Significance of π–electrons in the Design of Corrosion Inhibitors for Carbon Steel in Simulated Concrete Pore Solution

A. Mohamed, D. P Visco, Jr., D.M. Bastidas*

Department of Chemical, Biomolecular, and Corrosion Engineering, The University of Akron, OH, USA

Aim

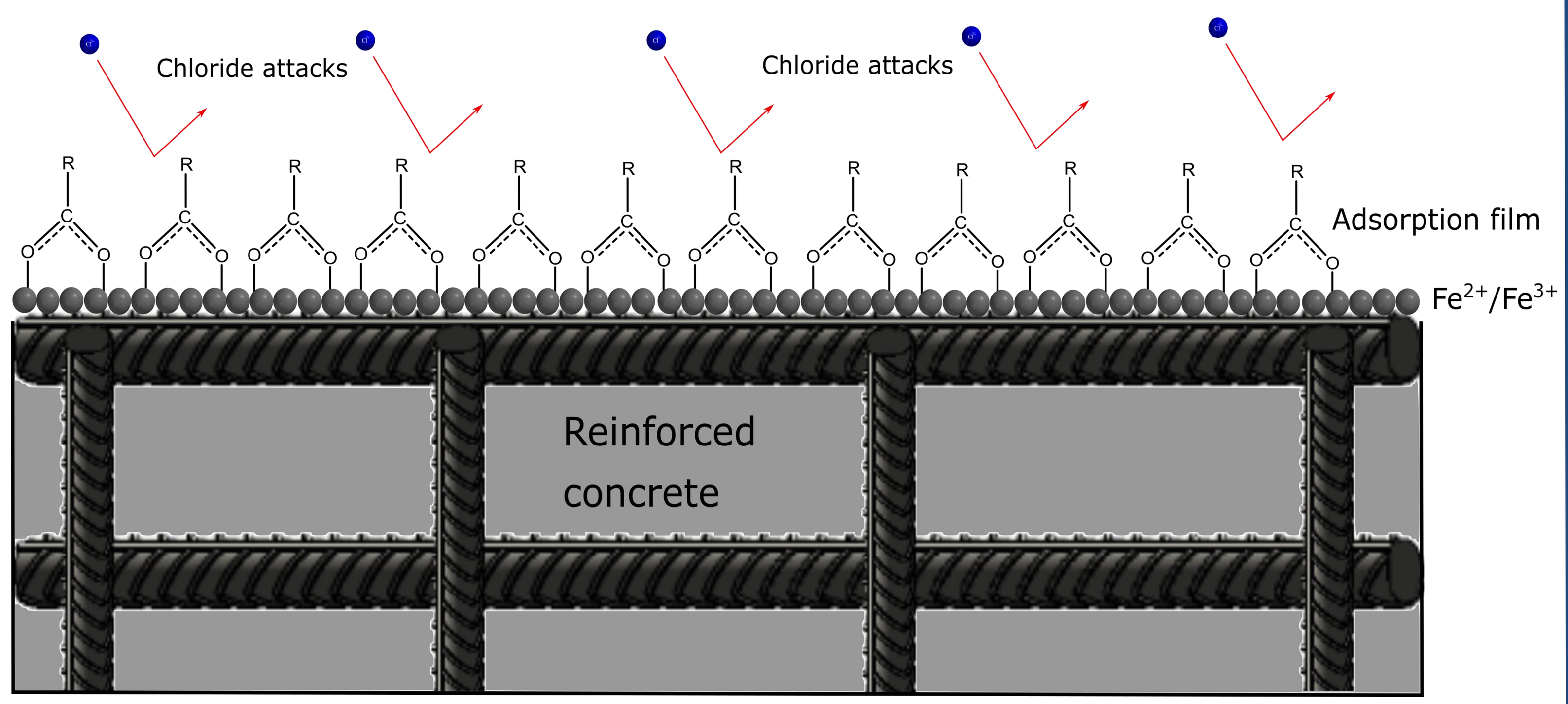
- To evaluate the significance of π– electrons on the anticorrosive properties of inhibitors through an experimental and a modelling approach.

