

1-1-1999

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Recommended Citation

ZOR, SİBEL; YAZICI, B.; and ERBİL, M. (1999) "The Effects of Detergent Pollution on the Corrosion of Iron and Aluminium," *Turkish Journal of Chemistry*. Vol. 23: No. 4, Article 6. Available at: <https://journals.tubitak.gov.tr/chem/vol23/iss4/6>

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The Effects of Detergent Pollution on the Corrosion of Iron and Aluminium

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Received 25.08.1997

The current-potential values were measured with iron or aluminium electrodes in solutions of 3.5 % NaCl containing 30, 150, 300 ppm linear alkylbenzene (LAB) and detergents (LAS) at pH8. Polarization resistances (R_p) were determined using the values of current and potentials. The corrosion rates of iron and aluminium were determined in 2 and 4 hour intervals using the Mansfeld-Oldham equation based on the Stern-Geary and Butler-Volmer equations.

Introduction

Corrosion of metals depends on the kind of metal and the prevailing conditions in the medium (temperature, pH, pressure, concentration, etc.) as well as the type of ions such as CO_3^{2-} , NO_3^- , Cl^- and NO_2^- present in the medium. It will be useful to briefly discuss the effects of some ions on metals.

The ions mentioned above have different effects on metals. For example, CO_3^{2-} is adsorbed on the metal surface and produces insoluble carbonates with iron. As a result, the metal is isolated from the medium and corrosion is prevented¹. Having an oxidizing character, NO_3^- increases the dissolution of the metal, and the protective effect of the oxide phase which is formed, similar to the effect of carbonate precipitations, decreases the corrosion².

On the other hand, ions such as Cl^- , Br^- and F^- which are adsorbed selectively on the metal surface, prevent the formation of the oxide phase on the metal surface, thus allowing continuous corrosion on the naked surface¹⁻¹⁰. The chloride ion produces metal chlorides in stationary parts of the metal and corrosivity of the medium increases as a result of hydrolysis. In short, chloride ions increase corrosion on many metals⁶⁻¹⁰. It is claimed that nitro compounds or nitrite ions adsorbed on metal surfaces decrease the free energy of the system, thus inducing the onset of passivity³.

Organic substances as well as inorganic ones affect the corrosion rate. It is claimed that if organic molecules have groups like -OH, -CHO, -COOH, -CN, -SCN, -CO, -NH₂, -SO₃, double or triple bonds or unpaired electrons, the substance and the metal interact easily, and changing the zero charge potential, an effective protection is provided^{2,11}.

Iron, aluminium and their alloys are the most useful materials in industry and for domestic needs. Their corrosive behaviour has been investigated for a long time^{1-11,16-27}. In domestic usage and in industry, linear alkylbenzene (LAB) and linear alkylbenzene sulfonate (LAS) are also widely used as detergents. They are found together in waste water¹²⁻¹⁵. It is claimed that LAB and LAS act as inhibitors for stainless steel and aluminium²⁷⁻³¹.

In this study, the effects of the organic molecules like linear alkylbenzene (LAB), which is a raw material of detergents and has surface active properties, and linear alkylbenzene sulfonate which is formed by the sulfonation of LAB, on metals were investigated.

In order to determine the corrosion rates of ferrous and aluminium containing materials caused by linear alkylbenzene (LAB) and detergent (LAS) at various concentrations in a 3.5 % NaCl solution, the measured polarization resistances (R_p) and current-potential (I-E) values were used. Then, applying the method presented by Mansfeld and Oldham, the results were evaluated. To obtain a fast result from the corrosion tests, it has been worked at the concentration of LAB and LAS a little higher than the natural environment.

Experimental

In order to determine the polarization resistances, a high purity iron bar, (99.9 % Fe Armco Iron) 1.2 cm in diameter was used as the working electrode. The iron bar was first kept in citric acid adjusted to a pH value of 4.5 (by means of concentrated NH_3) for 2 hours to clean it. Then it was put in polyester die excluding the surface which would be in contact with the electrolyte. Similarly, an aluminium bar was used as the aluminium electrode. The contact area of the aluminium electrode with the electrolyte was $1.5 \times 1.5 \text{ cm}^2$, and the remaining part of the electrode was covered with polyester similar to the iron electrode. The open surface of the electrodes was shined with DAP-8 Struers slender using emery paper (500 and 800 grit size).

