IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.8 No.3 (September 2007) 53-59
ISSN: 1997-4884

University of Baghdad
College of Engineering

Corrosion Inhibition of Aluminum Alloy in 50% Ethylene Glycol Solution

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Abstract

The present study was conducted to evaluate the effect of different inhibitors on the corrosion rate of aluminum in 50% (v/v) ethylene glycol solution at 80°C and pH 8.0 in which the electrochemical technique of linear sweep voltammetry was employed to characterize each inhibitor function and to calculate the corrosion rate from Tafel plots generated by a computer assisted potentiostat.

It is found that both sodium dichromate and borax reduces the corrosion rate by polarizing the anodic polarization curve while sodium phosphate, potassium phosphate, and sodium benzoate reduces the corrosion rate by polarizing both the anodic and cathodic polarization curve.

When inhibitor concentration increases from 1 g/l up to 3 g/l, the inhibitor efficiency increases from 50% up to 85% for borax, from 64% up to 71% for sodium dichromate, and from 66% up to 82% for sodium phosphate, while constant inhibitor efficiency of about 55% and 50% for potassium phosphate and sodium benzoate were obtained respectively.

Keywords: ethylene glycol, antifreeze, corrosion inhibition.

Introduction

An antifreeze and coolant is a substance that is added to a liquid – usually water – to provide year round protection for the cooling system. It prevents freeze-up in winter and boil-over in summer. It provides protection from rust and corrosion and does not harm rubber hoses and plastics. In addition, it must be relatively low in cost, chemically stable, does not have unpleasant odor, and does not affect the cooling system finishes [1,2].

Ethylene glycol which is produced by the reaction of ethylene oxide with water [3] was first produced for use as antifreeze and coolant in 1925 comes to share about 90% of the antifreeze and coolant market because of its high boiling point and flash point that reduces the risk of coolant loss when the cooling system undergoes overheating. Moreover, the vapors from a hot glycol solution contain mostly water, so that, the antifreeze base is not lost by evaporation and freezing protection is maintained [1].

Unfortunately, ethylene glycol which is the major antifreeze and coolant material oxidizes to a mixture of corrosive acids in which the formic acid and oxalic acid are the major constituents. This oxidation process is promoted by mechanical defects, such as air suction at pump shaft seal, bad hose connection, and exhaust gas leakage. The resulting solution will be much more corrosive than tap water to which no antifreeze has been added. The factors be responsible for the rapid oxidation of the antifreeze/coolant also are excessive aeration, the presence of local hot spots in the cooling system, and operating of the antifreeze/coolant at consistently high temperatures. It is proved that the addition of ethylene glycol gives higher corrosion rates for many metals than when water alone is used. This increase was especially the case for aluminum [4,5].

Aluminum used extensively in the construction of the cooling system parts because of its efficient heat transfer property, good electrical conductivity, and its passivity in many environmental media subjected to the cooling system. Gray cast iron has been the traditional material for cylinder block, heads and liners (in automobiles) for example is being replaced by lighter aluminum alloys that have better thermal conductivity. Traditional copper or brass radiators are also being replaced by aluminum radiators with cross-flow plastic tanks. This introduces new corrosion problems because several different aluminum alloys are being used for this purpose. The aluminum is much more susceptible to pitting and corrosion than conventional metals would be, and it is especially important that it must be protected with inhibitors [2].

There are a number of methods used on large scales for combating corrosion. These include cathodic protection, coatings, equipment design, changes in metallurgy, and so on. In many situations, the use of one or more of these measures is preferable to the use of inhibitors. The economics, the nature and use of the liquid to be inhibited, and the design of the system must be considered in making a decision as to which type of protective approach to take [6].

Corrosion inhibitors, come to solve the problem of corrosion in ethylene glycol-water solutions. These inhibitors must be present in sufficient concentration to provide metal protection. The amount needed depends on operating conditions, corrosivity of the water used, and length of time at operating temperatures. Since inhibitors are depleted with time through interaction with metals or other substances in the system, the antifreeze/coolant must be replaced periodically. Some of the typical inhibitors traditionally used in antifreezes are borates, phosphates, benzoates, nitrates, silicates, mercaptobenzothiazole, and polytriazole [2].

