

THE APPLICATION OF THE φ -SCALE OF POTENTIALS TO PROBLEMS OF THE CORROSION AND PROTECTION OF METALS†

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The aim of the present paper is to discuss a new method of studying inhibitors of metallic corrosion and to examine certain fundamental aspects of a combined method for protecting metals from corrosion, based on the simultaneous action of organic inhibitors and cathodic polarisation. The introduction of these methods is related to the φ -scale of potentials, proposed by the author¹⁻³ and first applied to problems of corrosion about ten years ago³⁻⁷.

The φ -potential of an electrode, i.e. the difference between the potential ϵ under the given conditions and the corresponding potential of zero charge $N\epsilon$, determines the charge of the metal relative to the surrounding solution^{3,8,9}:

$$\varphi = \epsilon - N\epsilon. \quad (1)$$

The two potentials ϵ and $N\epsilon$ should of course be given on the same scale. By definition [Eqn. (1)] the φ -potential is independent of the reference electrode chosen.

If the steady-state potential corresponding to the corrosion process $c\epsilon$ and the potential of zero charge of the corroding metal $N\epsilon$ are known, the difference

$$c\varphi = c\epsilon - N\epsilon, \quad (2)$$

which is the potential on the φ -scale, is also a measure of the charge on the metal surface under the corrosion conditions, and is easily measured. The concept of potential of zero charge was introduced by Frumkin about 40 years ago, and these potentials have been determined experimentally for many metals. It should be emphasised that the potential of zero charge $N\epsilon$ in this case is understood to be the particular value of the potential of the uncharged

metal surface, $q=0$, observed in a solution containing no surface-active substance¹⁰. Defined in this way, the potential of zero charge is a constant characteristic of a given metal and solvent, whereas the potential of an uncharged metal surface may vary over a wide range, depending on the nature of the dissolved substances. The potentials of zero charge, unlike the potential of the uncharged surface, can be calculated theoretically from the work function.

If the metal undergoing corrosion is not uniform and the decomposition process takes place by a heterogeneous electrochemical mechanism with spatial separation of the zones of the cathodic and anodic processes, an equation of type (2) can be written for each zone. In most cases $c\epsilon$ is almost the same for the cathodic and anodic regions, since the part played by the ohmic factor in corrosion phenomena is usually small. The values of $c\varphi$, however, may differ considerably, due to the difference in the potentials of zero charge $N\epsilon$. The adsorption of substances from solution or from the gaseous phase *via* a thin film of moisture will obviously be determined by the value of $c\varphi$ and not $c\epsilon$ or the nature of the process (anodic or cathodic) taking place on the metal. Application of the φ -scale to corrosion problems thus shows the erroneous character of a widespread view regarding the nature of adsorption in corrosion processes and the mechanism of action of corrosion inhibitors. According to this view, anions and negatively-charged colloidal particles should be adsorbed on anodic regions, and cations and positively-charged colloidal particles on cathodic regions. The former are often regarded as anodic inhibitors and the latter as cathodic inhibitors. In fact, however, the preferential adsorption of cations or anions will be determined by the charge of the metal under the corrosion conditions, i.e. by the value of the $c\varphi$ -potential. As an illustration, let us examine the corrosion of Fe, Zn, and Cd in acidic solutions. The values of the corrosion potentials on the φ -scale for these metals are $-0.26 - 0.00 = -0.26$ V (Fe), $-0.75 - (-0.60) = -0.15$ V (Zn), and $-0.50 - (-0.70) = 0.20$ V (Cd).

According to these $c\varphi$ values, we should expect that the surface of corroding iron should show preferential adsorption of cationic and molecular substances, the adsorption of

† The main contents of this paper were presented at the First International Congress on the Corrosion of Metals, London, April 1961.

anions being less marked. On the surface of corroding cadmium, however, no adsorption of cations will take place, and molecular and anionic compounds should here be regarded as potential inhibitors. All compounds, irrespective of their electrical character, may be adsorbed on the surface of corroding zinc, although the slight negative charge on its surface favours the adsorption of cations to a greater extent. If it is assumed, for example, that inclusions of Tl (cathodes) are present in Zn (anodes), the values of the $\epsilon\varphi$ -potentials lead us, contrary to the widespread view, to expect preferential adsorption of cations on the anode (Zn) and of anions on the cathode, *i.e.* on the inclusions of the more noble Tl.

It should however be emphasised that completely reliable conclusions regarding the electrical character of the substances adsorbed preferentially can be reached on the basis of the value of the $\epsilon\varphi$ -potential only in the following cases.

