting electrolyte. $v=3$ mV.s⁻¹.

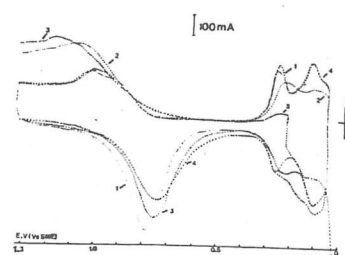


Fig.2. Potentiodynamic curves of Pt/Pt in 1 N H_2SO_4 (1) and in 0.024 M IMD solution after adsorption at different potential values: $E_a=60$ mV (2); $E_a=500$ mV (3); $E_a=-20$ mV during 30 min (4). All curves were obtained after washing the electrode with support electrolyte. $v=3$ mV.s⁻¹.

The different anodic potentiodynamic curves (Fig.1,2) and the electrooxidation charge curves in the electrical double layer region for different adsorption conditions (E_r) points out that the initial HOTMI particles were destroyed in a higher grade than IMD during adsorption. A complete oxidation of the adsorbed HOTMI even at anodic E_r potential sweep up to 1,4 mV cannot be carried. This happens even when the electrode has been polarized at -22mV during 30 min (curve 5, Fig.1). Fig.2 also shows that IMD easier undergoes electrodesorption.

These results may suggest that the adsorption capacity and electrodesorption can be related to the electronic density redistribution in the HOTMI ring and to the products chemical nature. The HPLC study of the product solutions showed that the electrochemical oxidation of HOTMI is rather complex and the products have very low stability (Fig.3).

The capacity curves C vs E (Fig.4) obtained for HOTMI on polycrystalline Au electrode by the faradaic impedance technique yield two pseudocapacity peaks in different potential regions. They appeared in the vicinity of the capacity curves maximum for the supporting electrolyte.

The pseudocapacity peak (0,45-0,65 V) for 0,01 M HOTMI in the C vs E curve corresponds to the electrooxidation of HOTMI on Au according with the potentiodynamic studies performed (Fig.5). These last curves show that HOTMI really presents electrochemical activity in the some region.

In dichloromethane medium the C vs E curves show the characteristic adsorption maximum of the supporting electrolyte (Fig.6). In presence of 0,01 M HOTMI this maximum decreases greatly owed to the adsorption of HOTMI and produces at the same time a shift to more cathodic potentials of the capacity minimum value. The pseudocapacity maximum at the C vs E (Fig.6) in the potential region from 0,60-0,70 V corresponds to the electrooxidation of HOTMI since it presents electrochemical activity in this region on the potentiodynamic curve (Fig.7).

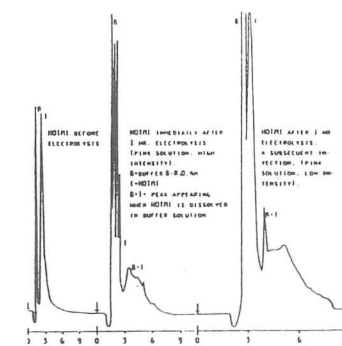


Fig.3. Chromatograms of HOTMI after electrolysis on a Pt electrode. Eluent: CH_3CN-H_2O (15:85); 0.75 M NaF; 200 mm x 1 mm I.D. column; 1.5 ml/min; 150°C.

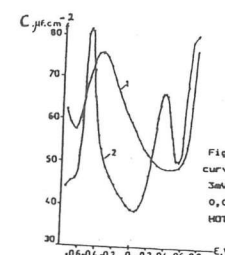


Fig.4. Differential pseudocapacity-potential curves for polycrystalline Au at sweep rate 3mV.s⁻¹ (anodic) and frequency 130 Hz (1) in 0,01 M NaOH+0,2 M NaClO₄ (2) in 0,01 M HOTMI.

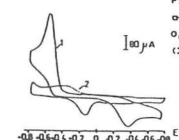


Fig.5. Cyclic voltammetry of 0,01 M of HOTMI (1) on Au electrode in 0,01 M NaOH+0,2 M NaClO₄ medium (2). $v=150$ mV.s⁻¹. E vs BCE.

