IMPEDANCE SPECTROSCOPY STUDY OF INHIBITIVE PROPERTIES OF QUATERNARY AMMONIUM SALTS

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ABSTRACT

Two quaternary ammonium di-bromides were investigated as corrosion inhibitors of mild steel in 1M HCl using impedance spectroscopy. Equivalent structure model of the interface metal/1M HCl+inhibitor was presented to describe the process. Independently the polarisation resistance was measured as well and compared with impedance data. Good agreement was found. Both investigated compounds show very good inhibitive properties.

Keywords: acid media, mild steel, corrosion, electrochemical impedance spectroscopy, inhibitors.

INTRODUCTION

Acid solutions are often used in many industrial technologies, as pickling before metal plating, descaling and others. A suitable method for decreasing the corrosion loses is the use of inhibitors. In acid media good inhibitive properties have a number of organic compounds [1 - 8]. Among them are quaternary ammonium salts [9, 10]. In this study two compounds of this group are for the first time investigated (Table 1).

The electrochemical impedance spectroscopy (EIS) provides exact and rapid information about the kinetics of the electrode processes and the properties of the metal surface. From the impedance diagrams one can deduce which steps play an important role in the overall corrosion process [11 - 13]. The method has been successfully applied for inhibitor investigations [14 - 23].

EXPERIMENTAL

The experiments were carried out using a conventional electrochemical three-electrode cell. All investigated compounds were synthesized for the purpose and purified by re-crystallisation from ethanol to analytical purity grade.

The mild steel used had the following chemical composition (mass %): 0.16 C, 0.35 Mn, 0.016 Si, 0.01 P, 0.029 S, 0.06 Cr, 0.10 Cu and balance Fe. The working steel electrodes were cylinders pressed into Teflon holders with an exposed area of 0.5 cm². A saturated calomel electrode connected through a salt bridge was used as reference electrode, while a large area platinum leaf served as counter electrode. Prior to each experiment the working electrode was wet polished with 600 grade emery paper, rinsed with distilled water and an
ethanol-ether mixture and immediately inserted into the
glass cell which contained 250 ml of the test solution.

The impedance measurements began 2 hours after
immersing the working electrode. The temperature was
maintained 22±1ºC. EG&G Instruments PAR model
273 potentiostat and 5208 two phase lock-in analyzer
connected to an IBM personal computer via GPIB-II
interface and M378 and M342 software were used to
run the tests, collect and evaluate the experimental data.

The response of the electrochemical system to ac
excitation with a frequency ranging mainly from 95
kHz to 0.07 Hz and peak to peak amplitude of 10 mV
was measured. Lock-in amplifier technique was used
in the frequency range of 95 kHz to 5 Hz with 5 points
per decade. Measurements below 10 Hz were performed
using FFT technique with eight data cycles. All EIS
data are recorded at the open circuit potential, i.e. at the
corrosion potential. One spectrum is recorded usually
within 8 minutes. An appropriate equivalent circuit
model is fitted to the impedance data using a non-linear
least squares fit procedure.

The polarisation resistance measurements were per-
fomed immediately after the impedance spectra on the
same electrode without any additional surface treatment.
The working electrode was polarized in the range from
±10 mV vs. E_{corr} at a sweep rate of 0.1 mV s^{-1}.

For every inhibitor concentration five independent
experiments were carried out. The mean values and the
standard deviations are reported.

RESULTS AND DISCUSSION

The recorded impedance spectra depend on the
type and the concentration of the inhibitor. All spec-
tra in presence of MTB and TFB have the shape of a
depressed semicircle in complex plane representation
(Fig. 1). In this case the transfer function Z(ω) can be
represented by:

\[ Z(\omega) = \frac{1}{R_1 + i\omega C} \]  \hspace{1cm} (1)

where to the parallel connected capacitance C and
resistance R_1 a resistance R_2 is added in series. Such
transfer function is common for describing homogene-
ous systems with only one time constant. The depression
of the semicircle does not allow the use of an “ideal”
capacitance, so it can be replaced by a distributed ele-

![Fig. 1. Impedance diagrams in presence of 1M HCl + 1x10^{-3}
M MTB: a) Niquist plot; b) Bode plot. ◊ - experimental
data; ..... – calculated.](image-url)
The equivalent circuit, used to describe this type of impedance spectra is illustrated in Fig. 2.

The values of the model parameters are given in Tables 2 and 3. The double layer capacitance is evaluated according to eq. 3. In the tables are presented also the relaxation times, a measure for the time required for return to the equilibrium state (in this case to the stationary state) calculated as \( \tau = C/R_{ct} \), as well as the values of polarisation resistance \( R_p \), determined by means of the direct current polarisation method.

In the whole concentration range the increase of concentration of MTB and TFB increases the values of \( R_{ct} \), indicating amelioration of the inhibitive properties. This effect is connected with diminishing of the double-layer capacitance, often observed by adsorption of organic molecules on electrode surfaces. In presence of MTB \( n \) shows a tendency to shift towards lower values, indicating an increase of the surface heterogeneity as a result of the adsorption. In the case of TFB \( n \) remains
almost constant.

In presence of MTB the relaxation time increases slowly with concentration, while almost no changes are observed in presence of TFB.

The total resistances are compared with the values of the $R_{p, DC}$, determined by means of the direct current polarisation resistance method. When the transfer function has only one time constant (Fig. 2) the sum $R_{\alpha} + R_\Omega$ is very close to $R_{p, DC}$.

At all concentrations the inhibitor TFB is better than MTB.

**CONCLUSIONS**

The inhibition of the corrosion of mild steel by quaternary ammonium salts is studied using electrochemical impedance spectroscopy and polarisation resistance measurements. The spectra in presence of MTB and TFB are described well by a structural model of the interface mild steel/1M HCl + inhibitor with one time constants - they are attributed to the double layer charging (combined with charge transfer reaction) - $R_{\alpha} || C_d$.

The double-layer capacitance is imitated by a constant phase element due to surface inhomogeneity.

The values of $R_{p, DC}$, determined by the independent direct current polarisation resistance method are very close to the total resistance $R_{\alpha} + R_\Omega$, calculated from the impedance data.

**REFERENCES**

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