1. When the solution contains no surface-active substances. In this case if $\varphi > 0$, surface-inactive anions will be preferentially adsorbed, and if $\varphi < 0$, surface-inactive cations will be adsorbed. This is the case in the corrosion of metals in solutions of most mineral acids and salts.
2. If the absolute value of φ is extremely high, all adsorption forces, except electrostatic forces, can be neglected, and in any solution we should expect adsorption of anions when $\varphi \gg 0$ and adsorption of cations when $\varphi \ll 0$. This appears to be the case for the corrosion of Zn and Al in alkali³.

If $\varphi = 0$, we should expect preferential adsorption of uncharged species.

In the more general case the value of the φ -potential alone cannot serve as a reliable criterion for estimating the nature of the species being adsorbed. It has been known since Gouy's time that surface-active substances can be adsorbed in appreciable quantities on a mercury surface carrying a charge of the same sign. This phenomenon has been called specific adsorption and has been interpreted as the result of non-coulombic forces of interaction between the metal and the dissolved substance predominating over the forces of electrostatic repulsion so long as the charges on the surface are not too high. At each value of the φ -potential the surface concentration of the substance will therefore be determined by the superposition of the specific adsorption forces on the electrostatic forces.

If the φ -potentials of different metals are the same, the electrostatic interaction between the metal surface and adsorbed species will be approximately the same, and forces of a specific nature will play a decisive part. There is reason to assume, however, that this specific character, if we exclude the extreme case of chemical compound formation, depends to a greater extent on the properties of the substance being adsorbed than on the nature of the metal. This is indicated by the following considerations.

1. The change in the adsorbability of most surface-active substances on a mercury surface under conditions corresponding to its potential of zero charge is parallel to the change in their adsorbability at a solution-vacuum interface¹¹.
2. Many organic compounds with clearly defined π bonding show specific adsorption on a positively charged mercury surface¹². A similar specific adsorption has been shown for the case of cadmium¹³. Some indications of an analogous effect were obtained in a study of the influence of a

number of nitrogen-containing organic compounds on the corrosion of iron in acid solutions¹⁴. In this case the specific character is evidently due primarily to the compound and not to the metal.

3. The change in the shape of the electrocapillary curve observed in the presence of surface-active substances can be described by Frumkin's equation¹⁵ or Butler's equation¹⁶. Neither of these equations contains quantities specific for mercury, and they show that for a given substance the relative change in the shape of the electrocapillary curve should be determined only by the deviation of the potential of the metal from its potential of zero charge. At equal values of φ the change in the adsorbability relative to that observed at the potential of zero charge should be independent of the nature of the metal.

Thus the introduction of the φ -scale gives a basis for using data obtained for a given metal to interpret results for other metals, and for predicting the possible influence of a surface-active substance on various electrochemical processes. Some applications designed to describe the influence of organic inhibitors on the corrosion of metals are given below.

The Possibility of Determining the Retardation Coefficient and the Rate of Corrosion of Iron from Electrocapillary Measurements on Mercury

The corrosion of iron was studied in 1 N H₂SO₄ containing different concentrations of inhibitors. This made it possible to determine the retardation coefficient $k = j_c/j'_c$, where j_c is the rate of corrosion in the original acid containing no inhibitor and j'_c the rate of corrosion at a given inhibitor concentration. The electrocapillary curves for mercury in the same solutions were then recorded and the decrements in the surface tension of mercury $\Delta\sigma$ were found at the φ -potential corresponding to the $\epsilon\varphi$ corrosion potential (as shown for the case of caffeine in Fig. 1). The corrosion potential depends on the presence of inhibitor, but these small changes were not taken into account; and in all cases we used the value of the standard potential of iron in 1 N H₂SO₄ ($\epsilon\varphi_{Fe} = -0.26$ V). The values of k were

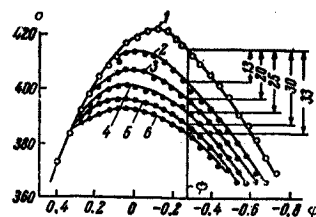


Fig. 1. Electrocapillary curves for 1 N HCl containing the following concentrations of caffeine (M): 1) 0; 2) 2.15×10^{-3} ; 3) 4.30×10^{-3} ; 4) 8.60×10^{-3} ; 5) 1.72×10^{-2} ; 6) 3.44×10^{-2} . The vertical straight line corresponds to the corrosion potential of iron in 1 N HCl, expressed on the φ -scale. The numerals on the right denote the values of $\Delta\sigma$ observed in the presence of the appropriate quantity of caffeine at $\epsilon\varphi_{Fe}$.

