Ascorbic Acid as Corrosion Inhibitor for Steel in Alkaline Media Containing Chloride Ions

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The investigation of nature-designed molecules and blends of naturally synthesized chemical compounds as possible inhibitor candidates for reinforcing steel in concrete is of raising interest due to the health and environmental hazards involved in the use of most inorganic corrosion inhibitors. In the alkaline media of concrete pore solution, the oxide film is present on the surface of the reinforcing steel. The ingress of chloride ions and/or carbon dioxide into the concrete destabilizes the passive film leading to a higher rate of metal dissolution through the appearance of localized forms of corrosion.

This study investigates pitting inhibition with ascorbic acid (AA), by analyzing the polarization curves in the presence and absence of the inhibitor. Inhibition action was evaluated from its ability to suppress the cathodic reaction of oxygen reduction as well as from its ability to suppress the onset of pitting. The mechanism of the inhibitor action was deduced by comparative interpretation of the inhibitor's molecular properties and the data obtained from electrochemical experiments.

Key words:
Reinforcing steel, corrosion, inhibition, alkaline media, ascorbic acid

Introduction

Corrosion of reinforcing steel due to the presence of chloride ions is one of the major causes of deterioration of concrete structures.[1] In the absence of chloride ions in concrete, a protective passive film composed of iron oxides and oxy-hydroxides forms at the steel surface.[2] However, passivity may be lost in the presence of the chloride ions, due to the change in composition, thickness and density of the passive film. The most common method of decreasing and preventing reinforcement corrosion is application of corrosion inhibitors. An ideal inhibitor would be a compound preventing corrosion without unfavourable effects on the properties of concrete and also without environmental hazards.[1] Generally, the inhibitors used in concrete are inorganic compounds such as phosphates, chromates, nitrites and nitrates, although some of them have toxic effects and pollute the environment. Organic inhibitors often considered as possible substitutes, are based on amines[3–5] or organic acids.[1,6,7] It is well known that the presence of an organic molecule in the corrosive media inhibits corrosion of metals by adsorbing at the metal-solution interface.

Modes of adsorption are dependent on the chemical structure of the molecule, chemical composition of the solution, nature of the metal surface and electrochemical potential at the metal solution interface. Among alternative corrosion inhibitors, organic compounds containing one or more polar functional groups, (with N, O, and S atoms) as well as heterocyclic compounds containing polar groups and π electrons have shown to be quite efficient corrosion inhibitors.[8] Polar functional groups usually act as reaction centres for the adsorption processes, where the adsorption bond strength is determined by electron density and polarizability of the functional group.

Application of small biomolecules such as ascorbic acid (AA) as environmental-friendly, low-cost, readily available corrosion inhibitors of rebar corrosion would be favourable. AA has already been proved as a good steel corrosion inhibitor in acidic[9,10] and neutral media[11,12] but no investigations of alkaline media have been done. The AA effect on the corrosion of mild steel in pH 2 – 6 solutions was investigated by *Ferreira* et al.[9] and AA was shown to act as a mixed type inhibitor. *Goncalves* et al.[10] have found that the presence of AA decreases the anodic current values of steel in 0.5 mol dm^{-3} Na$_2$SO$_4$ at pH 2.7, and have related

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the effect to the adsorption of AA at the active sites of the electrode surface and blocking of the water adsorption reaction that is involved in the oxide layer formation. *Sekine* et al.[11] tested the effect of several vitamins in $w = 0.3$ % NaCl solution and showed that AA had the best inhibition effect. The mechanism of corrosion inhibition was considered to be due to the chemisorption of AA molecules obeying the Langmuir adsorption isotherm. The inhibition effect decreased at higher concentrations due to the formation of iron chelate resulting in accelerated corrosion of steel.

In the present work, ascorbic acid was tested for its inhibition properties against rebar corrosion in alkaline media contaminated with chloride ions. The mechanism of adsorption has been deduced by means of electrochemical measurements and molecular electronic properties.