Abstract

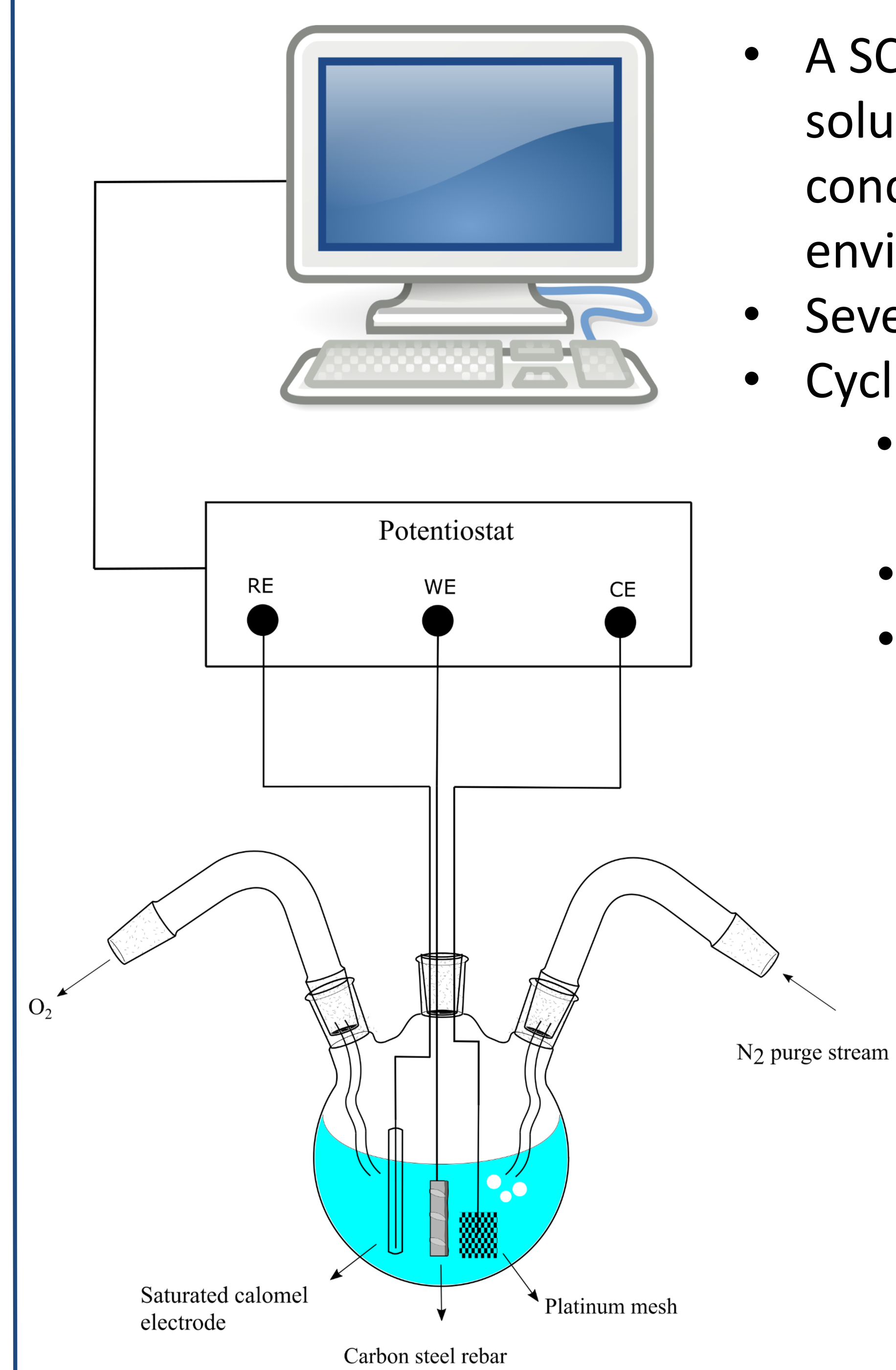
Corrosion inhibitors from different organic groups were tested on carbon steel in 0.1 M Cl^- contaminated simulated concrete pore solutions (SCPS). It was found that inhibitors possessing π–bond electrons in a functional group had better performance. This is attributed to the high tendency of donating π– electrons to the metal surface. Thus, creating a protective adsorption film during the chemisorption process. Another way to show the significance of this phenomena is by using a quantitative structure-property relationship (QSPR) using Signature descriptors. It was found that the atomic signature fragment that captures π– bond was the most influential - corroborating experimental results.