plotted against the corresponding values of $\Delta\sigma$. Some typical results are given in Fig. 2. For each substance studied, the plot of the retardation coefficients against surface activity ($\Delta\sigma$) is linear. These data confirm the basic principle of the method and indicate that it is possible to use results obtained for one metal (Hg) to describe the conditions of adsorption for another metal (Fe) at the same value of the φ -potential. It is evident, however, that the surface activity of a substance cannot be regarded as the only factor determining its efficiency as an inhibitor of metal corrosion. If this were the case, all substances, irrespective of their nature, should give the same retardation coefficient at a given value of $\Delta\sigma$. Fig. 2 shows that the values of k for a given value of $\Delta\sigma$, and the slopes of the plot of k against $\Delta\sigma$, are different for different substances. The quantity δ in the equation

$$k = \delta \Delta\sigma \quad (3)$$

for the two metals chosen (Hg and Fe) depends on the chemical properties of the compound. As a first approximation, however, we can regard δ as constant for similar compounds. Thus, for example, for three nitrogen-containing compounds (Fig. 2), $\log \delta = \text{const}_s$ is approximately the same and equal to -0.8 . For anthranilic acid, a compound with two functional groups, $\text{const}_s = -0.1$ (Fig. 3). In the general case

$$\log k = \text{const}_s + \log \Delta\sigma, \quad (4)$$

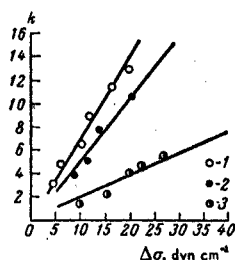


Fig. 2. Dependence of the retardation coefficient k on the decrease in surface tension $\Delta\sigma$ in 1 N H_2SO_4 containing: 1) sulphathiazole; 2) sulphidine; 3) *o*-hydroxyquinoline.

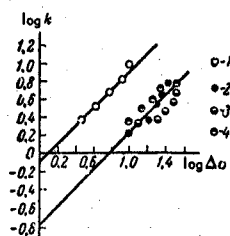


Fig. 3. Plot of $\log k$ against $\log \Delta\sigma$ for: 1) anthranilic acid; 2) *o*-hydroxyquinoline; 3) pyrimidone; 4) caffeine.

where const_s is a quantity which remains approximately the same for a group of similar substances. Eqn. (4) can be used to calculate the retardation coefficients from the value of $\Delta\sigma$, if const_s is unknown. For practical purposes it is more convenient to modify Eqn. (4) so that it includes the volume concentration of inhibitor. The experimental dependence of the retardation coefficient on the volume concentration of inhibitor c can be expressed as follows¹⁷⁻¹⁹:

$$\log k = \text{const}_k + \beta_k \log c. \quad (5)$$

According to experimental data¹⁷⁻²⁰, the dependence of $\Delta\sigma$ on c is given by the equation

$$\log \Delta\sigma = \text{const}_\sigma + \beta_\sigma \log c. \quad (6)$$

Under the conditions defined earlier, i.e. when $\varphi_{\text{Hg}} = c\varphi_{\text{Fe}}$, the quantity β_k for a given organic compound is equal to β_σ . Substituting the value of $\log \Delta\sigma$ from (6) in (4), we obtain

$$\log k = \text{const}_s + \text{const}_\sigma + \beta_\sigma \log c. \quad (7)$$

Comparison of (5) and (7) shows that

$$\text{const}_k = \text{const}_s + \text{const}_\sigma. \quad (8)$$

where const_s should be the same for any group of similar compounds. Eqn. (7) can be used to calculate the retardation coefficients k from electrocapillary measurements†. The applicability of the method is illustrated by Figs. 4 and 5 and Table 1. Fig. 4 shows that, in accordance with the above assumption, the value of const_s remains the same (-0.8) for different nitrogen-containing organic compounds. Thus the values of k for any organic compound containing nitrogen as $-\text{NH}_2$, $=\text{NH}$, or $\equiv\text{N}$ as the only functional group can be found from electrocapillary measurements alone.

Fig. 5 shows, for example, that Eqn. (7), on substitution of electrocapillary data for mercury¹⁸, describes fairly satisfactorily the values of k for the corrosion of iron in the presence of diethylamine^{21,22} and quinoline²¹⁻²⁵. Table 1

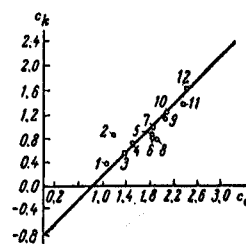


Fig. 4. Relationship between const_k and const_σ for nitrogen-containing organic compounds. 1) Piperazine; 2) diethylamine; 3) pyridine; 4) aniline; 5) quinoline; 6) di-*n*-butylamine; 7) dimethylaniline; 8) ethylaniline; 9) 2-methylquinoline; 10) diethylaniline; 11) brucine; 12) β -naphthoquinoline.

† If the rate of corrosion in the pure acid is known, we can find not only the value of k , but also the rate of corrosion for any inhibitor concentration.

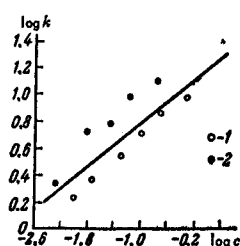


Fig. 5. Plot of $\log k$ against $\log c$ for diethylamine. The straight line was drawn in accordance with Eqn. (7). The points correspond to the experimental data of: 1) Ride; 2) Mann.