Many standard industry tests and modern electrochemical techniques were used to help and identify corrosion inhibitors to optimize the selection of inhibitor combinations and to evaluate the performance of the antifreeze and coolant.

In this investigation, a linear sweep voltammetry was used to study the corrosion by aqueous 50% (v/v) ethylene glycol solution on aluminum specimens used by a specific cooling system at 80°C and pH 8.0 to evaluate the function of sodium dichromate, borax, sodium phosphate, potassium phosphate, and sodium benzoate and to calculate the corrosion rate also.

Experimental Work

The test cell

Fig. 1 represents the apparatus arrangement during the test. The test cell (supplied from Princeton Applied Research) includes the metal specimen (working electrode) and the solution in which the specimen is to be tested. The reference electrode contacts the solution via the bridge tube, a compartment filled with test solution which provides optimum positioning of the reference electrode. An auxiliary electrode (counter electrode) is used to supply the current flowing at the electrode during the test. The test cell can holds also the contact thermometer to maintain the temperature of the test solution within 80±2°C.

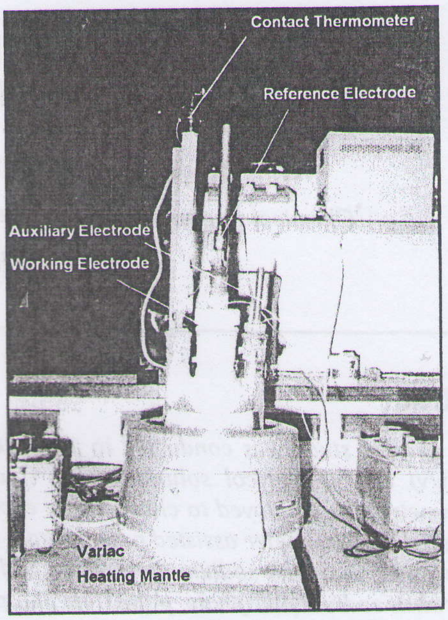

Fig. 1 The electrochemical apparatus arrangement during the test

Electrodes

The working electrode

Table 1 shows the composition of the test specimens used during a test.

Table1 Test specimens' composition

Compound	*Weight percent, %*
Al	94.00
Mn	0.12
SiO_2	3.50
Others	Traces

Specimens were cut to approximately 50 × 10 × 1 mm, and 3 mm hole was drilled, 5 mm from one end. Sharp edges and imperfections in the surface were removed by sand paper (a separate sand paper was used for each specimen).

All test specimens were degreased in benzene for 30 minutes, etched in 10% sodium hydroxide, rinsed in distilled water and dipped in concentrated nitric acid for 5 seconds. After etching, specimens were rinsed in distilled water, wiped with a cloth to remove excess moisture, dried, and stored in a desiccator.

The reference electrode

Saturated calomel electrode (SCE) was used in carrying out the electrochemical tests. The reference electrode is an important part of the electrochemical cell and must be operate properly to get an accurate detector response. So that, a fresh reference electrode was used to check the reference point of the reference electrode. With a digital voltmeter, the potential difference between the two electrodes was measured and found to be less than 20 mV. A drift value less than 20 mV is acceptable in an electrochemical test [7].

The auxiliary electrode

Graphite rod was used as an auxiliary (counter) electrode which acts to source or sink electrons in the electrochemical circuit formed with working electrode. The auxiliary electrode was rinsed with distilled water between each test to remove any encrusted buffer salts from the electrode surface. Applying several drops of acetone to the surface of the electrode whenever required. This simple chemical cleaning procedure may clean the electrode enough to bring back a suitable response rapidly.

Test Solution

Technical grade ethylene glycol was used in all tests. 50% (v/v) solutions were prepared with tap water. Tap water used in the test solution had a conductivity of 743 µS/cm and chloride ion concentration of 74.5 ppm. The pH of solutions was adjusted with oxalic acid and sodium hydroxide solutions to maintain the pH within 8.0±0.5 unit. Solution temperature was kept at 80±2°C during the test.