Introduction

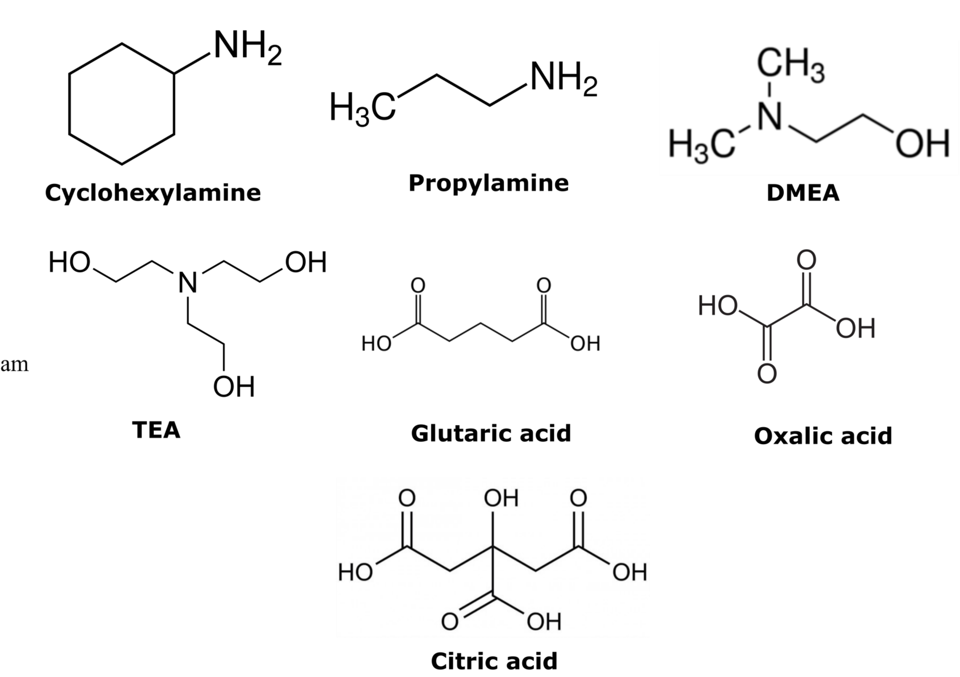
- Chlorides near marine environment diffuse into the concrete matrix creating an autocatalytic acid hydrolysis reaction, decreasing the local pH from 12 to 4, causing pitting corrosion.
- Formation of corrosion products on the surface of carbon steel in concrete causes an increase in volume and pressure. As a result, the concrete will crack and spall, thus losing its structural integrity.
- Many corrosion preventions methods have been introduced. However, corrosion inhibitors are one of the most popular as they are less costly and easy to use.
- Organic inhibitors create an adsorption film on the surface of the carbon steel rebar protecting it from chloride induced pitting corrosion, as seen in the figure below.