The solutions of 3.5 % NaCl containing 30, 150, 300 ppm LAB and detergent were prepared in advance. The solution was put in a beaker of 500 ml and the pH was adjusted to 8. The iron electrode or aluminium electrode reference electrode (saturated calomel electrode, SCE) and platinum electrode, as the auxiliary electrode, were placed in the solution, thus forming a corrosion cell. The reference electrode was brought close to the working electrode by means of a lugin capillary. The corrosion cell was then connected to a Corrovit and two measurements with 2 and 4 hour intervals were conducted. During the experiment the solution was stirred by a magnetic stirrer continuously revolving at the same speed.

First the corrosion potential (E_{cor}) was determined with the Corrovit. After reaching a stable value for this potential, 1.25, 2.5, 5.0, 12.5 and 25.0 mV potentials were applied to the electrode. The anodic and cathodic current values corresponding to these potentials were measured. These measurements were carried out two or three times for every pollutant concentration. Average currents for each potential were calculated, and a current-potential (I-E) curve was drawn. R_p values for anodic and cathodic branches were calculated from the slope of the curves. From these R_p values the corrosion rate (I_{cor}) was determined by the method developed by Mansfeld and Oldham⁵.

Results

The time variations of corrosion potentials (E_{cor}), polarization resistances (R_p) and corrosion rates (I_{cor}) of iron and aluminium in 3.5 % NaCl solutions with an initial pH of 8 and containing 30, 150, 300 ppm LAB

are shown in Table 1a. The corrosion potentials of iron in 3.5 % NaCl solution containing 30, 150 and 300 ppm LAB with pH=8 shifted to more positive values compared with the potentials in 3.5 % NaCl solution (Table 1a). For example while the E_{cor} values measured at the end of 2 and 4 hours for iron in 3.5 % NaCl solution were -618 mV and -659 mV respectively, these values were -569 and -594 mV in 3.5 % NaCl solution containing 30 ppm LAB for the same time intervals.

The polarization resistances (R_p) of iron in 3.5 % NaCl solutions containing 30, 150, 300 ppm LAB increased by increasing concentration, as shown in the third column of Table 1a. These values decreased with time for every concentration. The corrosion rate of iron in 3.5 % NaCl solution containing 30, 150 and 300 ppm LAB decreased with the increasing concentration of LAB compared with 3.5 % NaCl solutions (Table 1a). Corrosion rates of the iron in 3.5 % NaCl in the first 2 and 4 hours were 130×10^3 and 206.7×10^{-3} mA/cm² respectively, while the values for 3.5 % NaCl solution containing 30 ppm LAB decreased 7.27×10^{-3} and 6.9×10^{-3} mA/cm². A similar decrease in corrosion rates was also observed in other concentrations.

There was no significant difference between the corrosion potential of aluminium in 3.5 % NaCl solution containing 30, 150, 300 ppm LAB with the corrosion potential in 3.5 % NaCl solution, as shown in the second column of Table 1a. The variation interval of the corrosion potential was generally between -860 mV and -986 mV.

The polarization resistance of the aluminium in 3.5 % NaCl solutions containing 30, 150 and 300 ppm LAB increased with the increasing concentration. However, the increase in polarization resistance was generally time-independent (Table 1a). For example, the polarization resistance (R_p) in 3.5 % NaCl solution containing 30 ppm LAB in the first 2 and 4 hours was $3.865 \times 10^3 \Omega$ and $3 \times 10^3 \Omega$, respectively (Table 1a).

Table 1. The Time Variation of Iron and Aluminium Corrosion Potentials (E_{cor}), Polarization Resistances (R_p) and Corrosion Rates (I_{cor}) in 3.5 % NaCl Solutions Containing 30, 150 and 300 ppm LAB with on Initial pH Value of 8 and in 3.5 % NaCl Solution.