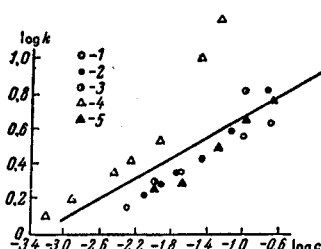


Fig. 6. Plot of $\log k$ against $\log c$ for quinoline. Straight line drawn in accordance with Eqn. (7). The points correspond to the experimental data of: 1) Ride; 2) Mann; 3) Rhodes and Kuhn; 4) Hoar and Holliday; 5) Okamoto *et al.*

TABLE 1. Comparison of the values of k found experimentally and calculated theoretically from Eqn. (7) for the corrosion of Fe in 1 N H_2SO_4 at 25°.

$10^4 c, M$	1.07	2.15	4.30	8.60	17.20	34.40
Anthranilic acid						
k_{exp}	—	2.26	3.21	4.77	6.42	0.79
k_{theor}	—	2.34	3.24	4.47	6.15	8.51
Deviation, %	—	5.3	0.9	6.3	3.9	3.2
(const _s = -0.1; const ₀ = -1.70; β_{σ} = 0.46)						
o-Hydroxyquinoline						
k_{exp}	1.65	2.42	3.80	4.55	5.43	—
k_{theor}	1.66	2.57	3.24	4.27	5.49	—
Deviation, %	0.60	6.2	13.6	6.2	1.1	—
(const _s = -0.8; const ₀ = -2.17; β_{σ} = 0.36)						
Trimethylsilylmethyl-diethylallylammonium iodide						
k_{exp}	4.17	5.22	7.95	10.44	11.98	—
k_{theor}	4.17	5.49	6.50	9.12	11.80	—
Deviation, %	0.0	5.2	18.2	12.6	1.1	—
(const _s = -0.8; const ₀ = -2.10; β_{σ} = 0.37)						

compares the experimental and calculated values of k for three different substances. The agreement is no poorer than that usually observed in the comparison of corrosion measurements.

The empirical equation (6) can be derived theoretically^{17,18} from the Gibbs adsorption formula and the Freundlich adsorption isotherm:

$$\log \Delta\sigma = \log \frac{RT}{\beta_{\sigma}} f k_{\text{Hg}} + \beta_{\sigma} \log c, \quad (9)$$

where $f k_{\text{Hg}}$ is the Freundlich constant for adsorption of mercury and $\log (RT/\beta_{\sigma}) f k_{\text{Hg}} = \text{const}_{\sigma}$ and depends on the properties of the compound.

Eqn. (5) can be obtained^{17,18} from general kinetic considerations, with the assumption that the surface of the corroding metal is equipotential, that the steady-state potential is independent of the inhibitor concentration, that the surface and volume concentrations of the inhibitor are related by the Freundlich equation, and that the exchange current with respect to hydrogen is inversely proportional to the surface concentration of inhibitor. With these assumptions, the theoretical equation can be written in the form

$$\log k = \log f k_{\text{Fe}} \gamma + \beta_k \log c, \quad (10)$$

where $f k_{\text{Fe}}$ is the Freundlich constant for adsorption on iron and γ a specific coefficient depending on the nature of the inhibitor.

Better agreement with the actual relationships can be obtained if allowance is made for the change in $c\epsilon$ with inhibitor concentration and k is compared with the values of $\Delta\sigma$ found at corresponding values of $c\epsilon$ ($c\phi$). For the present accuracy of corrosion measurements, this correction is superfluous and the theory can be used in the form of the simplified equations (9) and (10). Recently, qualitative agreement was observed between the influence of different compounds on the capacity of the electrical double layer and their behaviour as inhibitors of the corrosion of iron²⁶.

Combined Protection and the ϕ -Scale of Potentials

Use of the ϕ -scale of potentials makes it possible to suggest a new method for protecting metals from corrosion, based on the simultaneous action of inhibitors and cathodic polarisation^{5,6,27,28}. Under the influence of cathodic polarisation the potential of a corroding metal will be displaced to more electronegative values, leading to an increase in the adsorption of cations and certain polar organic molecules. The total protective effect may therefore be greater than the sum of the individual effects. Various experiments confirm this assumption. Tables 2-5 give some results obtained in a study of the combined protection of iron and zinc^{27,28}. Here it is more convenient to express the efficiency of protection not by the value of k but by the degree of protection P , defined as

$$P = \frac{\text{initial rate of corrosion} - \text{reduced rate of corrosion}}{\text{initial rate of corrosion}}, \quad (11)$$

and related to the retardation coefficient k by the equation

$$P = 1 - \frac{1}{k}. \quad (12)$$

The subscripts e , i , and m in Tables 2-5 indicate whether the protection is due to cathodic polarisation, inhibitor, or both. The quantity P_m can be regarded as

TABLE 2. Combined protection of Fe at 25°; P_e in pure acid solution = 30%.