Experimental

The investigation of non alloy special prestressing steel (EN 10020) corrosion inhibition by ascorbic acid in a chloride-contaminated, simulated pore solution was performed using the electrochemical polarization method. Measurements were conducted on a manually constructed electrode ($d = 5$ mm), embedded in epoxy resin, with edges protected by an inert coating. The electrode was first mechanically abraded by 600 and 1200 grade emery paper, then degreased with ethanol and rinsed in redistilled water. The counter electrode was a carbon rod and the reference electrode was saturated calomel electrode (SCE). All the potentials reported, refer to SCE. Experiments were performed in saturated $Ca(OH)_2$ with the addition of NaCl (pH 12.5). The anodic and cathodic polarization curves were measured in separate experiments performed after half an hour of electrode immersion, starting from the OCP and proceeding towards the cathodic potentials or to the anodic potentials with a scan rate of $\nu = 1$ mV s^{-1}. Fast anodic scans were also done, at a scan rate of $\nu = 20$ mV s^{-1}. Potentiostatic transients were measured at the cathodic potential of $E = -900$ mV vs. SCE instantly after electrode immersion into the solution.

Results and Discussion

Fig. 1 shows segments of the fast anodic polarization scans in the presence of various chloride concentrations. Pitting was accompanied by almost vertical current increase and an accumulation of corrosion product at pitting sites permitted visual confirmation of localized attack.
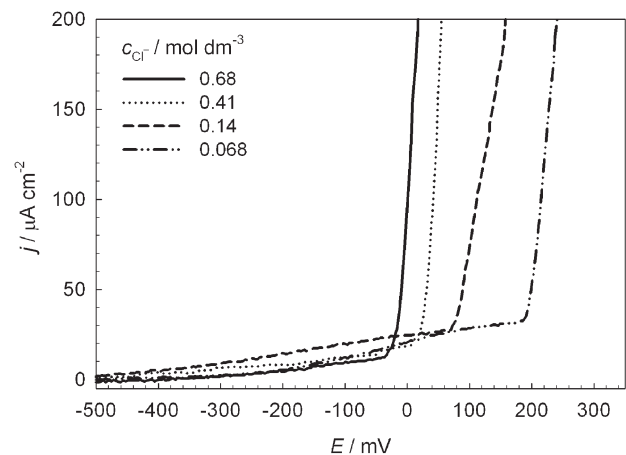

F i g . 1 – *Anodic polarization curves, for reinforcing steel in sat. Ca(OH)$_2$ with various chloride concentrations, recorded at a scan rate of $\nu = 20$ mV s^{-1}*

Under present experimental conditions, the pitting potentials were between -40 and +200 mV in the chosen range of chloride concentrations. Measured E_{pit} values are comparable to those in literature[12,13] obtained on reinforcing steel in sat. $Ca(OH)_2$ under similar conditions (chloride to hydroxide ion concentration ratio, pH, electrode preparation, scan rate).

Fig. 2 shows segments of fast anodic polarization scans recorded in the presence of various AA concentrations sat. $Ca(OH)_2$ + 0.14 mol dm^{-3} Cl$^-$. Maximum pitting potential, E_{pit}, shift has been measured for $c = 10^{-3}$ mol dm^{-3} AA. Maximum efficiency of 69 % at the same AA concentration has been observed previously by *Ferreira* et al.[9] in the case of the corrosion of mild steel in sulphate solutions of pH 2 – 6. Knowing that the localized corrosion initiation may be viewed as the outcome of a competitive process between the inhibiting properties of OH$^-$ and the breakdown-inducing effect of
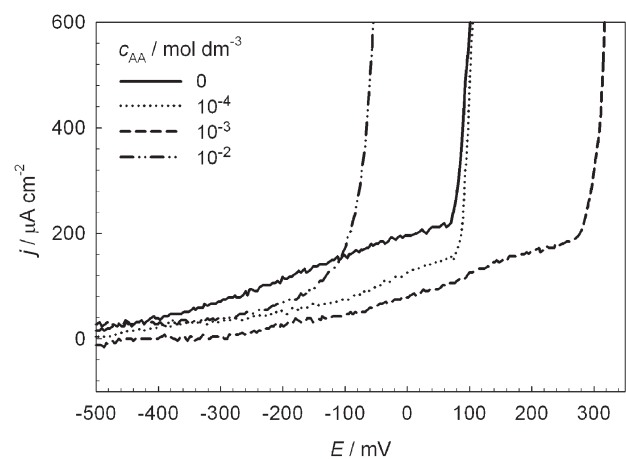

