

THE CORROSION AND ELECTROCHEMISTRY OF IRON IN AQUEOUS GLYCOL MIXTURES

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Summary

A multi-faceted approach to the determination of the electrochemical characteristics of iron in aqueous glycol mixtures has overcome many of the problems associated with the use of a single technique. From a comparison of the behaviour of a 19th century steel and pure iron it is clear that any experiments made without reference to 'in-service' structures of the metal will be subject to significant errors of interpretation. Data collected from corrosion potential, linear and anodic polarisation experiments has established that under acidic and low oxygen conditions, ethylene glycol (EG), propylene glycol (PG) and polyethylene glycol 400 (PEG 400) all inhibit the corrosion of iron by screening active sites on the surface of the electrode. In the absence of glycol, chloride ions are inhibitory under 'steady-state' conditions at concentrations greater than 0.1 M. Chloride ions lose their inhibitory characteristics at concentrations $\geq 10^{-2}$ M under anodic polarisation and assist the anodic dissolution of iron. Addition of glycol increases the apparent activity of chloride ions in the order 40 v/v% PEG 400 > 4 v/v% PEG 400 > 5 v/v % EG. The combined effects of chloride and glycol on the electrode surfaces under 'steady-state' conditions reflect competitive adsorption phenomena.

Keywords: inhibitors, glycols, steel, corrosion, chloride.

Introduction

The primary aim of this applied research was to develop an understanding of the processes controlling the deterioration of archaeological iron with special reference to the complex environment associated with composite wood/iron artefacts. This work reports on the behaviour of iron in aqueous solutions of polyethylene glycol 400 (PEG 400) which are used in preserving waterlogged wood. Because the objects came from historic shipwreck sites the effects of chloride ions over the range 10^{-6} M to 1 M were examined. This concentration range covers chloride levels found in completely treated to untreated artefacts. The degassed and acidic nature of the solutions was chosen in order to eliminate the effects of hydrolysis of corrosion products and to enable the specific effects of molecular weight and structure of the glycols to be determined. Further work needs to be done in the near neutral to mildly acidic solutions associated with objects in-situ and in treatment.

The upper concentration limit of chloride was chosen because the marine concretion causes chlorinity levels at the corroding iron surface to be significantly elevated above 0.5 M normally found in seawater. During corrosion on historic shipwreck sites the typical microenvironment of iron is pH 4.2 and 1.5 M chloride (1). Because it is essential to understand the interfacial phenomena associated with chloride and glycol at a corroding iron surface, the metal coupons of 19th century steel and pure iron were examined using E_{corr} and R_p measurements. Linear anodic polarisation studies were also performed to understand why, under certain conditions, iron composite materials recovered from archaeological sites undergo rapid and extensive corrosion.

Experimental

Distilled de-ionised water was used in the preparation of the solutions which contained AR quality electrolytes and ethylene glycol (EG). The propylene glycol (PG) and polyethylene glycol 400 (PEG 400) were general purpose reagents. It should be noted that 'polyethylene glycol' is a misnomer since it is in fact a polyether of the formula $\text{HOCH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{OH}$. Solutions were prepared with a formal ionic strength of 1.1 M which consisted of 1 M NaClO_4 , 0.1 M HClO_4 and the required concentration of chloride ions. When 1 M chloride solutions were used no NaClO_4 was added. All solutions were de-aerated by passing high purity nitrogen through the solution for 15 minutes before any measurements were made, and a nitrogen atmosphere was maintained above the solution during measurement. All measurements were made at the laboratory temperature of $22 \pm 1^\circ\text{C}$.

Iron electrodes were prepared from a 99.98% (Aldrich) iron rod with a final outside diameter of 5.00mm. The other electrode material came from reinforcing steel lintels in the Commissariat building (1856) in Fremantle. The elemental analysis gave the following composition (%): Fe 98.91; S 0.06; Si 0.06; Mn 0.69; Cu 0.02; Ni 0.02; P 0.06 and C 0.18. The low sulphur, silicon and phosphorous levels are consistent with a good quality steel with a carbon equivalent $[\text{CE} = \text{C} + \frac{1}{3}(\text{Si} + \text{P})]$ of 0.22 – the manganese increases the hardness of the low carbon steel. Samples were cut from a large flat bar, existing corrosion products were mechanically removed and the samples machined into rods of a known diameter of approximately 5 mm. The rods