Time h		Fe E_{cor} , mV	Al E_{cor} , mV	Fe R_p (Ω)	Al R_p (Ω)	Fe I_{cor} mA/cm ²	Al I_{cor} mA/cm ²
120	3.5% NaCl	-618	-879	$0.15 \cdot 10^3$	$12.4 \cdot 10^3$	$130 \cdot 10^3$	$13.47 \cdot 10^{-3}$
240	3.5% NaCl	-659	-986	$0.168 \cdot 10^3$	$4.17 \cdot 10^3$	$206.7 \cdot 10^{-3}$	$24.98 \cdot 10^{-3}$
120	3.5% NaCl+30 ppm LAB	-569	-949	$0.353 \cdot 10^3$	$3.86 \cdot 10^3$	$73.8 \cdot 10^{-3}$	$8.4 \cdot 10^{-3}$
240	3.5% NaCl+30 ppm LAB	-594	-921	$0.267 \cdot 10^3$	$3.9 \cdot 10^3$	$73.15 \cdot 10^{-3}$	$6.68 \cdot 10^{-3}$
120	3.5% NaCl+150 ppm LAB	-498	-889	$3.47 \cdot 10^3$	$4.58 \cdot 10^3$	$7.47 \cdot 10^{-3}$	$4.26 \cdot 10^{-3}$
240	3.5% NaCl+150 ppm LAB	-567	-885	$1.7 \cdot 10^3$	$4.47 \cdot 10^3$	$10.2 \cdot 10^{-3}$	$4.37 \cdot 10^{-3}$
120	3.5% NaCl+300 ppm LAB	-517	-861	$3.07 \cdot 10^3$	$8.71 \cdot 10^3$	$7.27 \cdot 10^{-3}$	$2.99 \cdot 10^{-3}$
240	3.5% NaCl+300 ppm LAB	-535	-861	$2.83 \cdot 10^3$	$7.89 \cdot 10^3$	$6.8 \cdot 10^{-3}$	$2.79 \cdot 10^{-3}$

The corrosion rate of aluminium in 3.5 % NaCl solutions containing 30, 150 and 300 ppm LAB decreased with time and concentration compared with the corrosion rates in 3.5 % NaCl. For example, corrosion rates of aluminium in 3.5 % NaCl in the first 2 and 4 hours were 13.47×10^{-3} mA/cm² and 24.98×10^{-3} mA/cm², respectively while the corrosion rates of the aluminium in 3.5 % NaCl solution

containing 30 ppm LAB were 8.4×10^{-3} mA/cm² and 6.68×10^{-3} mA/cm².

The time variation of the corrosion potentials (E_{cor}) of iron polarization resistances (R_p) and corrosion rates (I_{cor}) in 3.5 % NaCl containing 30, 150 and 300 ppm detergent with an initial pH value of 8 are shown in Table 1b.

Table 1b. The Time Variation of Iron and Aluminium Corrosion Potentials (E_{cor}), Polarization Resistances (R_p) and Corrosion Rates (I_{cor}) in 3.5 % NaCl Solutions Containing 30, 150 and 300 ppm Det (LAS) with an Initial pH Value of 8 and in 3.5 % NaCl Solution.

Time h		Fe E_{cor} mV	Al E_{cor} mV	Fe R_p (Ω)	Al R_p (Ω)	Fe I_{cor} mA/cm ²	Al I_{cor} mA/cm ²
120	3.5% NaCl	-618	-	$0.15 \cdot 10^3$	-	$130 \cdot 10^{-3}$	-
240	3.5% NaCl	-659	-	$0.168 \cdot 10^3$	-	$206.7 \cdot 10^{-3}$	-
120	3.5% NaCl+30 ppm LAS	-625	-	$0.29 \cdot 10^3$	-	$77 \cdot 10^{-3}$	-
240	3.5% NaCl+30 ppm LAS	-612	-	$0.26 \cdot 10^3$	-	$65.8 \cdot 10^{-3}$	-
120	3.5% NaCl+150 ppm LAS	-596	-	$1.01 \cdot 10^3$	-	$22.1 \cdot 10^{-3}$	-
240	3.5% NaCl+150 ppm LAS	-606	-	$1.14 \cdot 10^3$	-	$17.2 \cdot 10^{-3}$	-
120	3.5% NaCl+300 ppm LAS	-606	-	$0.892 \cdot 10^3$	-	$14.6 \cdot 10^{-3}$	-
240	3.5% NaCl+300 ppm LAS	-611	-	$1.035 \cdot 10^3$	-	$15.42 \cdot 10^{-3}$	-