F i g . 2 – *Anodic polarization curves, for reinforcing steel in sat. Ca(OH)$_2$ + 0.14 mol dm^{-3} Cl$^-$ solution containing various AA concentrations, recorded at a scan rate of $\nu = 20$ mV s^{-1}*

Cl^{-14}, the higher E_{pit} in the system containing 10^{-3} mol dm^{-3} AA is suggestive of competitive adsorption of the inhibitor and Cl$^-$ anions. On the other hand, the decrease of E_{pit} at higher AA concentrations may be associated with the formation of soluble complexes. *Das* and *Sudresanan*[15] studied the electrochemical properties of carbon steel magnetite coating in 10^{-2} mol dm^{-3} AA. Impedance data showed that the interaction between magnetite and AA is associated with an incubation period, where the adsorption of ascorbate onto the oxide surface occurs, after which reductive dissolution takes place, where the ferric surface complex undergoes reduction to the soluble ferrous species and is transferred to the bulk solution. Formation of soluble AA – Fe(II) complex at AA fraction $> 200 \cdot 10^{-6}$ mol dm^{-3} has been confirmed by Mössbauer spectroscopy.[16]

The change of the open circuit potential (OCP) during the immersion period in the sat. Ca(OH)$_2$ + 0.14 mol dm^{-3} Cl$^-$ with different concentrations of AA is shown in Fig. 3. The sample without the addition of AA shows relatively steady potential shifting slightly, in time, towards the anodic direction and finally attaining values around –450 mV. However, the addition of 10^{-3}, $5 \cdot 10^{-3}$ and 10^{-2} mol dm^{-3} AA shifted the OCP significantly to cathodic direction, i.e. to the values around –520 mV, –900 mV and –670 mV, respectively. In the presence of lower AA concentrations ($c = 5 \cdot 10^{-4}$ and 10^{-4} mol dm^{-3}) the OCP is slightly shifted to anodic direction compared to the sample without inhibitor addition (OCP amounts to – 420 mV).

Corrosion properties of the reinforcing steel were further investigated by the method of quasi-potentiostatic linear polarization. Polarization curves with the addition of various AA concentrations are presented in Fig. 4. By observing the anodic side of the polarization curves, it could be de-
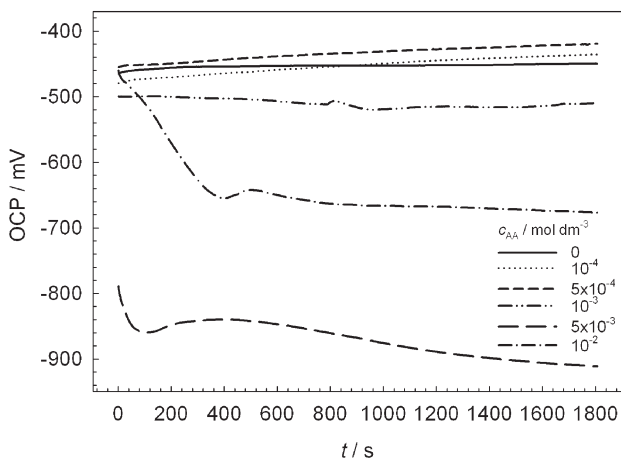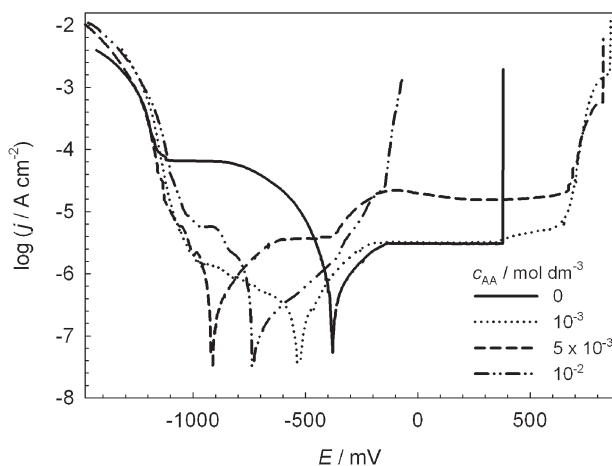