The Potentiostat

The potentiostat used in this investigation had been designed for computer-assist operation. It can accept a computer generated waveforms rather than predefined waveforms found in usual potentiostats. A computer-assisted measurement systems offer an important advantage over semi-automatic instrumentation. When the data is plotted on a recorder, we must perform manual calculations to obtain the plot and results. Of course, once the data is collected by a computer, it is in the ideal place for automatic reduction and calculation. Fig. 2 shows a screenshot for a typical scanning results obtained using the computer assisted potentiostat.

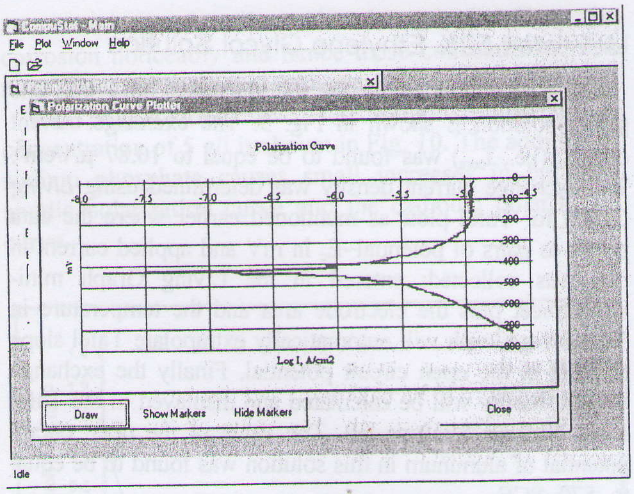

Fig. 2 typical screenshot for scanning results

Calculation of Corrosion Rates from the Corrosion Current

Tafel plot is generated by beginning the scan -250 mV~E_{corr} and scanning continuously to +250 mV~E_{corr}. The resulting curve is a plot of the applied potential vs. the logarithm of the measured current.

The corrosion current, I_{corr}, can be determined by superimpose a straight line along the linear portion of the anodic and cathodic curve and extrapolate them through the open circuit potential (E_{corr}). Encompassing both the anodic and cathodic Tafel regions, the two straight line extrapolations should intersect at E_{corr}. The point of intersection at E_{corr} gives the I_{corr} value [8,9].

A good application program was used also in determining the corrosion current available for on-line calculations in the internet as Living Graph [10]. It has the advantage in that it support additional parameters/plots required to analyze the electrode kinetics from Tafel data points.

To determine the corrosion current, data points from a test must be entered on the Tafel Data mini-spreadsheet, electrode area, and the temperature when the applet was started. After obtaining the corrosion current, the corrosion rate was readily for calculation according to Faraday's law.

Results and Discussion

Instead of comparing different inhibitor concentration with uninhibited solution, and to avoid the interference between the curves, it was decided to compare one inhibitor concentration with that of uninhibited solution to show the effect of the inhibitor on the polarization characteristics of aluminum clearly.

Untreated 50% Ethylene Glycol Solution

The polarization curve for the untreated 50% ethylene glycol solution is shown in Fig. 3. The exchange current density (i.e., i_{corr}) was found to be equal to 10.87 μA/cm^2. The exchange current density was determined using *Living Graph* for Tafel plots as mentioned earlier where the data points as pairs of potential~E_c in mV and applied current in mA was collected; entered in the Living Graph mini-spreadsheet plus the electrode area and the temperature in °K. Living Graph will automatically extrapolate Tafel slope to meet at the open circuit potential. Finally the exchange current density will be calculated and displayed in the Tafel Least Squares Analysis tab. The value of the open circuit potential of aluminum in this solution was found to be equal to -570~SCE.

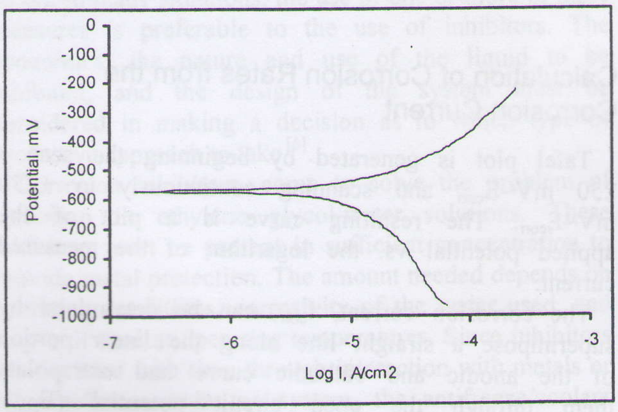

Fig. 3 Polarization curve for aluminum in untreated 50% ethylene glycol solution

Effect of pH

The effect of pH on the corrosion rate for 50% ethylene glycol solution in case of absence of inhibitors is shown in Fig. 4. The corrosion rate in the range of 6-9 gives the best pH for operation. High pH values (>9) cause aluminum to corrode rapidly because new secondary reactions will take place. This phenomenon found in all amphoteric metals such as Zn, Pb, Sn, and the aluminum [11]