were cut to a length of 10 mm and made into electrodes by attaching them to a stainless steel plate and mounting them in an epoxy resin (Ciba-Giegy Araldite LC 191/LC 226). The interface between the metal and epoxy was regularly inspected for signs of attack. If interfacial corrosion was detected the results were discarded. The electrodes were attached via a threaded section to a Teflon coated, brass electrode holder when being used for measurements. This allowed the electrodes to be easily removed for preparation and examination whilst maintaining the exposure of a disc of known diameter to the solution. The electrodes were prepared by abrasion on a Struers Planopol polishing wheel using silicon carbide paper to a final 1200 grit. They were rinsed in acetone, cleaned in 1 M HClO₄ for 30 seconds and rinsed in distilled deionised water immediately prior to immersion in the test solution. No attempt was made to remove any air-formed oxidation layer which may have developed on the metal surface between the last cleaning stage and immersion in solution during the few seconds which elapsed between these operations.

Electrochemical Measurements

A rotating disc electrode assembly similar to that described by Power et al (2) was used during all measurements. The working electrode design was adapted to incorporate a threaded section in the base of the holder (Figure 1.) and on the shaft of the electrode as described above. All electrochemical measurements were made in a Metrohm 100cm³ cell with provision for a Luggin probe to be added through the base. This was used in conjunction with a Metrohm cap that allowed the working electrode, counter electrode and gas inlet access to the solution.

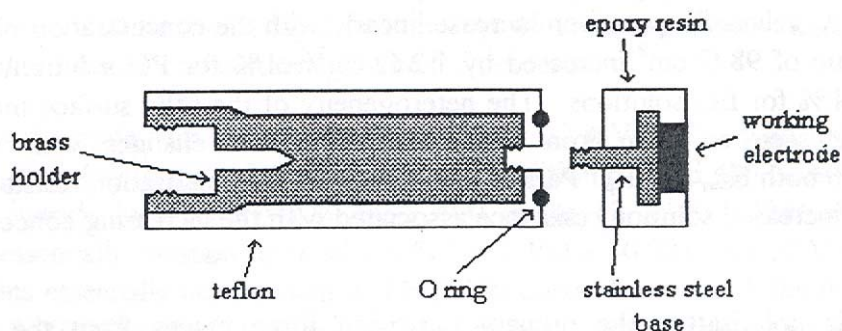


Figure 1. The working electrode and electrode holder

The corrosion potential (E_{corr}) was measured using a Hewlett-Packard E2373A Multimeter connected through a Princeton Applied Research (PAR) Model 173 potentiostat to obtain a sufficiently high impedance. Polarisation curves and Stern-Geary measurements were obtained using this instrument with a PAR Model 376 Logarithmic Current/Voltage Converter, Model 178 Electrometer Probe and Model 175 Universal Programmer. A 100mS filter (on the PAR model 376 Logarithmic Current/Voltage Converter) was incorporated into the current circuit to reduce noise associated with the measurement. All measurements were made, and are reported against a Hg/Hg₂SO₄,K₂SO₄(sat) reference electrode which has a formal potential of 0.654 V vs NHE. A platinum wire (150 mm x 0.5 mm diameter) was used as the counter electrode.

E_{corr} measurements were carried out by immersing the electrode in the solution of interest for 30 minutes, by which time a reasonably stable and reproducible potential was reached. Once a stable E_{corr} was established, the measurement of the polarisation resistance (R_p) was performed by scanning at 0.1 mV s^{-1} in the range $E_{\text{corr}} \pm 7 \text{ mV}$. The most reproducible results were obtained by scanning initially in the cathodic direction. All E_{corr} and R_p measurements were carried out at a stationary electrode and the slope $\Delta E/\Delta i$ (R_p) was measured from the current-voltage curve.

Measurement of the anodic dissolution current was carried out by scanning anodically at 5 mV s^{-1} from -1100 mV to -300 mV on a freshly prepared electrode surface. All anodic polarisation experiments were performed with the electrode rotating at 1000 rpm . The slope, $\Delta E/\Delta i$, was measured from the recorded curve.