There was no significant difference between the corrosion potentials of iron in 3.5 % NaCl solution containing 30, 150 and 300 ppm detergent with pH=8 and in 3.5 % NaCl solution. Corrosion potentials, shown in the table, varied between -590 mV and -660 mV (Table 1b).

The polarization resistances of the 3.5 % NaCl solutions containing 30, 150 and 300 ppm detergent increased slightly with time, as shown in Table 1b. Polarization resistances also increased with increasing concentration. Corrosion rates generally decreased with time and increasing concentration of detergent. For example, corrosion rates of the iron in 3.5 % NaCl solution containing 30 ppm detergent in the first 2 and 4 hours were 77×10^{-3} and 66.8×10^{-3} mA/cm², respectively. It is also possible to observe similar values for other concentrations from the table. Due to the aluminium electrode surface being unstable, no measurements could be carried out in 3.5 % NaCl solution containing 30, 150 and 300 ppm detergent.

The Method Used to Evaluate the Experimental Results

In order to determine the corrosion rates, various methods are used. In the polarization resistance method, the Stern-Geary equation is utilized to determine the corrosion rate.

$$I_{cor} = B \cdot R_p^{-1} = B \left(\frac{dI}{dE} \right)_{E_{cor}} \quad (1)$$

where R_p is the polarization resistance, and B is a constant depending on anodic (b_a) and cathodic (b_c) Tafel slopes. B is defined as,

$$B = \frac{b_a \cdot b_c}{2.3(b_a + b_c)} \quad (2)$$

For the situations where B can not be determined accurately Oldham and Mansfeld have developed a new method using the Butler-Volmer equation to determine the corrosion rates precisely (5). According to this method, the Butler-Volmer equation can be rewritten depending on the Tafel constant, as shown below:

$$I = I_{cor} \left\{ \exp \frac{2.3(E - E_{cor})}{b_a} - \exp \frac{2.3(E - E_{cor})}{b_c} \right\} \quad (3)$$

where I_{cor} is corrosion current, E_{cor} is corrosion potential, b_a is anodic Tafel constant, and b_c is the cathodic Tafel constant. Combining equations (1), (2), (3) and rearranging, equation (4) is obtained.

$$2.3R_p I = \frac{b_a \cdot b_c}{b_a + b_c} \left\{ \exp \left(\frac{2.3\Delta E}{b_a} \right) - \exp \left(\frac{2.3\Delta E}{b_c} \right) \right\} \quad (4)$$

In this method, introduced and developed by Mansfeld and Oldham, the determination of the corrosion rate consists of four steps where Eq. (1) and (3) form the base. These steps are as follows:

- 1) Polarization resistances (Rp) for each concentration are calculated utilizing current-potential curves.
- 2) Using experimental Rp values and current values corresponding to applied potentials, experimental 2.3 RpI values are determined.
- 3) Theoretical 2.3 RpI values are calculated by equation (4). In Eq. (4) ΔE is the experimentally applied potential and b_a and b_c are theoretical Tafel constants (Table 2).

Table 2. Theoretical Tafel constants used in calculations.

b_a (mV)	30	40	60	90	120	240
	60	90	90	90	90	90
b_c (mV)	90	60	60	60	60	60
	120	120	120	120	120	120

Table 3. Theoretical and Experimental 2.3 RpI values for the iron electrode in 3.5 % NaCl solution containing 30 ppm LAB with pH=8.

