TENSAMMETRIC STUDIES ON CORROSION INHIBITORS

Part I. Dicyclohexylamine Nitrite

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ABSTRACT

The study of adsorption by the alternating current polarographic method is known as 'tensammety'. This technique has been extended to the study of the adsorption characteristics of organic corrosion inhibitors with a view to elucidate the mechanism of inhibition by such compounds. The usefulness of such studies in elucidating the mechanism of inhibition by dicyclohexylamine nitrite, which is now widely used as a vapour phase corrosion inhibitor, is brought out. For this purpose, results obtained by tensammetric studies have been compared with potential measurements on the one hand and direct corrosion tests on the other and discussed.

INTRODUCTION

A large number of organic compounds are known to inhibit corrosion in aqueous media. The mechanism of inhibition by these compounds has been studied by polarization measurements. Direct measurement of the extent of adsorption of the inhibitor on the metal surface has also been attempted. Direct studies on adsorption characteristics of organic corrosion inhibitors, however, involve the use of fine metal powders, the surface condition of which is generally difficult to reproduce. This difficulty may be overcome by studying the adsorption behaviour of organic compounds at the mercury surface. Among metals, mercury is unique in that it can be obtained in a highly pure chemical form and its surface characteristics are easily reproduced because of its liquid state. It is for this reason that mercury has been so widely used for the study of various metal-liquid interface phenomena including the changes in surface tension caused by capillary active substances. Electro-capillary data have been employed for the study of corrosion inhibitors. Purely electrochemical methods of studying adsorption using mercury surface have also been put forward. One approach that has
been made in this direction is that of Gatos based on the suppression of polarographic maximum by surface-active substances which are, otherwise, known as maxima suppressors. While this method appears to have been quite fruitful in regard to the behaviour of certain types of organic compounds having corrosion-inhibiting properties, it suffers from two important drawbacks. Firstly, the polarographic maximum is not an easily reproducible phenomenon and secondly, the mechanism of maxima suppression is not yet adequately understood. A more elegant approach to the study of adsorption of organic compounds on mercury surfaces is that of Proskurnin and Frumkin and Grahame who have made use of the capacity of the electrical double layer of mercury for following adsorption. They observed capacitance peaks when surface-active substances were desorbed at the metal-solution interface of a mercury electrode. The measurements were made by superposing a small low-frequency alternating voltage on to the direct potential applied to the electrode. Subsequently, Breyer and Hacobian and Doss and Gupta showed that the alternating current polarographic method can be used with advantage for this type of investigation. The technique consists in applying simultaneously a D.C. potential as well as a small A.C. voltage on the dropping mercury electrode of the type commonly used in polarography. The magnitude of the A.C. component of the pulsating current thus produced is a direct measure of the capacity of the electrical double layer. Percentage decrease in capacity values indicate the extent of adsorption. A new term “tensammetry” has been coined to denote studies of this kind. The present paper deals with the relationship between adsorption measurements made in this manner, potential and polarization measurements and the corrosion inhibiting property of some inhibitors. The study has been particularly useful from the point of view of elucidating the mechanism of inhibition by dicyclohexylamine nitrite which is widely used as a vapour phase corrosion inhibitor.

**Experimental**

(a) *Compounds studied.*—(1) p-toluidine, (2) a-naphthylamine, (3) morpholine, (4) cyclohexylamine, (5) dicyclohexylamine, (6) dicyclohexylamine nitrite, and (7) sodium nitrite. Dicyclohexylamine nitrite is the active constituent of the trade product known as V.P.I. 260 and was obtained by recrystallisation from alcoholic solution of the trade product. The other chemicals were obtained from trade and used as such.