Effect of Simple Glycols

The effects due to ethylene glycol (EG) and propylene glycol (PG) in the concentration range 0 to 40 vol % in water, have been grouped together as their results are remarkably similar. The addition of small amounts of glycol causes very little change in the R_p and E_{corr} values of both pure iron (Fe) and nineteenth century steel ($^{19\text{th}}\text{C Fe}$) principally because of their hydrophilic nature. The anodic shift of E_{corr} values of Fe with increasing glycol concentrations is probably due to the de-stabilisation of Fe(II) in solution. The E_{corr} for Fe shifts anodically by $0.4 \text{ mV/wt } \%$ increase in EG concentration, and by half this value for the ($^{19\text{th}}\text{C Fe}$). The R_p data shows no discernible glycol dependence for ($^{19\text{th}}\text{C Fe}$) in either EG or PG solutions, providing some support for the argument that the changes in E_{corr} are due to solvation effects on the Fe/Fe $^{2+}$ couple. The R_p values for pure iron increase linearly with the concentration of glycol; the initial value of $98 \text{ } \Omega \cdot \text{cm}^2$ increased by $1.2 \text{ } \Omega \cdot \text{cm}^2/\text{vol } \%$ for PG solutions and by $1.5 \text{ } \Omega \cdot \text{cm}^2/\text{vol } \%$ for EG solutions. The heterogeneity of the ($^{19\text{th}}\text{C Fe}$) surface masks the subtle effects seen on pure iron which shows greater changes with solution composition in both E_{corr} and R_p . Part of the increase in the polarisation resistance will be due to the increased solution resistance associated with the increasing concentration of the glycols.

During anodic polarisation the primary corrosion force comes from the applied voltage, rather than from dissolved oxygen or from acid dissolution. The addition of EG results in the oxidation of both Fe and ($^{19\text{th}}\text{C Fe}$) becoming increasingly difficult as the concentration of EG is increased. Since the slope ($\Delta E/\Delta i$) of the anodic polarisation curve is directly related to the ease of oxidation, the linear decrease of 1.5 % of the corrosion rate, as measured by ($\Delta E/\Delta i$), for every 1 % increase in EG concentration is a clear demonstration of the effectiveness of EG in lowering the corrosion rate. Similar percentage changes were observed via the R_p measurements. The combination of EG's de-stabilising effect on the Fe(II) species in solution and its lower dielectric makes it harder for the iron to be removed from the surface of the electrode. Given the established similarity in behaviour it would seem reasonable to suggest that PG would have a similar effect, but this was not experimentally verified.

Effect of Polyethylene Glycol 400

The effects of polyethylene glycol 400 (PEG 400) on the electrochemistry of iron was studied in the range 0 - 40 vol % in aqueous acid solutions. In these solutions significant differences in the behaviour of the two types of electrode material were noted. The R_p data for (^{19}C Fe) shows a sharp increase from 55 to 185 $\Omega\cdot\text{cm}^2$ as soon as 1.4 vol % PEG 400 was added. This indicates that the PEG 400 has a major effect on the double layer at low concentrations since the PEG 400 decreased the reactivity of the surface by more than a factor of three. At 1.4 vol % PEG 400 the effects on bulk parameters such as viscosity have not yet significantly changed. At the same concentration of PEG 400 the anodic polarisation behaviour is also significantly affected and the $(\Delta E/\Delta i)$ value fell by 12.5 % indicating significant inhibition at low concentrations of glycol. The smaller effect of the PEG 400 on anodic polarisation is due to the different nature of the double layer at these voltages. The apparent inhibitory effect could occur by partial blocking of the active sites on the electrode surface. This effect, as are all adsorption related processes, is strongly influenced by the micromorphology of the surface and so the effects are much less significant on the Fe electrode. Pure iron needed 7.5 vol % PEG 400 to reach the same R_p value as the (^{19}C Fe) reached at 1.4 vol %. Once the initial adsorption is complete, the R_p values are similar for both types of iron (possibly indicating that the reaction rate is limited by the ability of the proton to reach active sites on the electrode surface). However the R_p of (^{19}C Fe) increases with PEG 400 concentration at twice the rate of Fe. Since the solution compositions are the same the differences in the behaviour of the two electrodes must be due to the different nature of the adsorption phenomena at the corroding surfaces. This is the reverse of the apparent sensitivities of (^{19}C Fe) and Fe in the simple glycol solutions. The further increase in the R_p values is possibly due to the de-stabilising effect of PEG 400 on the Fe(II) solvation. At 40 vol % PEG 400 the R_p for (^{19}C Fe) is 75 % higher than the corresponding value for pure iron.