Solution	$10^4 j_c$ A cm ⁻² ($U_e = 0$)	$10^4 j_c$ A cm ⁻² ($U_e = 1.0 \times 10^{-2}$ V cm ⁻²)	P_i , %	P_m , %	$P_i + P_e$, %	P'_i , %
1 N H ₂ SO ₄	2.60	1.80	—	—	30	—
Ditto + 5.0 g litre ⁻¹ thiourea	1.55	1.20	38	54	68	24
Ditto + 0.01 g litre ⁻¹ <i>p</i> -tolylthiourea	0.63	0.11	77	95	107	65
Ditto + 0.1 g litre ⁻¹ anthranilic acid	2.37	2.02	9	25	39	—5
Ditto + 1.0 g litre ⁻¹ tetrabutylammonium sulphate	1.99	0.40	23	85	53	55
Ditto + 0.1 g litre ⁻¹ tribenzylamine	1.22	0.00	53	100	83	70

TABLE 3. Combined protection of Fe at high temperatures; P_e at 40° = 22%; P_e at 60° = 10%.

Solution	$10^4 j_c$, A cm ⁻²		P_i , %	P_m , %	$P_i + P_e$, %	P'_i , %
	$j_e = 0$	$j_e = 9.0 \times 10^{-4}$ A cm ⁻²				
1 N HCl						
40°	8.3	6.5	—	—	22	—
60°	22.6	20.3	—	—	10	—
1 N HCl + 1.0 g litre ⁻¹ quinoline						
40°	3.3	1.1	60	87	82	65
60°	10.6	7.5	54	67	64	57
1 N HCl + 0.5 g litre ⁻¹ <i>o</i> -hydroxyquinoline						
40°	4.0	2.1	52	77	73	55
60°	14.3	9.0	37	62	47	52
1 N HCl + 0.1 g litre ⁻¹ tribenzylamine						
40°	3.2	0.9	61	89	83	67
60°	6.7	4.1	70	82	80	72

TABLE 4. Combined protection of Fe in neutral solutions (artificial seawater) at 25°.

Solution	$j_e = 0$	$j_e = 8.0 \times 10^{-4}$ A cm ⁻²			
	P_i , %	P_e , %	P_m , %	$P_i + P_e$, %	P'_i , %
Salt solution	—	39.7	—	39.7	—
Ditto + 1.0 g litre ⁻¹ caffeine	0	—	92.4	39.7	52.7
Ditto + 1.0 g litre ⁻¹ ethylammonium benzoate	0	—	60.0	39.7	20.3

TABLE 5. Combined protection of Zn in 1 N H₂SO₄ at 25°. Inhibitor: 0.1 g litre⁻¹ tribenzylamine; $P_i = 48\%$.

j_c , A cm ⁻²	0.00	2.0×10^{-3}	2.0×10^{-2}	3.0×10^{-2}	3.4×10^{-2}	9.0×10^{-2}
j_c , A cm ⁻²	$1.28 \cdot 10^{-1}$	$1.26 \cdot 10^{-1}$	$1.02 \cdot 10^{-1}$	$0.82 \cdot 10^{-1}$	$0.75 \cdot 10^{-1}$	0.00
j'_c , A cm ⁻²	$0.66 \cdot 10^{-1}$	$0.62 \cdot 10^{-1}$	$0.30 \cdot 10^{-1}$	$0.75 \cdot 10^{-2}$	0.00	—
P_e , %	—	1.6	25.5	35.9	41.21	100
P_m , %	—	51.0	76.5	93.8	100.0	—
$P_i + P_e$, %	48	49.6	73.5	83.9	89.4	—
P'_i , %	—	49.4	51.0	57.9	58.6	—

the sum of P'_i and P'_e , attained under conditions of combined protection

$$P_m = P'_i + P'_e. \quad (13)$$

In some cases it is more convenient to assume that only one of the quantities changes under the combined protection conditions. Thus in Tables 2–5 the values of P'_i were calculated on the assumption that P'_e is independent of the presence of inhibitor, i.e. that $P'_e = P_e$.

Table 2 shows that, in agreement with theory, the effect of combined protection is a maximum when surface-active cations (tetrabutylammonium sulphate and tribenzylamine) are used as inhibitors. In this case P'_i is always greater than the corresponding value of P_i and $P_m > P_i + P_e$. On the other hand, the ability of anions to protect iron from corrosion (thiourea) decreases when cathodic polarisation is applied ($P'_i < P_i$ and $P_m < P_i + P_e$). Cathodic polarisation has only a slight effect (a decrease) on the inhibiting action of molecular substances of a slightly predominant anionic character, such as *p*-tolylthiourea. The anomalous behaviour of anthranilic acid (the negative value of P'_i) must be due to secondary effects, probably involving an increase in the surface area of iron.