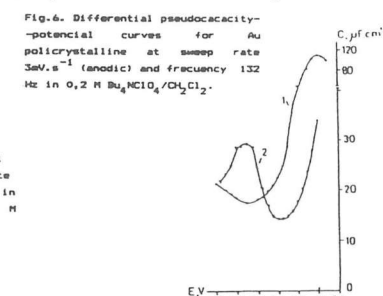


Fig.6. Differential pseudocapacity-potential curves for Au polycrystalline at sweep rate 3mV.s⁻¹ (anodic) and frequency 132 Hz in 0,2 M Bu₄NClO₄/CH₂Cl₂.

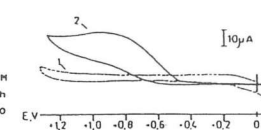


Fig.7. Cyclic voltammetry of 0,2 M Bu₄NClO₄ in CH₂Cl₂ (1) and with 0,01 M HOTMI on Au electrode. $v=200$ mV.s⁻¹.

At the mercury/electrolyte interphase, the HOTMI behaviour varies greatly with the nature and pH of the medium (4). In aqueous solution it was found that HOTMI adsorbs strongly in neutral medium on the mercury electrode in the potential interval -0,20-0,80 V since the C vs E curves show two sharp peaks, characteristic for adsorption-desorption phenomena (Fig.8).

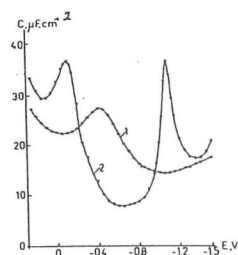


Fig.8. Differential capacity curves for Hg at sweep rate 3 mV.s^{-1} and frequency 130 Hz in $0,2 \text{ M NaClO}_4$ (1) and $0,01 \text{ M HOTMI}$.

These results lead to the conclusion, that the electrooxidation of HOTMI on mercury, gold and platinum electrodes are joined with the adsorption-desorption phenomena.

IR-spectroscopy, NMR and H-MS analyses allowed the identification of the main HOTMI electrooxidation products, which in water were diacetylmonoxime and in dichloromethane: dimethylglyoxime and 2-ketoxiimino-3-oximin butanone.

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AN ELECTROCHEMICAL APPROACH TO THE STUDY OF DYNAMIC PROCESSES AT THE INSULATOR/LIQUID INTERFACE

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ABSTRACT

A novel flow cell is described which allows the determination of the heterogeneous kinetics of calcite dissolution to be quantified.

INTRODUCTION

Heterogeneous reactions between a liquid phase reactant (R) and a solid (S) may be regarded as proceeding via a sequence of elementary steps involving, for example, (i) mass transport of R to the Outer Helmholtz Plane of the double layer of S, (ii) adsorption of R, (iii) surface diffusion of adsorbed R to a reaction site on the solid surface, (iv) heterogeneous reaction with the formation of adsorbed product (P), (v) desorption of P and (vi) transport of P into bulk solution. The kinetics of the process may be characterised with a heterogeneous rate law,

$$\text{flux, } j/\text{mol.cm}^{-2}\text{s}^{-1} = k_n[R]_{\text{ohp}}^n \quad (1)$$

where k_n is the nth order heterogeneous rate constant and $[R]_{\text{ohp}}$ relates to the Outer Helmholtz Plane. In the case when S is a metal then a diverse range of electrochemical methods have been developed to characterise reactions and their kinetics within the framework given above and this has been possible since the current flowing provides a direct measure of j . However for insulators no ready analogue exists. Accordingly we have developed a novel channel flow cell method to characterise the kinetics and mechanisms of processes at the insulator/liquid interface [1-3]. In this paper we illustrate its use in the quantification of the kinetics of calcite (CaCO_3) dissolution.

The technique uses a cell (figure 1) through which solution is pumped, under laminar flow conditions, along a rectangular duct. A block of calcite (in this application) forms part of one wall of the channel. Material consumed or released by calcite dissolution is detected