



CONCERNING THE EFFICIENCY OF CORROSION INHIBITORS AS GIVEN BY SVET

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INTRODUCTION

The Scanning Vibrating Electrode Technique (SVET) was firstly used in the life sciences [1-3] being introduced later in the corrosion field [4-7]. The ability to measure ionic fluxes in aqueous solutions makes the technique suitable to study many corrosion systems, particularly those that show a clear separation between anodic and cathodic regions. So far, most SVET studies in corrosion focused on the qualitative or semi-quantitative comparison of currents and the distribution of the anodic and cathodic activities in space and time. The present work explores and discusses the possibility of obtaining more quantitative data from SVET measurements, namely, the efficiency of corrosion inhibitors in aqueous solution. Values obtained by several parameters are tested and compared to those obtained by Electrochemical Impedance Spectroscopy (EIS).

EXPERIMENTAL

Materials and Reagents

The metal electrodes were prepared with pure iron (99.5%) and pure zinc (99.95%), both supplied by Goodfellow (UK). The corrosive medium was aqueous 0.05M NaCl prepared with distilled water and p.a. grade reagent. Two corrosion inhibitors, one of organic nature (benzotriazole, BTA, 99%, Aldrich) and one of inorganic nature (cerium nitrate, 99%, Aldrich) were added to the corrosive medium at a concentration of 0.5 g L⁻¹.

Electrochemical Impedance Spectroscopy (EIS)

Measurements

Experimental set-up

FemtoStat FAS2/PC14 (Gamry Instruments, USA)
Reference electrode: Hg/Hg₂Cl₂, KCl_{sat} (Radiometer XR110)
Counter Electrode: Pt plate (Radiometer M140), 1cm²
Working Electrode: Pure iron or zinc, 1cm²

Experimental Conditions

Frequency range: 100 kHz - 5 mHz
(7 points per decade with log distribution)
a.c. signal: 10 mV rms at o.c.p.

Calculations

The inhibition efficiency, IE, of a substance can be estimated by comparing the corrosion rate in the presence and in the absence of that substance [8]:

$$IE(\%) = \frac{\text{Rate uninhibited} - \text{Rate inhibited}}{\text{Rate uninhibited}} \times 100 \quad \text{Eq. (1)}$$

The charge transfer resistance, R_{ct} , obtained by EIS, is inversely proportional to the corrosion rate [9]. The figure on the right shows graphical ways of obtaining those values from Bode and complex plane representations of a simple impedance response, where the subscript "cto" denotes the uninhibited medium and "ct" denotes the inhibited medium.

When the response is more complicated, numerical fitting using equivalent electric circuits should be used. Common complications come as additional time constants due to surface films and mass transport of charged species. The inhibition efficiency can be determined from the values of charge transfer resistance using,

$$IE(\%) = \left(1 - \frac{R_{cto}}{R_{ct}}\right) \times 100 \quad \text{Eq. (2)}$$

Scanning Vibrating Electrode Technique (SVET)

Measurements

Experimental set-up

SVET manufactured by Appliable Electronics, USA
Cell:



Experimental Conditions

Distance from the surface: 200 μm
Probe tip: 20 μm
Vibration amplitude: 20 μm
Frequency: 122 Hz
N° points: 100x50

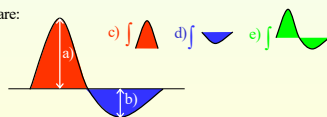
Calculations

The SVET detects the electric fields in solution associated with the ionic currents generated at the metal surface [5]. A prior calibration permits to present the results in local current densities [6]. The % inhibition can be calculated according to Eq. 3 where i is the current of sample in the inhibiting medium and i_0 is the current measured in the corrosive medium,

$$IE(\%) = \left(1 - \frac{i}{i_0}\right) \times 100 \quad \text{Eq. (3)}$$

Different ways to obtain i and i_0 from SVET maps are:

- maximum height of anodic peak,
- maximum height of cathodic peak,
- integration of anodic currents,
- integration of cathodic currents,
- overall activity in electrode.