(b) *Capacity measurement.*—The method used was the same as that described in reference 10. Measurements were made in N/10 KCl solutions to which the inhibitor had been added. 0.1% solution of the inhibitor was...
usually employed but where the inhibitor was not soluble to this extent as in the case of dicyclohexylamine and α-naphthylamine, a saturated solution of the inhibitor was used. Decrease in capacity was calculated by deducting the capacity (A.C. current) measured in solution containing inhibitor from that measured at the same potential in N/10 KCl solution only and this difference converted into a percentage on the original value to enable comparison. Measurements of capacity were made over a wide range of potentials on both sides of the electro-capillary zero. Decreases in capacity at different potentials are shown in Figs. 1 and 2. The capacity peaks on either side have been omitted from consideration here as the concentration of the inhibitor is not under study.

![Fig. 1](image1.png)

![Fig. 2](image2.png)

**Fig. 1.** Percentage decrease in capacity by inhibitor at different potentials. (a) Cyclohexylamine. (b) Morpholine. (c) p-Toluidine. (d) α-Naphthylamine.

**Fig. 2.** Percentage decrease in capacity by inhibitor at different potentials. (a) Sodium nitrite. (b) Dicyclohexylamine nitrite. (c) Dicyclohexylamine neutralised to pH 7. (d) Dicyclohexylamine.

(c) Potential and polarization measurements.—The potentials were measured by the Poggendorf method using a Beckman pH meter as the zero reading instrument. This made it possible to make potential measurements without passage of more than $10^{-11}$ amperes on off balance. Polarization measurements were carried out by external application of current with a duplicate specimen as the auxiliary electrode. The procedure followed in the preparation of steel specimens for potential and polarization measurements was similar to that described by Brasher. All measurements were
made at 35 ± 0.1°C. The finish given to these specimens is similar to that given in the case of specimens used in corrosion test.

(d) Corrosion tests.—3" × 2" mild steel specimens were cut, uniformly abraded with 0 emery, degreased with methanol, benzene and acetone and used. The electrolyte used for the corrosion tests was 0.001% NaCl with and without inhibitor. The solution was aerated before test. The experiments were carried out in triplicate and the specimens were suspended in the electrolyte with the help of glass hooks such that the top edge of the specimens was more than 1" below the water line.

RESULTS

(a) Changes in capacity.—The percentage decrease in capacity at various potentials on both sides of the electro-capillary zero of the various inhibitors studied are given in Figs. 1 and 2. In the case of dicyclohexylamine the values were also determined after neutralizing the solution to pH 7 with dilute sulphuric acid solution to enable comparison with dicyclohexylamine nitrite which in its pure form gives a neutral solution. It may be seen from the two figures that (i) all the compounds studied excepting sodium nitrite show adsorption on mercury surface, (ii) the adsorption is on both sides of the electro-capillary zero, (iii) the extent of adsorption at different potentials varies from inhibitor to inhibitor, (iv) α-naphthylamine and p-toluidine show adsorption preferentially on the negative side of the electro-capillary zero, (v) morpholine, cyclohexylamine and dicyclohexylamine are adsorbed to the maximum extent at the electro-capillary zero, and the adsorption on both sides extends over a wide range, (vi) the range of potentials over which adsorption takes place and the extent of adsorption is highest in the case of dicyclohexylamine and least in the case of morpholine, (vii) this adsorption decreases at the lower pH and, lastly (viii) the adsorption characteristics of dicyclohexylamine nitrite and dicyclohexylamine at pH 7 (i.e., when the dicyclohexylamine has been converted into sulphate) are very similar to each other.

(b) Potential and polarization measurements.—Steady potentials of mild steel specimens in 0.001% NaCl solutions containing the inhibitors are given in Table I. It may be seen from Table I that changes in potential in the nobler direction, which usually indicates passivation of the metal surface, are observed only in the case of sodium nitrite, dicyclohexylamine nitrite, cyclohexylamine and morpholine. No such shift is observed in the case of the other chemicals.