The (^{19}C Fe) electrode showed an initial increase of 22 mV in E_{corr} with the addition of 1.4 vol % PEG 400 to the solution. Continued addition of PEG 400 caused the E_{corr} to increase linearly by 0.9 mV/vol % PEG 400 up to 12 vol %. Thereafter the E_{corr} remains essentially constant up to 40 vol % PEG 400 at -0.921 ± 0.002 V. The E_{corr} of Fe remains essentially independent of PEG 400 concentration with the mean value of -0.902 ± 0.003 V vs Hg_2SO_4 over the entire range, which indicates that any effects of changing liquid junction potentials are insignificant (Figure II). This is consistent with the findings of other workers studying the liquid junction potentials in mixed aqueous solvent systems(3). The magnitude of the changes for (^{19}C Fe), is greater for PEG 400 compared to EG and PG. Since PEG 400 is a much larger molecule than the two glycols, it is probably capable of causing greater disruption to the water structure. The likelihood of this is increased as both ends of the molecule are hydrophilic so a micellar type structure cannot be achieved. Due to the size of the PEG 400 molecule compared to the water molecule, it would seem reasonable to assume that at low concentrations the hydrophobic nature of the ether linkages of PEG 400 forces it out of the regular water structure.

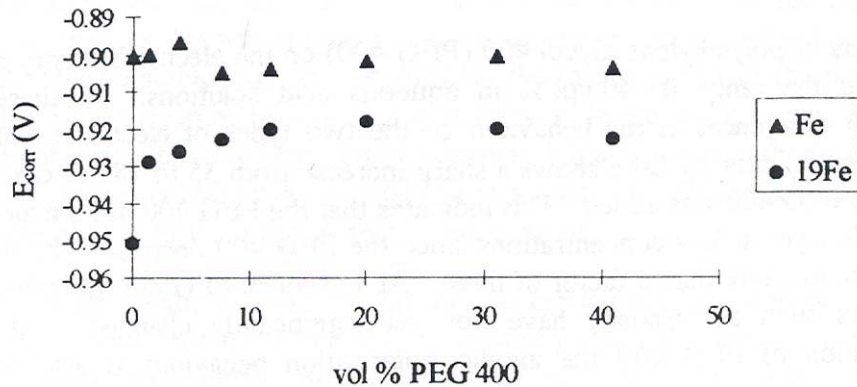


Figure II. The effect of PEG 400 on E_{corr} of Fe and ^{19}C Fe.

It is interesting to note the changeover in the relative rates of corrosion as derived from the R_p values for the different electrodes. (^{19}C Fe) corrodes faster in water but less rapidly in the presence of PEG 400, presumably because PEG 400 adheres better to (^{19}C Fe)'s less uniform surface than to the more homogeneous Fe surface where the inhibitory effects are less marked.

The anodic polarisation data shows marked inhibition of the dissolution rate of Fe and (^{19}C Fe) by PEG 400 with the value of $(\Delta E/\Delta i)$ falling by 1.9 % per unit increase in the vol % of PEG 400. The magnitude of the inhibition is greater than the corresponding 1.5 % fall found with EG solutions. The addition of 40 vol % PEG 400 causes a drop in the $(\Delta E/\Delta i)$ values of 76 % which is the same as the 75 % increase in the R_p values at the same concentration. Thus in the case of aqueous PEG 400 solutions the addition of PEG 400 causes the same order of corrosion inhibition whether it was measured under '*steady-state*' R_p methods or under active transport in the anodic polarisation. Once the concentration range of 0-7.5 vol % PEG 400 has been passed the solvent sorting and viscosity effects on the $(\Delta E/\Delta i)$ curves settles down to a monotonic trend.

Owing to equipment and other experimental problems it was not possible to perform further experiments in the Tafel controlled region or to carry out AC impedance studies on the corroding surfaces. Such data is needed to help determine the mechanism of apparent inhibition of the corrosion process by the PEG 400 solutions. There is danger in extrapolating data obtained in acidic media to more alkaline conditions where the cathodic process may be dominated by oxygen reduction as, in neutral conditions, where PEG 400 has been shown to increase the corrosion rate of ferrous materials (4). Part of the cause of the apparent inhibitory effects of PEG 400 and glycol solutions will be due to the falling value of the dielectric constant.

Effect of Chloride

The effect of chloride concentration was studied in the range 10^{-6} (background) to 10^0 M, at pH = 1 in water. At this pH our studies have shown that there is no complication due to film formation, so any observed effects are probably due to the presence of chloride ions. The way in which the R_p values change with concentration suggests that chloride ions have a noticeable inhibitive effect at concentrations > 0.1 M. 'Steady-state' conditions require hydrogen ions to be present at the active sites on the electrode surface for corrosion to occur. The apparent inhibitory action of chloride is consistent with the blocking of active sites by adsorbed chloride. This effect is not as marked on (^{19}C Fe) as this material has a higher number of active sites, as previously seen in the effects of adsorption of PEG 400 on the electrode surface.

