CHAFTER - 1

INTRODUCTION

1.1. Ceneral

Efforts towards understanding of corrosion processes have increased enormously during the past two decades. This has happened so, because, corrosion loss to the economy has increased tremendously in consequence of the extensive use of metals which is often accepted as an index for the progress in civilization. Increased public interest in this aspect of metal degradation has also enhanced the importance of corrosion study. The understanding of the fundamentals of corrosion processes that started with the works of C.Waoner, has undergone substantial development as a result of the availability of new techniques of study. It is recognised that all corrosion processes are electrochemical in nature and the advancements in electrochemical studies have enriched the present day corrosion research while introducing a very quantitative change in it. Potentiostatic and Galvanostatic techniques have been applied by numerous investigators for evaluating corrosion behaviour of metals and alloys in various environments and a vast amount of informations are now available with regard to this.

The control and prevention of corrosion is a subject with tremendous technological significance. Amongst the available methods for mitigation of metal corrosion, the use of inhibitors has not only become a new independent mode of protection, but also has altered significantly many classical protective media (oils, greases, polymeric coatings etc.). With every passing year corrosion inhibitors are becoming increasingly important for the anticorrosive protection of metals in diverse branches of technology and the economy. The use of inhibitors to protect metals against corrosion is based on the ability of certain specific chemical compounds, or mixtures of them, to reduce the rate of corrosion process, or to completely suppress this process, when they are introduced in small concentrations into the corrosive medium.

While some inorganic chemicals are certainly useful for controlling corrosion in specific cases, organic chemicals have gained primary importance as inhibitors and are widely used for preventing corrosion.

Effectiveness of organic inhibitors has been determined by many ways. But the electrochemical measurements employing polarization techniques have dominated as the principal techniques for evaluation and characterisation of organic inhibitors. The effectiveness of a corrosion inhibitor is often expressed in terms of percent protection, that is, the inhibited corrosion

rate is related to the uninhibited one. Measurements of corrosion rates in presence and in absence of the inhibitor in the corrosive media are thus of primary importance.

There are two basic electrochemical techniques which are widely used for such measurements :

- High-field approximation of the Stern-Geary equation can be used to derive corrosion rates. This method is equivalent to the Tafel's extrapolation method.
- 2. Corrosion rates can also be obtained by low-field approximation of Stern-Geary equation which is termed as the 'Linear polarization' method. The correlation used in this approach is given by the equation.

$$I_{corr} = \left(\frac{\Delta I}{\Delta E}\right) \cdot \frac{\dot{\beta}_{a} \cdot \dot{\beta}_{c}}{2 \cdot 3 \left(\beta_{a} + \beta_{c}\right)} ,$$

where β_a and β_c are anodic and cathodic Tafel slopes respectively and $E = E_{corr}$.

Both these methods have been extensively used by corrosion investigators and occasionally corrosion rates determined by such electrochemical measurements have been compared with the results obtained from conventional methods such as measurements of weight loss. It is generally accepted that the polarization measurements are quite reliable as a tool for corrosion rate estimation and

also for the evaluation of inhibitor performance. Only recently, opinions contrary to this general view has been expressed by $R.H.Hausler^{83}$.

Measurements of corrosion rates by polarization technique using Tafel's extrapolation method for uninhibited solutions, especially for acid solutions, where the mechanism of hydrogen evolution and metal dissolution is well guessed, is accepted in a general way. But in the presence of inhibitors, such evaluations have many difficulties that need scrutiny.

A major objection addingt the use of polarization techniques for inhibitor evaluation is based on the observation of the non-Tafel behaviour of the polarization curves in the inhibited situation. In absence of true Tafel relation in the inhibited situation, obviously, Tafel extrapolation or the intercept method fails to meet the object of deriving corrosion rates from polarization measurements. It appears that the large number of publications on electrochemical corrosion rate measurements using the Tafel extrapolation technique, that have been written in the past two decades, were based on rather arbitrary values of Tafel slopes for the inhibited situation.

The problem of getting true values for the Tafel parameters also creats difficulties for the conventional or modified Linear Polarization methods when used to derive corrosion rates

in presence of inhibitors. Absence of Tafel behaviour in the experimental polarization curves raises the very basic question about the physical significance of β_a and β_c values that are used to fit best the experimental data for Linear Polarization measurements.

The non-Tafel behaviour of polarization curves has been partially explained by Hausler⁸³ for the case of acid corrosion of iron in presence of phenylthiourea. He has suggested that a change in the mechanism of hydrogen evolution in presence of phenylthiourea might have a reflection in the current-potential relation resulting in non-Tafel behaviour of the polarization curves. This explanation, which puts stress on a plausible change in the rate control process may be true for the case of strong chemisorption of the inhibitor molecules. But for the majority of organic inhibitors, it is more likely that the potential dependent adsorption/desorption processes exert major influence on the shape of the polarization curves. The potential of zero charge (PZC) of the corroding metal has an important role to play in this connection.

If the PZC lies close to the corrosion potential well within the Tafel region (as is the case with iron), polarization is expected to have marked influence on the electrosorption/ desorption behaviour of the organic inhibitor, especially if the adsorption forces are physical in nature. In such a situation

true Tafel behaviour can not be expected in the usual polarization curves obtained in presence of the inhibitor. In this case it may not be possible to get true Tafel slopes from the polarization curves and unambicuous values for corrosion current can not be obtained by using the extrapolation method. With these ideas in view, the present investigation was undertaken to correlate the polarization characteristics of metal electrodes with the potential of zero charge in electrolytes containing organic adsorbates.