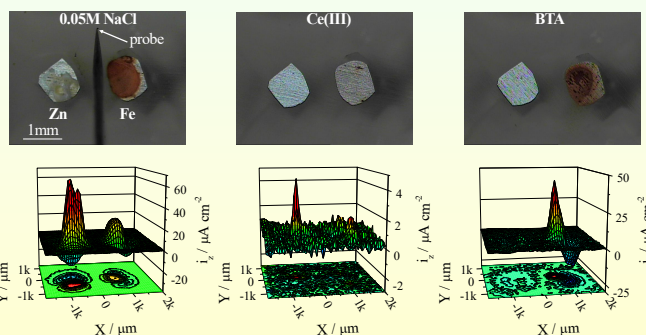
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RESULTS

EIS. The figure on the right gives the impedance, in Bode and complex plane representations, of Fe after 24 hours of immersion in the corrosive medium and in the two inhibitive solutions. In NaCl and BTA a single time constant is observed, being attributed to the response of the double layer capacitance, C_{dl} , and the charge transfer resistance, R_{ct} . R_{ct} is smaller for BTA which is explained by the adsorption of inhibitor that decreases the active metal area. R_{ct} is slightly higher in BTA than in NaCl. For iron immersed in Ce(III), a second time constant appears at higher frequencies that is attributed to the formation of a passive layer. C_{dl} is much smaller and R_{ct} much higher compared to the other two media. In this system the pure resistive response of R_{ct} was not observed. For that, measurements at lower frequencies would be necessary. The value of R_{ct} for iron and zinc in the three solutions was obtained by numerical fitting using the software package ZView2 (Scribner, USA).

SVET. Shown below are video images and current maps obtained by SVET, above zinc and iron electrodes after 24 hours of immersion in the three solutions. Both metals corrode in NaCl, but the activity is much reduced in Ce(III). In BTA, Fe corrodes and Zn shows very little attack.



DISCUSSION

The table below summarizes the inhibition efficiency determined in the different ways presented above. Assuming the value calculated by EIS as the true value, the error (%) of estimation using SVET can be calculated by,

$$\text{Error}(\%) = \frac{EIS - SVET}{EIS} \times 100 \quad \text{Eq. (4)}$$

The error for each case is included in the table, in green for variations below 5% and in red for major discrepancies. The closest values were obtained for the inhibition with Ce(III) and for zinc, i. e., for the cases when inhibition was significant. Large errors were found for iron in BTA. The precipitation of corrosion products introduces an underestimation of the current measured. A fraction of the ions generated at the metal surface precipitate and are not detected by SVET. This was more pronounced for the iron electrode in NaCl. The efficiency thus calculated is affected by this error and gives negative values, as if the inhibitors favoured the corrosion of iron. These results show that in optimal conditions SVET can give accurate inhibition efficiency. However, in other circumstances, gross errors can be produced. Video images obtained in the SVET measurement can anticipate the accurateness of the inhibition efficiency calculated by SVET. It is clear that it is possible to get more quantitative information from SVET, but the technique cannot, at this stage, replace the traditional ways to determine the inhibition efficiency.

		SVET				
		EIS	a)	b)	c)	d)
			e)			
Fe	BTA	13.40	-84.33	-19.20	14.40	-30.30
			(-730)	(-243)	(7.0)	(-326)
Ce		96.16	79.26	93.02	83.00	94.90
			(-18.0)	(-3.3)	(-13.7)	(-1.3)
Zn	BTA	99.60	94.96	85.20	92.20	81.44
			(-4.7)	(-14.4)	(-7.4)	(-18.2)
Ce		99.20	98.36	97.81	94.20	98.00
			(-0.8)	(-1.4)	(-5.0)	(-1.2)

CONCLUSIONS

The use of SVET to obtain the efficiency of corrosion inhibitors was analysed. Good correlation was encountered for high levels of inhibition. Discrepancies existed when corrosion products were formed, leading to an underestimation of the currents to be measured. Visual inspection of the samples can identify the cases more susceptible to error. The approaches discussed here can be used to obtain more quantitative information when performing SVET measurements but cannot replace the traditional ways to determine the inhibition efficiency, like EIS, polarization curves or mass loss.