F i g . 4 – *Polarization curves of reinforcing steel in sat. Ca(OH)$_2$ + 0.14 mol dm^{-3} Cl$^-$ solution containing various AA concentrations, recorded at a scan rate of $v = 1$ mVs^{-1}*

duced that in the presence of AA, at all tested concentrations, no lowering of the passive currents occurs. The positive shift in the pitting potentials, in the presence of the inhibitor, indicates adsorption which retards pit nucleation. Also, in the presence of the inhibitor, significantly smaller pits were formed at the electrode surface compared to those formed in the solution without the inhibitor. In the $c = 5 \cdot 10^{-3}$ mol dm^{-3} AA solution, significantly higher anodic currents were obtained due to the dissolution of iron increased through the chelate formation. In the presence of $c = 10^{-2}$ mol dm^{-3} AA, a passive behaviour is not seen at all, probably due to the reductive dissolution taking place accompanied by oxidation of AA. Polarization results are consistent with a shift in the OCP being a direct consequence of the processes taking place at the interface.

The difference between the pitting potential and the corrosion potential, E_{corr} may be considered as a measure of the metals resistance to pitting corrosion,[17,18] i.e. the larger the difference between those two potentials, the higher resistance to pitting. The dependence of $E_{pit} - E_{corr}$ on AA concentration obtained from the polarization measurements is shown in Fig. 5.

A pronounced influence of the presence of the inhibitor on the cathodic oxygen reduction reaction is also apparent in Fig. 4. The cathodic current densities at – 1000 mV for various AA concentrations are shown in Fig. 5. The cathodic reaction inhibition probably works by blocking the oxygen reduction active sites.

For both the cathodic and the anodic reaction, the inhibitive effect increases with the increase in AA concentration up to $c = 5 \cdot 10^{-3}$ mol dm^{-3}. The highest effect was obtained in the 5×10^{-3} mol dm^{-3}

F i g . 3 – *Open circuit potential vs. time, for steel in sat. Ca(OH)$_2$ + 0.14 mol dm^{-3} Cl$^-$ solution containing various AA concentrations*
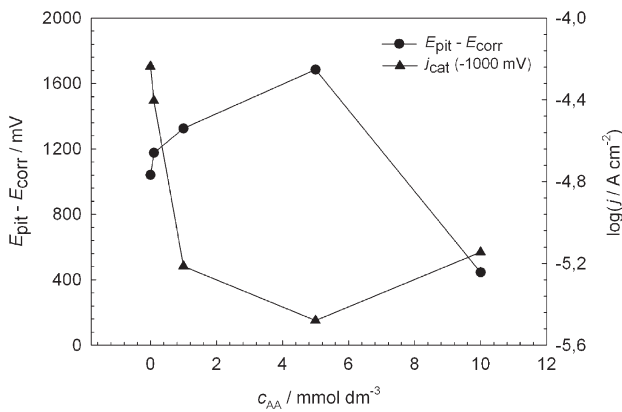
F i g . 5 – E_{pit}-E_{cor} and j_{cat}(–1000 mV) dependence on the AA concentration

F i g . 7 – *Surface coverage dependence on the AA concentration (symbols-experimental results; line – fitted results)*

AA solution, but due to the pronounced increase of the metal dissolution in the passive region, the protective properties when considering general corrosion are questionable, in spite of the pitting retardation. Lower concentrations have also shown some retardation of pit nucleation, e.g. for the 10^{-3} mol dm^{-3} AA solution, E_{pit} is almost 300 mV higher than that obtained without inhibitor addition.