Effect of Borax

The corrosion rate – concentration curve for borax is shown in Fig. 5. The addition of 1 g/l borax causes a sharp decrease in the corrosion rate, an indicative of film formation. Further increase of borax causes a gradual decrease in corrosion rate to about 5 g/l and levels off to a constant value for concentration greater than 7 g/l, which indicates that the higher concentration of borax is less effective as shown in Table (2).

The polarization curve for borax at concentration of 7 g/l is shown in Fig. 6. The addition of borax to the 50% ethylene glycol solution effects little change in the slope of the cathodic polarization curve, but a marked change in the slope of the anodic polarization curve (steeper anodic slope). The inhibitive action of borax in 50% ethylene glycol solution is primarily due to the increase in the polarization of the anode. It retards or arrests the anodic reaction, therefore, it is classified as an anodic inhibitor.

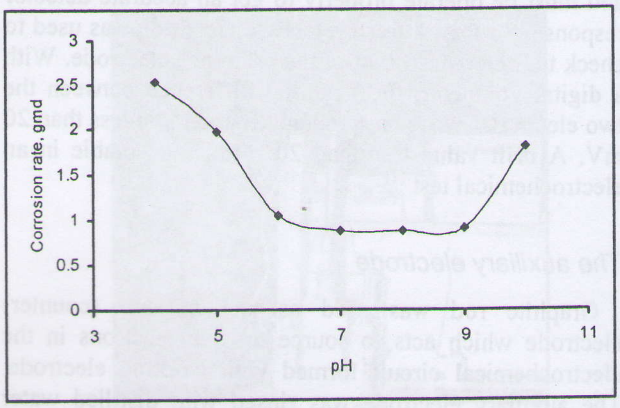

Fig. 4 Corrosion rate as a function of pH

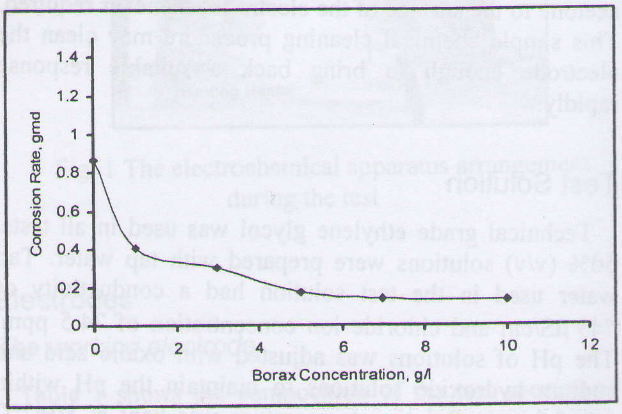

Fig. 5 The effect of borax on the corrosion rate of aluminum in 50% ethylene glycol

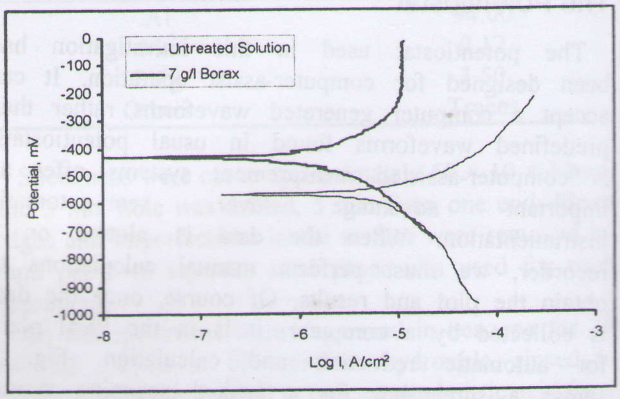

Fig. 6 Influence of borax on polarization characteristics of aluminum in untreated 50% ethylene glycol

Effect of Sodium Dichromate

The corrosion rate – concentration curve for sodium dichromate is shown in Fig. 7. The addition of sodium dichromate reduces the corrosion rate sharply until it levels off to a constant value. Dosage levels of 1 to 3 g/l of sodium dichromate seem to be sufficient to give the desired protection.