	Anodic Branch					Cathodic Branch				
3.5 % NaCl+ 30 ppm LAB	1.25 mV	2.5 mV	5.0 mV	12.5 mV	25.0 mV	1.25 mV	2.5 mV	5.0 mV	12.5 mV	25.0 mV
Experimental 2.3 RpI	2.64	5.96	11.92	29.14	56.3	-3.37	-6.37	-12.7	-31.11	-61.85
Theo. $b_a=120$ mV 2.3 RpI $b_c=90$ mV	2.89	5.71	11.31	27.9	55.64	-2.89	-5.71	-11.31	-27.9	-55.64
Theo. $b_a=240$ mV 2.3 RpI $b_c=90$ mV	2.88	5.76	11.50	28.81	57.55	-2.88	-5.76	-11.5	-28.81	-57.55

- 4) Experimentally determined 2.3 RpI values are compared with the theoretically calculated 2.3 RpI values, in order to determine the closest ones to each other. In spite of the large margins of error involved in the selection of the theoretical 2.3 RpI values, we tried to select the theoretical values closest to the experimental ones. b_a and b_c values used in calculating theoretical 2.3 RpI values are determined. These b_a and b_c values are substituted in Eq. (1), and I_{cor} is calculated.

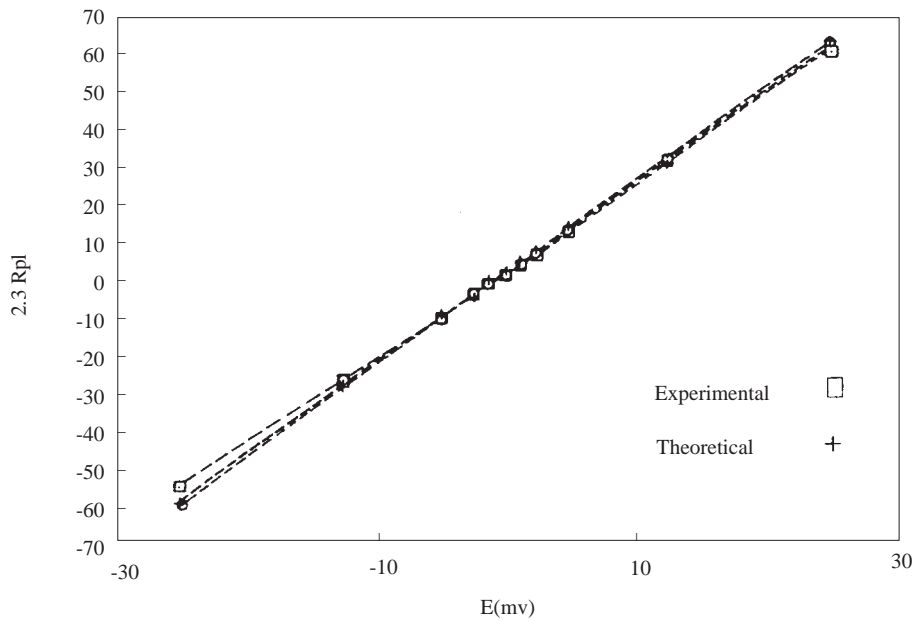


Figure 1. The variation of the experimentally calculated (□) 2.3 RpI and theoretical (+) with potential in the Fe/3.5 % NaCl + 30 ppm LAB system.