In order to investigate more thoroughly the mechanism of cathodic reaction suppression in the presence of different AA concentrations, potentiostatic transients were measured at the potential $E =$ –900 mV in the region of the oxygen diffusion current (Fig. 6). The curves suggest a very fast adsorption process, especially at higher concentrations, since the constant currents were reached after only a few seconds. Electrode surface coverage, θ, was calculated from the cathodic current values after 60 s of immersion according to the formula $\theta = (j_{cat} - j_{0,cat})/j_{cat}$.[19] The dependence of the surface coverage on the AA concentration is presented in Fig. 7.
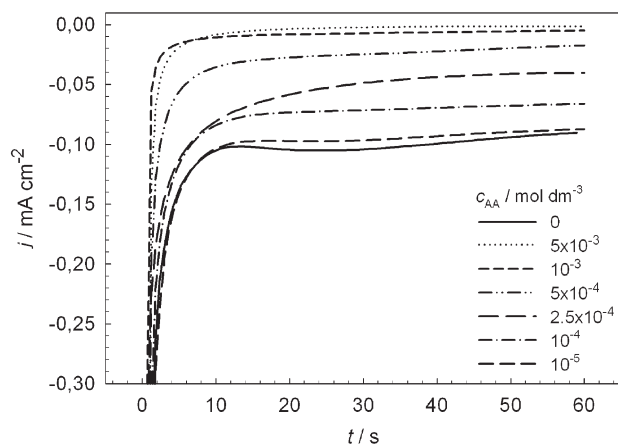

F i g . 6 – *Potentiostatic transients of the reinforcing steel in SPS measured at cathodic potential –900 mV vs. SCE with different AA concentrations*
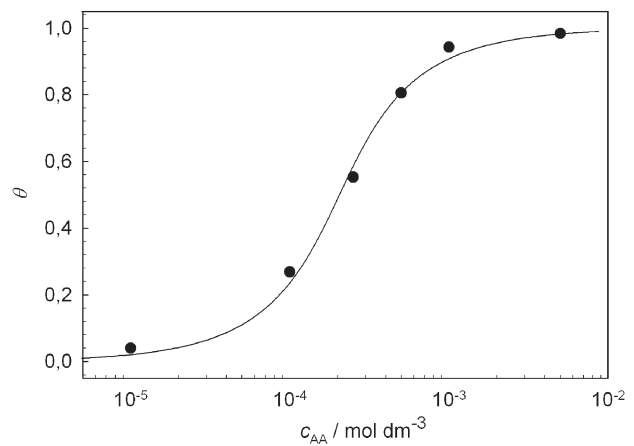
Since the inhibition works through the mechanism of adsorption of the inhibitor molecules on the metal surface, the use of adsorption isotherms provides useful insight into the cathodic reaction inhibition mechanism. The Frumkin adsorption isotherm:[8]

$$B\,c = \frac{\theta}{1-\theta}\,e^{-2a\theta} \qquad (1)$$

gave the best fit to the potentiostatic transient results. In Eq. (1), c is the inhibitor concentration, θ is the surface coverage, a is the attraction constant and B is the adsorption-desorption equilibrium constant linked to the free energy of adsorption, ΔG_{ads} by the equation:

$$B = \frac{1}{55.5}\exp\left(\frac{-\Delta G_{ads}}{R\,T}\right) \qquad (2)$$

Application of a nonlinear fitting procedure to the potentiostatic transient results yielded the values of ΔG_{ads} and a. The value of $\Delta G_{ads} = $ –28.5 kJ mol^{-1} indicates spontaneous adsorption of the AA at the metal surface, while the positive value of the attraction constant ($a = 0.866$) points to the presence of attraction forces between the adsorbed molecules.[20]

It is known that AA is unstable when present in a solution at pH higher than 4.[11] AA, being a weak organic acid, is readily doubly deprotonated at pH 12.5 forming the ascorbate anion. Since ascorbate anion is unstable and easily-oxidizable it is expected to be rapidly air-oxidized to dehydro-ascorbic acid (DAA) and eventually to 2,3-diketogluconic acid (DGA).[21,22] The final products of further decomposition are threonic (TA) and oxalic acid (OXA). The reaction is shown in Fig. 8.
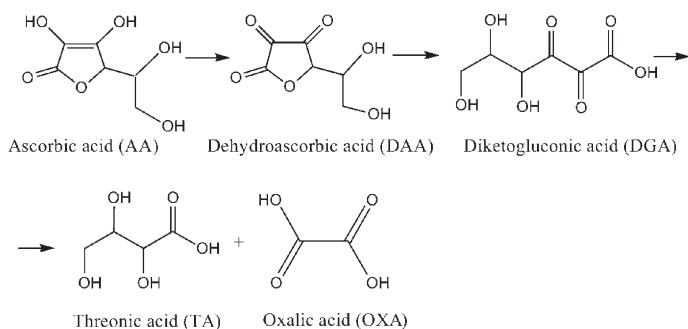
F i g . 8 – *Reaction pathway of ascorbic acid decomposition*