The efficiency of ordinary cathodic protection decreases sharply with increase in temperature (Table 3), but the efficiency of the combined protection depends little on temperature and remains fairly high at higher temperatures.

Particularly interesting results were obtained in a study of the corrosion of iron in neutral solutions²⁹. It was found (Table 4) that organic substances which have no corrosion-inhibiting action in neutral solutions become effective when a sufficiently high external current is applied. This sudden change in behaviour can be attributed to the fact that the diffusion limitations (oxygen supply) typical of the corrosion of iron in neutral solutions are replaced by limitations determined by the kinetics of hydrogen liberation when cathodic polarisation is applied. The adsorbed species of the organic substance, covering only a relatively small proportion of the surface, cannot change the rate of diffusion[†]. Their influence on the anodic dissolution of the metal cannot be detected under these conditions until the rate constant of the anodic dissolution becomes greater than the rate of diffusion. The picture changes significantly, however, when kinetic limitations predominate, and the organic compound, by influencing the anodic dissolution of the metal and the cathodic formation of hydrogen, begins to act as an inhibitor.

Iron is not the only metal which can be successfully protected by the simultaneous action of cathodic polarisation and an inhibitor. The protection of zinc, for example, is more effective when cathodic polarisation is combined with the use of inhibitors[†] (Table 5). No change in the weight of a zinc specimen could be observed in an experiment at a current density of 3×10^{-2} A cm⁻² in a solution containing 0.1 g litre⁻¹ of tribenzylamine. In pure acid solution the corresponding current density was three times greater. In

§ The electrical nature of the organic substances was assessed from the corresponding electrocapillary curves.

† This apparently also explains the fact that many organic compounds, despite their ability to decrease the capacity of the electrical double layer on mercury, are quite ineffective as inhibitors of the corrosion of iron in NaCl solution²⁶.

† A similar observation was made by Machu³¹, who gave no data, however, on the nature of the inhibitor or the values of the polarisation current.

accordance with theory, an increase in P_i' for the cationic compound chosen is observed with increase in the current density.

Further independent confirmation of the efficiency of combined protection was given by Rajagopalan and Row³², who used a Hall cell.

The above results were explained on the assumption that the adsorbability changes with potential. Other explanations may be given, however, and some of these are considered below.

1. The increase in the efficiency of inhibitors, observed under the influence of cathodic polarisation, can be related to the decrease in the rate of dissolution of the metal. As a result of this decrease the adsorbed species will have more time and greater opportunity for forming a strong bond with the metal surface and producing a more complete covering layer. This possibility cannot be excluded completely, particularly for organic substances with large molecules and a low rate of adsorption, but it cannot by itself explain many of the experimental facts. For example, it is difficult on this basis to understand the difference in the behaviour of cationic, anionic, and molecular substances, the fact that the temperature dependence of k is only slight, etc.

2. It may be suggested that the change in the pH of the solution close to the corroding metal, produced by the external current, will be revealed in different ways, depending on the nature of the inhibitor. There are some grounds for this explanation, if we consider the action of inorganic inhibitors on corrosion in neutral media^{33,34}, but it can hardly apply to acidic solutions, where the pH does not change appreciably under the influence of a small external current. This explanation is also unlikely for neutral solutions containing organic inhibitors which do not give insoluble compounds with OH^- ions.

3. External cathodic polarisation may lead to partial reduction of surface oxides and thus change the conditions of adsorption of organic compounds. This factor, which does not explain the difference in the behaviour of different organic substances, cannot be decisive, although it may play some part in cathodic protection. Moreover, it follows from tabulated data (Table 6) that the effect of combined protection is slightly greater when an oxide film is present. The complete or partial reduction of oxides cannot therefore be the reason for the increased efficiency of combined protection.

Thus the action of organic inhibitors under the conditions of combined protection should be attributed chiefly to their adsorption, which changes with change in potential. The adsorbed species of inhibitor do not form a compact covering layer and do not change the diffusion conditions (see results obtained for neutral solutions). They cannot create an appreciable ohmic resistance. The inhibiting action of adsorbed organic substances must be related to their influence on the kinetics of the electrochemical reactions involved in corrosion. This can be illustrated by the corrosion diagram (Fig. 7) drawn on the assumption that a semilogarithmic function of the Tafel type applies both to the anodic dissolution of metal and to the cathodic liberation of hydrogen. The diagram is based on the Frumkin-Wagner-Shul'tin theory of electrochemical corrosion and represents the acidic corrosion of metals such as iron. Fig. 7 indicates that the current necessary for any given degree of protection should decrease when inhibitor is added, in accordance with its influence on the cathodic and anodic

TABLE 6. Combined protection of bright and oxidised specimens of iron at 25° in artificial sea water containing 0.5 g litre⁻¹ dextrin.