Coming to anodic and cathodic polarization measurements at different current densities given in Figs. 3 and 4, one finds that the results closely
TABLE I

Potentials of mild steel specimens in 0·001% NaCl solution containing organic chemical at the end of 3 hours of immersion

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>System</th>
<th>Potential vs. saturated calomel electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Without inhibitor</td>
<td>-0.66</td>
</tr>
<tr>
<td>2</td>
<td>Solution saturated with α-naphthylamine</td>
<td>-0.53</td>
</tr>
<tr>
<td>3</td>
<td>0·1% p-Toluidine</td>
<td>-0.67</td>
</tr>
<tr>
<td>4</td>
<td>Solution saturated with dicyclohexylamine</td>
<td>-0.60</td>
</tr>
<tr>
<td>5</td>
<td>0·1% Morpholine</td>
<td>-0.32</td>
</tr>
<tr>
<td>6</td>
<td>0·1% Cyclohexylamine</td>
<td>-0.13</td>
</tr>
<tr>
<td>7</td>
<td>0·1% Sodium nitrite</td>
<td>-0.02</td>
</tr>
<tr>
<td>8</td>
<td>0·1% Dicyclohexylamine nitrite</td>
<td>+0.02</td>
</tr>
</tbody>
</table>

Fig. 3. Potential current density curves in 0·001% NaCl solution. (a) No inhibitor. (b) p-Toluidine. (c) Morpholine. (d) Cyclohexylamine.

Fig. 4. Potential current density curves in 0·001% NaCl solution. (a) Dicyclohexylamine nitrite. (b) Sodium nitrite. (c) Dicyclohexylamine.
paralleled potential data and corrosion data given in the next section. The only chemicals which bring about increased polarization of the steel specimens are sodium nitrite, dicyclohexylamine nitrite, cyclohexylamine and morpholine. The extent of polarization follows the same order as corrosion inhibition data. Both sodium nitrite and dicyclohexylamine nitrite polarize to the same extent, cyclohexylamine to a lesser extent and morpholine to a still lesser extent.

(c) Corrosion inhibition data.—The period for which complete protection is given by the different inhibitors in the corroding medium, and loss in weight at the end of 15 days of test are given in Table II.

**Table II**

*Data on corrosion inhibition*

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>System</th>
<th>Period for which complete protection is obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Without inhibitor</td>
<td>... &lt; One hour</td>
</tr>
<tr>
<td>2</td>
<td>a-Naphthylamine</td>
<td>... &lt; One hour</td>
</tr>
<tr>
<td>3</td>
<td>p-Toluidine</td>
<td>... &lt; One hour</td>
</tr>
<tr>
<td>4</td>
<td>Morpholine</td>
<td>... Two days</td>
</tr>
<tr>
<td>5</td>
<td>Cyclohexylamine</td>
<td>... Three days</td>
</tr>
<tr>
<td>6</td>
<td>Dicyclohexylamine</td>
<td>... &lt; One hour</td>
</tr>
<tr>
<td>7</td>
<td>Dicyclohexylamine nitrite</td>
<td>&gt; One month</td>
</tr>
<tr>
<td>8</td>
<td>Sodium nitrite</td>
<td>... &gt; One month</td>
</tr>
</tbody>
</table>

It is seen from Table II that practically no inhibition is given by p-toluidine, a-naphthylamine and dicyclohexylamine, in neutral solution containing chloride. Morpholine gives protection for a short duration but once rusting commences at the glass-metal contact, it spreads quite rapidly to the rest of the metal surface. Cyclohexylamine gives considerable inhibition and localizes rusting even when it has commenced. Sodium nitrite and dicyclohexylamine nitrite both containing nitrite ion give complete inhibition during the entire duration of test.
Discussion