The corresponding E_{corr} data (^{19}C Fe) and Fe is shown in Figure III. For pure iron there is a trend in E_{corr} towards more cathodic values even at low chloride concentrations due to the stabilisation of Fe(II) by chloride ions. (^{19}C Fe) shows no change until a chloride concentration > 0.1 M is reached, suggesting that the less uniform surface requires a critical concentration of chloride to affect its behaviour.

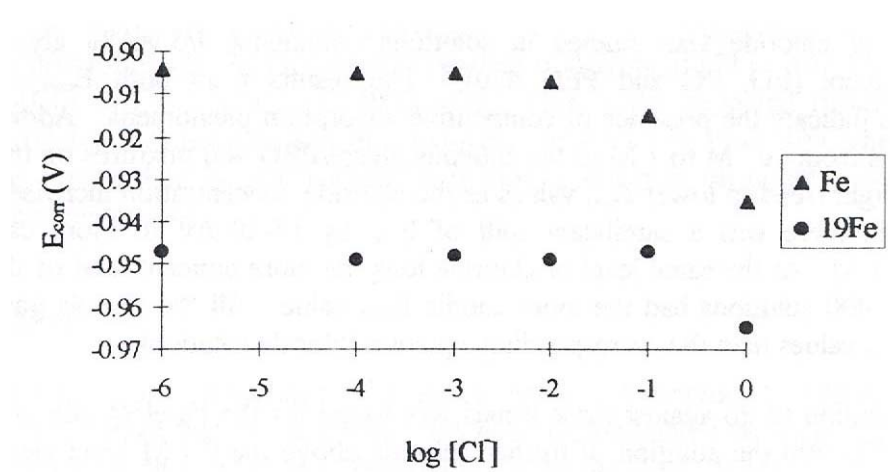


Figure III. The effect of chloride in water on E_{corr} of Fe and (^{19}C Fe)

The anodic polarisation data, summarised in Figure IV, shows that for concentrations of $[\text{Cl}^-] \leq 10^{-2}$ M the presence of chloride inhibits the dissolution of iron but that at higher concentrations, chloride accelerates iron dissolution (5). The differences between this set of data, measured under dynamic conditions, and the E_{corr} and R_p data, emphasises the apparent differences which arise due to experimental design. Both electrode materials showed similar behaviour and rates of dissolution.

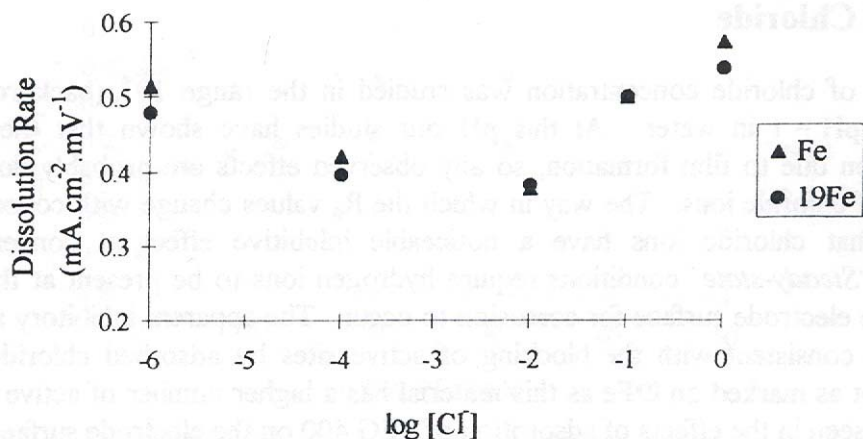


Figure IV. The effect of chloride in water on the dissolution rate ($\Delta E/\Delta i$) of Fe and ^{19}C Fe.

Effect of Chloride in Solutions Containing Glycols

The effect of chloride was studied in solutions containing 4/5 vol % glycol and 40 vol % glycol (EG, PG and PEG 400). The results from both E_{corr} and R_p experiments indicate the presence of competitive adsorption phenomena. Addition of chloride ions from 10^{-6} M to 1 M to the aqueous glycol/PEG 400 mixtures on the (^{19}C Fe) showed a slight trend to lower E_{corr} values as the chloride concentration increased until 10^{-1} M when there was a significant shift of E_{corr} by 15-20 mV to more cathodic voltages at 1 M. At the same level of chloride ions the more concentrated of the two glycol/PEG 400 solutions had the more anodic E_{corr} value. All the glycols gave less negative E_{corr} values than the corresponding aqueous chloride solutions.