The polarization curve for sodium dichromate is shown in Fig. 8. The addition of sodium dichromate to the ethylene glycol solution causes a little change in the cathodic polarization curve. However, there is a marked increase in the slope of the anodic polarization curve. Sodium dichromate behaves as an anodic polarizer.

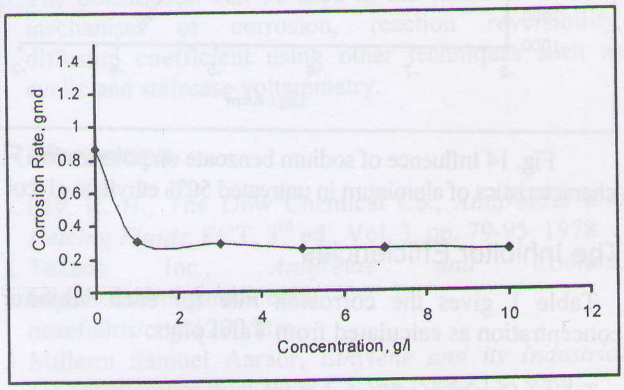

Fig. 7 The effect of sodium dichromate on the corrosion rate of aluminum in 50% ethylene glycol

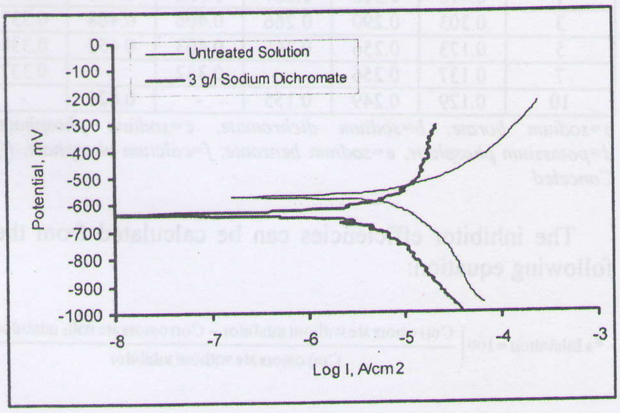

Fig. 8 Influence of sodium dichromate on polarization characteristics of aluminum in untreated 50% ethylene glycol

Effect of Sodium Phosphate

The corrosion rate – inhibitor concentration curve for the addition of sodium phosphate is shown in Fig. 9. The addition of sodium phosphate causes a decrease in the corrosion rate after the addition of 1 g/l, continues at the same rate until reaching a value of 5 g/l where a further decrease in the corrosion rate was detected. Further concentrations of sodium phosphate don't effects the corrosion noticeably and hence these concentrations are not efficient as compared with previous concentrations.

The polarization curve for sodium phosphate at concentration of 5 g/l is shown in Fig. 10. The addition of sodium phosphate causes small increases in both the anodic polarization curve and the cathodic polarization curve.

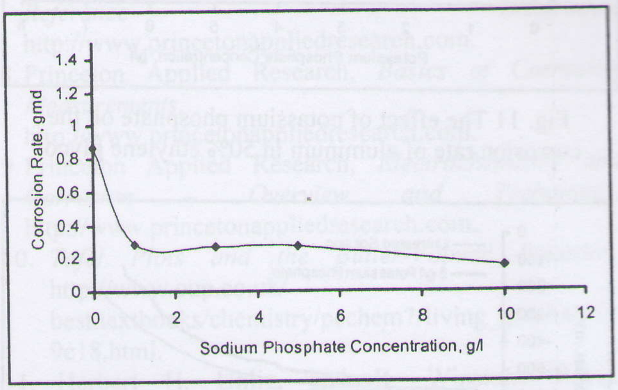

Fig. 9 The effect of sodium phosphate on the corrosion rate of aluminum in 50% ethylene glycol