However, *Nishikawa* et al.[21] have reported that at pH 7.4, DAA can be reduced by AA anion and consequently degradation of DAA to DGA is suppressed. Contrarily, in the solutions of low pH, AA is present as an undissociated molecule and incapable of reducing DAA. This has been explained by the chemical characteristics and structures of the molecules involved. It has been demonstrated, by the molecular orbital method, that the elements of the molecular structure of AA anion are very similar to the monocyclic tri-ketone structure of the DAA. Considering the great electron donating ability of the AA anion, it is reasonable to assume that it would reduce DAA more easily than undissociated AA. Moreover, interconversion between AA and DAA would preserve these compounds form oxidative decomposition allowing them to adsorb at the metal surface. This assumption is partly corroborated by the comparison of the AA and OXA inhibitive action shown in Fig. 9 and OXA showing considerably lower corrosion inhibition efficiency than AA. Because of its known electron donating ability as well as the Fe(II) and Fe(III) chelating properties,[23] AA anion would be the most probable adsorbing species in the investigated system.
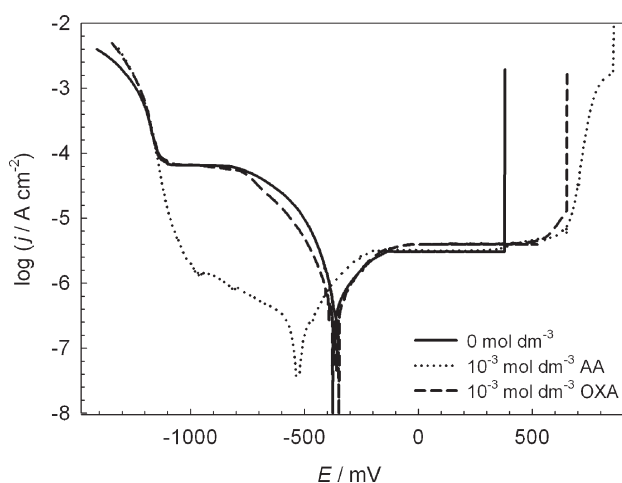

F i g . 9 – *Polarization curves for reinforcing steel in sat. Ca(OH)₂ + 0.14 mol dm⁻³ Cl⁻ solutions containing 10⁻³ mol dm⁻³ AA and 10⁻³ mol dm⁻³ OXA, recorded at a scan rate of 1 mVs⁻¹*

Conclusions

AA was proven as an excellent inhibitor for steel corrosion in the presence of chlorides in alkaline media in the time domain of the experiments. An optimal concentration of 10^{-3} mol dm^{-3} AA was shown to inhibit the cathodic oxygen reduction reaction with efficiency of 89 %, and retard the pitting nucleation with a shift of $E_{pit} - E_{cor}$ value by almost 300 mV compared to the solution without the addition of AA. In the presence of higher concentrations passivity of steel was distorted due to the reductive dissolution through the chelate formation. Reaction inhibition was shown to proceed through very fast adsorption process. Surface coverage following Frumkin adsorption isotherm enabled calculation of the value of $\Delta G_{ads} = -28.5$ kJ mol^{-1} indicating spontaneous adsorption of the AA at the metal surface. The positive value of attraction constant ($a = 0.866$) points to the presence of attraction forces between the adsorbed molecules.

List of symbols

a – Frumkin attraction constant

B – adsorption-desorption equilibrium constant, mol^{-1} dm^3

c – concentration, mol dm^{-3}

c_{AA} – concentration of ascorbic acid, mol dm^{-3}

d – diameter, mm

E – potential, V

E_{pit} – pitting potential, V

E_{corr} – corrosion potential, V

ΔG_{ads} – free energy of adsorption, J mol^{-1}

j – current density, A cm^{-2}

j_{cat} – cathodic current density, A cm^{-2}

OCP – open circuit potential, V

R – gas constant, (8.314 J mol K^{-1})

T – absolute temperature, K

t – time, s

χ – fraction, 10^{-6}

w – mass fraction, %

θ – surface coverage

ν – potential scan rate, mV s^{-1}

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