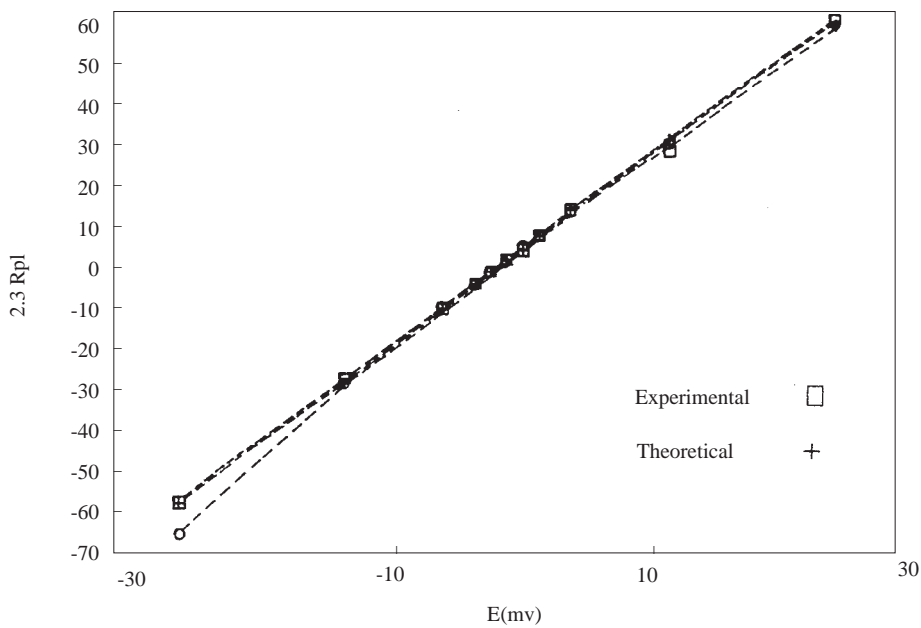


Figure 2. The variation of the experimentally calculated (□) and theoretical (+) 2.3 RpI values with potential in the Al/3.5 % NaCl + 30 ppm LAB system.

When the experimental 2.3 RpI values calculated by measuring current values corresponding to the applied potentials are compared with the theoretically determined 2.3 RpI values, it is seen that there is no significant variation. Some theoretical and experimental 2.3 RpI values are given in Table 3.

Theoretical and experimental results for other concentrations show a variation also in a similar interval.

In Fig. 1 the variation of experimental and theoretical 2.3 RpI values with potential is shown for the iron electrode in 3.5 % NaCl solution containing 30 ppm LAB. It is seen that theoretical and experimental 2.3 RpI values change in the same interval. A variation similar to that in Fig. 1 is also observed in Fig.2. In Fig. 2, the variation of the experimental and theoretical 2.3 RpI values for the aluminium electrode in 3.5 % NaCl solution containing 30 ppm LAB with potential is shown.

Discussion and Conclusions

Applying the method developed by Mansfeld and Oldham to the results obtained, it is seen that the corrosion rate of iron in 3.5 % NaCl solution containing 30, 150 and 300 ppm LAB with pH=8 decreased with time and concentration (Table 1a). As the concentration increased the corrosion potential (E_{cor}) shifted to more positive values, the polarization resistance (Rp) increased also.

The increase in the polarization resistance is possibly due to the film of active substance and corrosion products covering the surface of the electrode. In accordance with the Stern-Geary equation, the increase in polarization resistance causes a decrease in the corrosion rate. According to the results obtained, it can be stated that the corrosion rate decreases with time and concentration as a result of the adsorption of the LAB molecules on the electrode surface. This result is also supported by the values obtained with weight loss measurements¹¹.

The corrosion rate of iron in 3.5 % NaCl solutions containing 30, 150 and 300 ppm detergent (LAS) generally decreased with increasing concentration (Fig. 1b). This was probably due to the adsorption of the LAS molecules in the detergent on the metal surface, or due to the covering of the metal surface by these molecules.

There was no significant difference in the corrosion potentials of aluminium in 3.5 % NaCl solutions containing 30, 150 and 300 ppm LAB (Table 1a). The polarization resistance increased as the concentration of LAB increased (Table 1a) and this shows that the corrosion rate decreased with increasing concentration. It is claimed that the decrease in the corrosion rate of aluminium is due to the fact that surface-active substances like LAB replace the chloride ions on the metal surface and get adsorbed on the aluminium surface oxide⁴.

To calculate the corrosion rate by the polarization resistance method is more useful. It is simple and does not need more polarization of the metal sample. However, the B value is not known exactly (eq. 1). To determine the corrosion rate without using B the Mansfeld and Oldham method can be applied. This method was applied in this study and the obtained results are consistent with those in the literature and the estimated values.

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