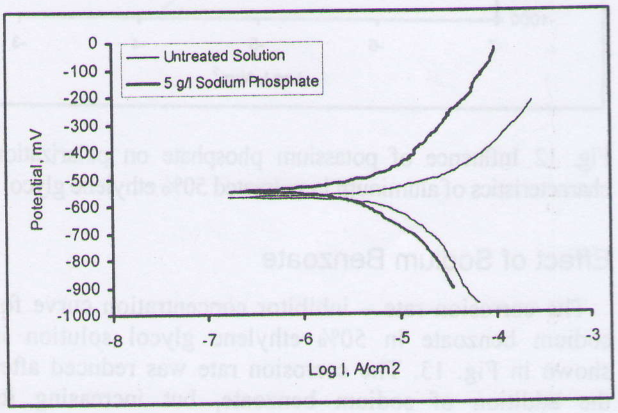

Fig. 10 Influence of sodium phosphate on polarization characteristics of aluminum in untreated 50% ethylene glycol

Effect of Potassium Phosphate

The corrosion rate – inhibitor concentration curve for potassium phosphate added to the ethylene glycol solution is shown in Fig. 11. The corrosion rate also decreases in the presence of potassium phosphate in concentration of 1 g/l, and then little increase in corrosion rate up to 5 g/l, finally it levels off to a constant value.

The polarization curve for potassium phosphate at concentration of 5 g/l is shown in Fig. 12. The addition of potassium phosphate causes small increases in both the anodic polarization curve and the cathodic polarization curve.

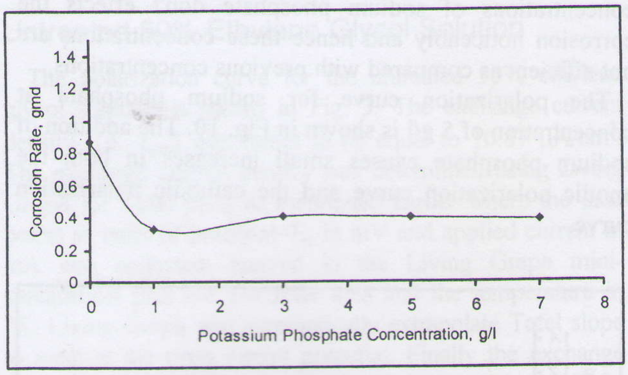

Fig. 11 The effect of potassium phosphate on the corrosion rate of aluminum in 50% ethylene glycol

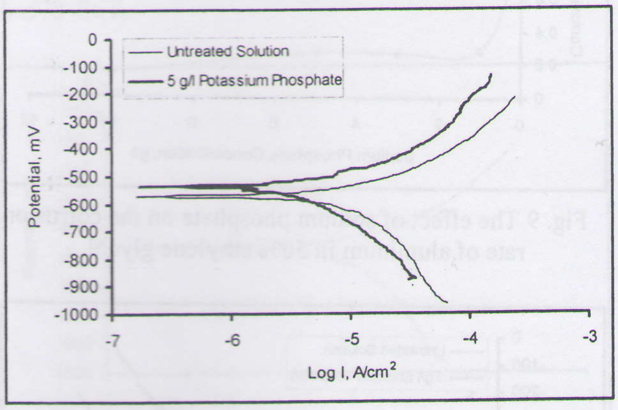

Fig. 12 Influence of potassium phosphate on polarization characteristics of aluminum in untreated 50% ethylene glycol

Effect of Sodium Benzoate

The corrosion rate – inhibitor concentration curve for sodium benzoate in 50% ethylene glycol solution is shown in Fig. 13. The corrosion rate was reduced after the addition of sodium benzoate, but increasing its concentration doesn't reduce the corrosion rate effectively. The corrosion rate after the addition of 1 g/l sodium benzoate seems to level off to a constant value.