Corrosion is retarded by the presence of a barrier between the metallic material and the environment and this barrier may be produced either by a protective oxide film formed at the metal surface or by adsorbed particles. The adsorption of gelatine on mild steel has been demonstrated by Rhodes and Kuhn\textsuperscript{14} in terms of the rate of hydrogen evolution from acid solution. Very similar inhibition is given by all types of amines and N-ring bodies. It has been suggested by Warner\textsuperscript{15} that amines are preferentially adsorbed at those points of the metal surface that are in its absence the most active for the cathodic discharge of hydrogen ions. The increase of hydrogen over potential produced by such substances at cathodes operating at much more negative potentials than those found in acid corrosion has been brought forward as evidence in support of this theory.\textsuperscript{16-18} But it is now known that very similar inhibition is produced by many other kinds of molecules, some of which can scarcely be supposed to accept protons even in the most acid solution. Machu,\textsuperscript{19} therefore, suggested general adsorption as the cause of inhibition by organic compounds which did not react with the metal surface. Hoar\textsuperscript{20} has pointed out that a mainly cathodic inhibitor acting merely by blocking cathodic sites must lead to a shift of the compromise or corrosion potential in the negative direction and conversely a mainly anodic inhibitor must lead to ennoblement of potential in accordance with the Evan's diagram. This has also lead Hoar\textsuperscript{21} to conclude that N-inhibitors including quinolines and substituted quinolines are readily adsorbed on the anodic than on the cathodic sites. Antropov\textsuperscript{22} has drawn pointed attention to his concept of $\psi$ potential of metals based on electro-capillary zero. According to him, adsorption is governed by the intrinsic charge of the metal surface and not in terms of the local cell theory of corrosion and the presence of anodic and cathodic sites on the metal surface. Depending upon the corrosion potential of a metal as given by the hydrogen scale both anodic and cathodic areas of the metal surface will be negatively or positively charged, or both negatively and positively charged. He has, therefore, suggested a new scale of potential known as $\psi$ potential obtained by the difference between the electro-capillary zero potential and the potential on the hydrogen scale. That this approach is considered more fundamental from the point of view of the study of adsorption has already been pointed out in the Introduction to this paper. The results obtained in this paper may also be satisfactorily understood in terms of this approach. The potential at the electro-capillary maximum of steel has been shown to be very near that of mercury. Steel in neutral chloride solution has an initial potential of $-0.45$ volts against saturated calomel electrode which quickly falls to a potential of $-0.65$ volts,
At the initial potential part of the surface may be expected to be slightly positively charged. Substances which are adsorbed on the positive side of the capacity curve are likely to give more inhibition under these conditions than those showing adsorption at the negative side. Of the different chemicals studied, it is seen that only morpholine, cyclohexylamine and dicyclohexylamine show pronounced adsorption on the positive side of the electro-capillary zero. Two of these chemicals cyclohexylamine and morpholine give inhibition to some degree; cyclohexylamine shows more adsorption and also shows more inhibition. The behaviour of dicyclohexylamine is not clear. In this case, as in the case of a large number of surface-active substances, adsorption has not been followed by corrosion inhibition. In the case of dicyclohexylamine nitrite, the observed corrosion inhibition may be attributed to the combined effect of adsorption of inhibitor as well as the property of the nitrite ion to form a protective oxide film of metal surface. The inability of a-naphthylamine and p-toluidine to give inhibition in neutral solution may also be explained on this basis. They show adsorption mainly on the negative side of the electro-capillary zero and this adsorption is favoured in acid solutions in which the corrosion potential of steel is more negative and the steel surface is also negatively charged.

It may also be noticed that such adsorption as those considered above shift the potential of the metal. When the potential is shifted in the nobler direction (adsorption of compounds like cyclohexylamine and morpholine) is further favoured that is why these chemicals which cause considerable changes in potential in the nobler direction are also the only amines among those considered which show inhibition to an appreciable extent in neutral solution. The same is observed in the case of dicyclohexylamine nitrite where adsorption enables the inhibitor being brought very near to the metal surface. However, the situation here is complicated by the existence of the nitrite group which really brings about the observed corrosion inhibition in the same way as sodium nitrite which by itself does not show any adsorption. The mechanism of inhibition by nitrite ion has been dealt with by other workers and it has been shown to form a protective oxide film on the metal surface.

**Conclusion**

The usefulness of adsorption studies by tensammetric measurements with corrosion inhibitors has been brought out. It has been shown that dicyclohexylamine nitrite gives corrosion prevention in neutral media both by the inhibitive action of the nitrite ion on the one hand and the property of adsorption displayed by dicyclohexylamine group on the other.
ACKNOWLEDGEMENT

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