The only solution to go against these trends was found for the Fe electrode where in 40 vol % PEG 400 the addition of further chloride above the 0.1 M level caused an increase in E_{corr} *ie.* it moved to more anodic voltages, which is the reverse of the effect of chloride in aqueous solution shown in Figure III.

The difference in behaviour is possibly due to changes in the solvation of the chloride ion caused by the high concentration of PEG 400. However it should be noted that all the R_p data showed the same effects of increasing values between 10^{-1} and 1 M chloride in the high and low glycol/PEG 400 solutions for Fe. For the ^{19}C Fe the changes in R_p values were only significant for the aqueous PEG 400 solutions. This indicates that once a sufficiently high concentration of chloride was reached it was able to effectively compete for adsorption sites on the electrode surfaces and displace H^+ ions, and so reduce the corrosion rate.

The anodic polarisation experiments in solutions containing 5 vol % EG show that for a chloride ion concentration greater than 10^{-2} M in the mixed solvent, higher dissolution rates are observed than in water (Figure V). Since EG in the absence of chloride inhibits anodic dissolution, this result represents an increase in the chloride ion activity in the mixed solvent (6). In solutions containing PEG 400, the concentration at which chloride promotes dissolution decreases with increasing PEG

400 concentration which suggests an increased chloride ion activity as PEG 400 inhibits anodic dissolution as the solvent composition is changed.

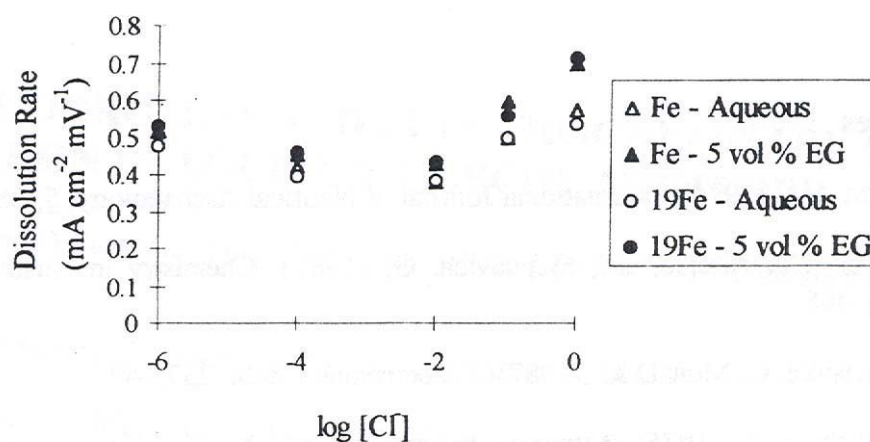


Figure V. The dissolution rate in aqueous and EG solutions.

At low (≈ 5 vol %) solvent concentrations in glycol/chloride media, the inhibition/promotion change is solvent dependent occurring at $[Cl^-] = 10^{-2}$ M in 5 vol EG and $[Cl^-] = 10^{-3}$ M in 4 vol % PEG 400. This is the expected result from the apparent relative a_{Cl^-} in these solvent mixtures. In 40 vol % PEG 400 when the a_{Cl^-} would be expected to be still higher, no inhibitive effect is observed, even at low chloride concentration.

Conclusion

A comparison of the electrochemical characteristics of a nineteenth century steel and pure iron has shown that the adsorption phenomena associated with the chloride ions and glycols are much more readily discernible on the old steel. It appears that many of the differences are due to surface inhomogeneities on the steel. Since the steel is close to the composition of the wrought iron encountered in composite wood-metal artefacts, the data obtained in this study has provided an insight into the complex way in which iron behaves in aqueous glycol solutions in the presence of chloride ions. The apparent change from chloride being an inhibitor of iron corrosion at some concentrations and an accelerant at others partially explains why the *in-treatment* corrosion of iron composite materials changes with time and with the concentration of polyethylene glycol. During conservation treatment there is simultaneous outward diffusion of chloride and inward diffusion of the polyethylene glycol. As the relative concentrations of chloride and glycol change different corrosion characteristics are observed. The effects of large concentrations of organic components in aqueous solutions is best understood in terms of the behaviour of a mixed aqueous solvent system controlling the electrochemistry. Faced with such complex solutions, the use of a range of measurement techniques can be of great assistance in discerning different influences on the system. Comparison of pure, 'theoretical' substances and more applied 'everyday' materials is essential to avoid significant errors of interpretation.

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