Pure silver was chosen as the principal meterial for the establishment of this correlation. The choice was determined mainly by the requirement of avoiding film formation on a freshly prepared electrode surface within a reasonably short period of handling the same during experiments. The determination of the PZC of silver and investigations on its polarization behaviour were carried out in 0.1 N KNO₃ solution. Potassium nitrate was chosen as the electrolyte because trials with silver showed an extensive Tafel region in 0.1 N KNO₃ and the PZC was observed to lie in the neighbourhood of the steady state potential. Moreover, the possibility of the formation of any insoluble compound on the silver surface could be avoided in the nitrate solution.

The correlation between the polarization characteristics of silver with its potentials of zero charge has been used to

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explain the polarization behaviour of iron in $1 \text{ M H}_2\text{SO}_4$ containing the inhibitor. Possible errors in estimating the corrosion rates from polarization data in the inhibited situation have been pointed out for the simple system of acid corrosion of iron.

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Mercury is considered to be the ideal metal for polarization studies and electrocapillary measurements on mercury have been extensively used for the determination of its PZC in different electrolytes. In the present work mercury-plated copper electrodes have been used for the determination of the PZC and for investigating the influence of the PZC on polarization behaviour in the same electrolytes as was used for silver (i.e. 0.1 N KNO₃).

1.2. Scope of the Work and Goal

The present work can be broadly divided into three parts. The first part comprises of the determination of the PZC of silver along with a study of its polarization behaviour in 0.1 N KNO_3 solution. The technique of measuring meniscus rise at partially immersed vertical plates with the variation of potential was employed for the determination of the PZC⁶⁷. The influence of the presence of some normal aliphatic acids (i.e., propoinic, butyric, caproic, heptoic and octoic) on the position of the PZC was also investigated. The choice of aliphatic acids as adsorbates were based on informations gathered from literature regarding their adsorbability on silver surface. For the polarization studies, potentiostatic technique was employed. The influence of the organic acids mentioned above on the polarization behaviour of silver has been investigated.

An attempt has been made to correlate the informations obtained from these two diverse fields of study, namely, polarization measurements and studies on the potential dependence of the liquid meniscus height. These correlations clearly demonstrate that the potential dependent adsorption/desorption behaviour of the organic acids on silver electrodes has a close relation with its potential of zero charge. The potential of maximum surface coverage by the organic substances, calculated from polarization data, corresponds closely to the PZC of silver in a particular electrolytic system. The polarization measurements also reveal marked influence of the organic acids on the shape of the polarization curves.

The second part of the work comprises of studies of the polarization behaviour of iron in 1 M H_2SO_4 containing various concentrations of thiourea as inhibitor. The influence of the presence of chloride ions in the electrolyte has also been investigated. The correlation between the PZC of silver and the maximum surface coverage as derived from polarization data has been used to explain the polarization behaviour of iron in 1 M H_2SO_4 containing thiourea and potassium chloride. The maximum surface coverage calculated from the polarization

measurements give values for the PZC of iron which are in good agreement with the results of capacitance measurements reported by other workers. These observations suggest that the data on polarization measurements, under suitable circumstances, can be conveniently used for the determination of the PZC of solid electrodes.

The presence of thiourea in H_2SO_4 exhibits conspicuous absence of true Tafel region in the polarization curves. Thus the electrochemical methods, especially the Tafel extrapolation method, apparently fail to give true corrosion rates in the inhibited situation. In connection with these studies on acid corrosion of iron, the role of the PZC in affecting the electrosorption processes and thereby imparting non-Tafel behaviour to the polarization curves has been brought to relief.

In the third part of the present work the polarization behaviour of mercury-plated copper electrode in 0.1 N KNO₃ containing various concentrations of the series of organic acids mentioned earlier has been investigated. The PZC of mercuryplated copper electrode in the electrolytes as influenced by the presence of organic acids has also been studied. A correlation of these results corroborates the observations on the role of the PZC in affecting the polarization behaviour in presence of organic adsorbates in the electrolytic solution.

1.3. Thesis Format

The main object of the present work has been to correlate the PZC of a solid electrode with its polarization behaviour in presence of organic adsorbates in the electrolyte. In addition, possible errors in inhibitor evaluation resulting from potential dependent adsorption/desorption processes of organic inhibitors during polarization have been brought to focus. A vast amount of informations are available in the literature in the related fields of adsorption studies, methods for PZC determination as well as polarization studies. As such it has not been possible to present a complete literature survey in this thesis; only the partinent literature is cited in Chapter 2. Theoretical aspects of some of the concerned topics have also been discussed in brief.

In Chapter 3 experimental procedure followed in this investigation has been outlined.

Chapter 4 of this thesis contains data on potential dependent meniscus rise on silver and mercury-plated copper electrodes along with polarization data for silver, mercury plated copper and Armco iron electrodes.

Results obtained from the data on meniscus rise measurements and the polarization measurements have also been discussed in Chapter 4. An attempt has been made to correlate these two sets of data for individual materials keeping in view the potential dependent adsorption behaviour of organic substances. A new method for the determination of the PZC of solid electrodes employing polarization technique has been suggested and the validity of the method has been discussed. The limitations of conventional procedures for the determination of corrosion rates and Tafel parameters in the inhibited situation from polarization data have also been discussed.

The observation of the present investigation have been summarized and interrelated in the general discussion incorporated in Chapter 5. The conclusions drawn from the present work have been listed in Chapter 6. It is expected that the correlation of the PZC with the polarization characteristics of solid electrodes as suggested in the present work will be much useful to scientists interested in scanning large number of inhibitors and designing proper inhibitors. The difficulties encountered with the conventional electrochemical methods for deriving corrosion rates in the inhibited situation, discussed in the present context, will perhaps, call for more active research in this field.