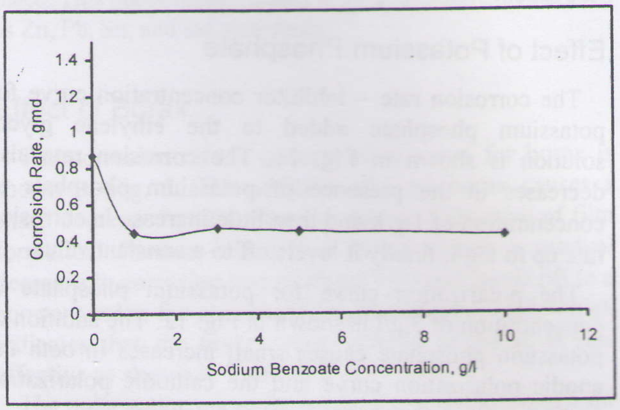

Fig. 13 The effect of potassium phosphate on the corrosion rate of aluminum in 50% ethylene glycol

The polarization curve for 1 g/l sodium benzoate in untreated 50% ethylene glycol solution was shown in Fig. 14. The addition of sodium benzoate affects the anodic polarization curve as well as the cathodic polarization curve.

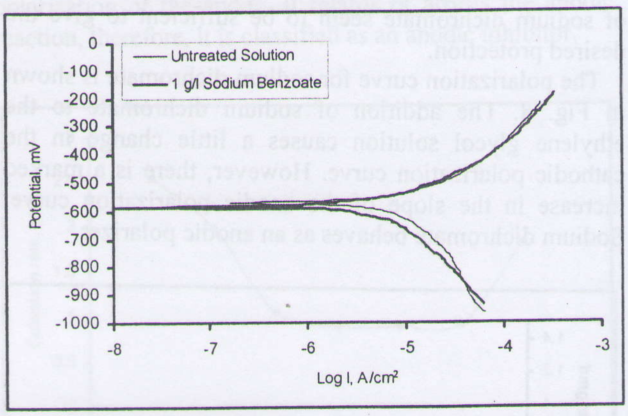

Fig. 14 Influence of sodium benzoate on polarization characteristics of aluminum in untreated 50% ethylene glycol

The Inhibitor Efficiencies

Table 1 gives the corrosion rate for each inhibitor concentration as calculated from Tafel plots.

Table 1 Corrosion rate for each inhibitor concentration

Conc.,	Corrosion Rate, gmd					
g/l	a	b	c	d	e	f
0	0.869	0.869	0.869	0.869	0.869	0.869
1	0.410	0.308	0.287	0.332	0.441	0.325
3	0.303	0.290	0.266	0.406	0.468	0.337
5	0.173	0.256	0.266	0.403	0.452	0.338
7	0.137	0.256	0.256	0.382	-	0.337
10	0.129	0.249	0.155	-	0.426	-

a=sodium borate, b=sodium dichromate, c=sodium phosphate, d=potassium phosphate, e=sodium benzoate, f=calcium phosphate, (-) Canceled

The inhibitor efficiencies can be calculated from the following equation:

$$\%\,\text{Inhibition} = 100\left[\frac{\text{Corrosion rate without inhibitor} - \text{Corrosion rate with inhibitor}}{\text{Corrosion rate without inhibitor}}\right]$$

Table 2 gives the inhibitor efficiency for each inhibitor concentration as determined from the above equation.

Table 2 Inhibitor efficiencies for each inhibitor conc.

Conc.,	Inhibition percent, %					
g/l	a	b	c	d	e	f
1	52	64	66	61	49	62
3	65	66	69	53	46	61
5	80	70	69	53	47	61
7	84	70	-	56	-	61
10	85	71	82	-	50	-

a=sodium borate, b=sodium dichromate, c=sodium phosphate, d=potassium phosphate, e=sodium benzoate, f=calcium phosphate, (-) Canceled

Conclusions

1. The optimum conditions for the antifreeze and coolant in the cooling system were 50% v/v ethylene glycol solution and at pH 8.
2. Borax, and sodium chromate are anodic polarizers, while others are both anodic and cathodic polarizers.
3. The results indicates that inhibitor effectiveness for the chromate is 82%, sodium benzoate 42%, and the rest studied inhibitors are around 62%.
4. Calcium phosphate reduces the corrosion rate but it can not be used in the cooling system because it forms insoluble compounds which may plugs the flow of the coolant in the cooling system.
5. The potentiostat can be used in the future to evaluate mechanism of corrosion, reaction reversibility, diffusion coefficient using other techniques such as cyclic and staircase voltammetry.

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