$10^6/i_c$, A cm ⁻²	Bright Iron	Oxidised Iron
4	37.4	37.5
6	59.5	61.0
8	89.3	90.5

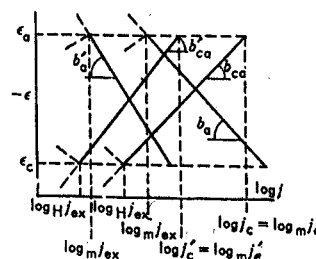


Fig. 7. Corrosion diagram for the application of an external current, given in semilogarithmic coordinates for pure acid solution (right) and for the same solution containing inhibitor (left); j_c , H/ex , m/ex , m/e , and ϵ_c denote respectively the rate of corrosion, the hydrogen exchange current, the metal exchange current, the current necessary for complete cathodic protection, and the corrosion potential in the acid solution. The same symbols marked with primes refer to the solution containing inhibitor.

polarisation. The relationships are simplified considerably if we restrict ourselves to the case of complete protection³⁵. The current ensuring complete protection can be defined³⁶ as the current necessary to displace the potential of the metal to a value corresponding to the equilibrium potential of the anodic process. It is evident that for the case of complete protection, the effect of the kinetics of dissolution of the metal becomes insignificant, since according to definition the metal is under equilibrium conditions and the resulting rate of dissolution should be zero. Thus the relationships corresponding to complete protection should be determined only by the kinetics of liberation of hydrogen and should be independent of the mechanism of anodic dissolution of the metal. For this particular case, the diagram in Fig. 7 can also be applied to metals whose anodic dissolution does not obey the Tafel formula, for example zinc. From the diagram we obtain the equation

$$m/e' = m/e \cdot \frac{j_c' a_{ca}/b_{ca}'}{H/ex' b_{ca}/b_{ca}'} \quad (14)$$

or

$$m/e' = m/e \cdot \frac{j_c' a_{ca}/a_{ca}'}{H/ex' a_{ca}/a_{ca}'} \quad (15)$$

where mje is the current necessary for complete protection, Hj_{ex} the hydrogen exchange current, b_{ca} the slope of the cathodic polarisation curve, α_{ca} a kinetic factor ($b_{ca} = 2.3RT/2\alpha_{ca}F$), and the prime refers to solutions containing inhibitor. Under the influence of inhibitor Hj_{ex} usually decreases, but the change in α_{ca} (b_{ca}) depends on the type of inhibitor. For surface-active cations $\alpha'_{ca}/\alpha_{ca} < 1$ ($b'_{ca}/b_{ca} < 1$) and the effect of cathodic polarisation is a maximum if an inhibitor of this type is used for the combined protection of metals. For many molecular organic substances, the ratio α'_{ca}/α_{ca} is close to unity, and the efficiency of combined protection is determined by the change in the hydrogen exchange current under the influence of the added inhibitor:

$$mje' = mje \frac{Hj_{ex}'}{Hj_{ex}} \quad (16)$$

CONCLUSION

1. The determination of the relationship between the electrocapillary data obtained on mercury and the results of corrosion measurements made on iron has been made possible only by the introduction of the φ -scale of potentials, based on the corresponding potentials of zero charge for the metals. The results depend on the reliability of the known values of $N\epsilon$. The potential of zero charge for mercury, determined by different methods, always lies between -0.19 V and -0.21 V on the hydrogen scale, i.e. the difference does not exceed 0.02 V. The values of $N\epsilon$ for iron, found from the position of the minimum on the plot of differential capacity against potential, differ from the values used in the present paper by 0.2–0.3 V. Birintseva and Kabanov³⁷ have shown, however, that this method cannot be used for metals whose surface is covered by adsorbed hydrogen³⁸. The values of $N\epsilon$ found in this way must therefore be regarded as incorrect. The potentials of zero charge for Zn, Cd, and Tl, used in the present work, were determined to about ± 0.05 V. An accuracy of 0.1 V is quite sufficient for even the quantitative application of the method described in the present work, although the error in the determination of $N\epsilon$ should be of greater significance when the adsorption of charged species is considered.

2. For two given metals, the values of $const_s$, determined by Eqns. (7) and (8), depend on the nature of the functional group and remain approximately the same for a series of similar organic compounds. At present $const_s$ has been determined fairly accurately only for amines, although it can also be found for other substances. The values of $const_s$ may serve as a basis for a theoretical approach to an intensive but as yet predominantly empirical choice of efficient inhibitors. This method is not restricted to any definite type of inhibitor and can be applied to any substances, so long as their action involves adsorption on the surface of the corroding metal. It should also be applicable to the study of industrial inhibitors of unknown composition, for example to find the optimum content of an industrial inhibitor and to establish the nature of its active ingredient.

3. In recent years the principles on which the method is based have been used by a number of authors. Thus in 1957 De³⁹ explained the behaviour of a number of inhibitors in terms of the potentials of zero charge of Hg and Fe and data obtained by electrocapillary measurements, as was done by the present author in 1951–1954. Although this paper was highly praised by Gatos⁴⁰, it contains a number

of unsatisfactory features. Without making a detailed criticism of De's work, it must be pointed out that the action of inorganic anions as inhibitors of the corrosion of iron in neutral media is due primarily to their ability to oxidise the iron surface, and cannot be related to simple adsorption. Blomgren and Bockris⁴¹ undertook certain studies because "there is apparently no information on the degree of adsorption of organic ions as a function of the potential and, particularly, the structure of organic groups" (Ref. 41, p. 1475). In fact, however, information of this type is available^{17,18} and electrocapillary curves covering a wide range of potentials and concentrations have been described for many organic ions, including four of the six compounds studied by Blomgren and Bockris. The main conclusion reached by these authors, namely that there is a parallelism between the adsorption of aromatic amines on mercury and their ability to decrease the rate of corrosion of iron, is not new. It was presented, in a more general form, in a report¹⁹ at the Conference on Electrochemistry in Moscow in 1956¹⁷, and one of the authors cited⁴¹ (Bockris) even took part in the discussion⁴² of the report. In connection with Blomgren and Bockris' articles, it should be noted that the parallelism which they mention is shown sufficiently rigorously only if the adsorption is measured at a φ -potential of mercury equal to the $c\varphi$ -potential of the corroding iron, but this important feature was not noted. Nevertheless, Blomgren and Bockris' work is of considerable interest, particularly the application of a modified Langmuir equation to describe the adsorption of organic substances.

4. The inhibitors most suitable for the combined protection of metals can be found on the basis of electrocapillary and polarisation measurements. As shown above, there are grounds for assuming that the most effective inhibitors in acidic and possibly in neutral solutions should be organic cations. The use of organic cations as inhibitors in combined protection, apart from its high efficiency, also has the advantage that their presence decreases the degree of absorption of hydrogen by the metal^{43–45}.

5. The efficiency of combined protection has been explained as follows: when cathodic polarisation is applied, the φ -potential of the corroding metal is displaced to more negative values, so that the adsorption of organic cations and certain organic molecular substances is facilitated. Under the conditions of combined protection this change in the φ -potential results from the displacement of the ϵ -potential of the corroding metal towards more negative values. Since $\varphi = \epsilon - N\epsilon$, an analogous effect may be attained if the value of $N\epsilon$ for the corroding metal is made more positive. This probably explains the increase in the inhibiting activity of organic cations and certain organic unionised substances in air compared with that in an inert gas. A similar explanation can apparently be given for the favourable effect of halides and certain other anions on the inhibiting power of a number of organic compounds^{44,46}.

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KINETICS OF DISSOLUTION OF METALS IN NITRIC ACID

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Knowledge of the relation between the kinetic and thermodynamic characteristics of the dissolution of metals in acids permits a deeper understanding of its mechanism. Thus it is known¹ that the kinetics of dissolution in hydrochloric acid of metals with a normal electrode potential more negative than -0.75 V are determined by diffusional factors whereas those of metals with a normal electrode potential more positive than -0.75 V are determined by chemical factors. Aluminium is an exception to this rule⁴. Dissolution is considerably facilitated by addition of an oxidising agent to the acid. For most metals diffusion of the oxidising agent is the rate-limiting stage⁵⁻⁷. The retardation of the evolution of hydrogen from acids is determined by the specific features of the action of both the proton and the oxidising agent.

In the present work an attempt is made to establish relations of this kind for the dissolution of metals in nitric acid. The Table lists the dissolution rates, whenever possible for 1 N unstirred nitric acid at similar temperatures, together with the activation energies E_a and the pre-exponential factors C_e . Although the rates of dissolution have been determined by different workers under somewhat different conditions, they are comparable to within a factor of 10.

The Figure shows a plot of the logarithms of the rates of dissolution against the normal potentials of the metals taken from Ref. 9; germanium, for which there is no tabulated value, lies between copper and silver¹⁰. The plot has the same shape as the potential-current curves for the anodic dissolution of metals, with a distinct limiting current region characteristic of the diffusional mechanism of the process. The Figure shows that for metals lying to the left of thallium in the potential series diffusion is the rate-limiting stage. This is in good agreement with the values of E_a and the nature of the relation between the rate of dissolution and stirring indicated in the Table. For dissolution of metals in hydrochloric acid the boundary between diffusional and chemical kinetics in the potential series occurs in the neighbourhood of zinc, and for dissolution in nitric acid to the right of thallium. This means that the interaction with acids of metals lying to the right of zinc in the potential series involves direct reduction of the acid by the metal. For electropositive metals this is