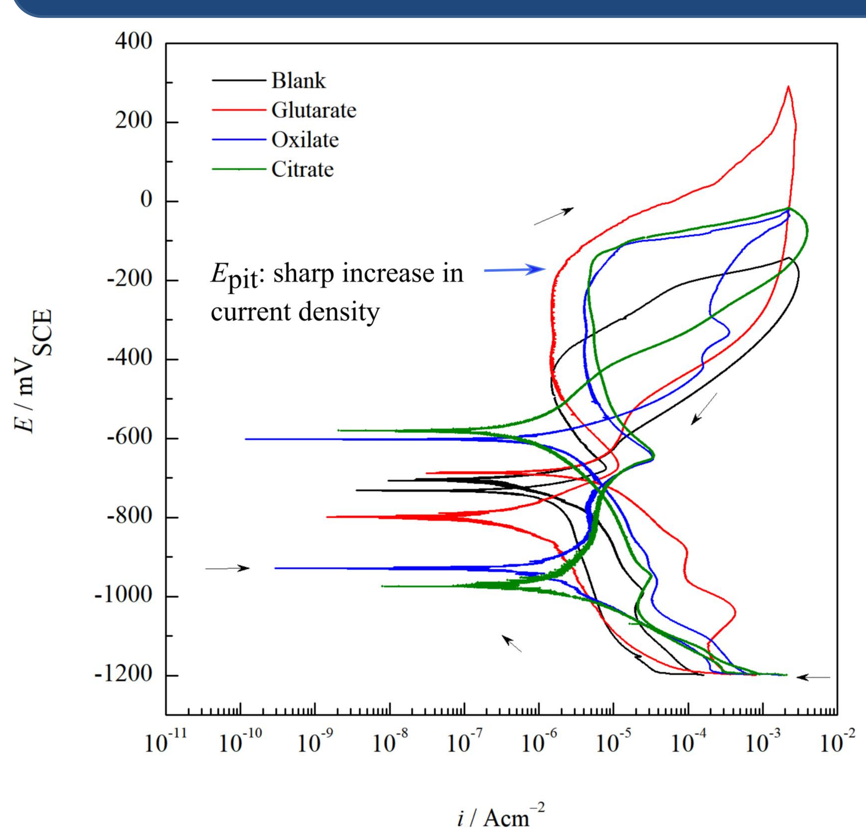
Experimental procedure



- A SCPS (pH=12.6) was used with 0.1M Cl^-. The solution was deareated to simulated buried concrete structures near marine environments.
- Seven 0.1 M inhibitors were used.
- Cyclic potentiodymanic polarization (CPP):
  - Forward/backward scan rate = 0.166 mV/s
  - Start and end potentials = −1.2 V_{SCE}
  - Current threshold = 2.2 mA/cm^2

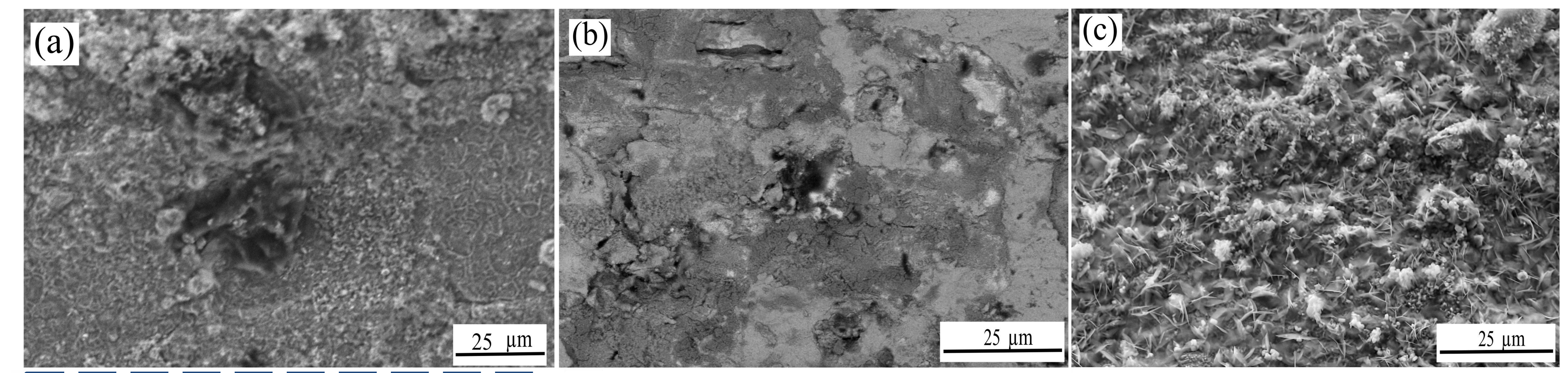


Results



- Poly-carboxylates increased the pitting potential significantly compared to the reference, as seen in the CPP. Thus, corrosion will be harder to initiate.
- Amines and alkanolamines showed moderate inhibition performance.
- The increased inhibition efficiency in poly-carboxylates is attributed the presence of π–bond electrons, making the inhibition process easier.

Inhibitor	Molecular Formula	Group	E_{pit} (mV_{SCE})
Reference (no inhibitor)	NA	NA	–430
Propylamine	C_3H_9N	Amines	–420
Cyclohexylamine	$C_6H_{13}N$	Amines	–200
Triethanolamine (TEA)	$C_6H_{15}NO_3$	Alkanolamines	–370
Dimethylethanolamine (DMEA)	$C_4H_{11}NO$	Alkanolamines	–410
Oxalic acid	$C_2H_2O_4$	Poly–carboxylates	–115
Glutaric acid	$C_5H_8O_4$	Poly–carboxylates	–150
Citric acid	$C_6H_8O_7$	Poly–carboxylates	–140



Reference	TEA	Glutaric acid
Clear formation of corrosion products and pit nucleation in unprotected carbon steel rebar.	Surface of the rebar shows lower signs of corrosion, as there are no corrosion products. However, pits were observed	Clear indication of an adsorption film on the surface of the rebar protecting it from corrosion

- Poly-carboxylates are chemically adsorbed on the surface of the metal through π–electrons in the delocalized hydroxyl group, due to ease of electron transfer. Thus, creating a protective adsorption film by forming different complexes on the surface.
- Amines and alkanolamines adsorb through lone pair electrons on the nitrogen atom causing water molecules to desorb from the surface of the rebar – protecting it.

Signature modelling

Variable	Height 1 Signatures	Regression coefficients
x_{19}	[O](=[C])	145.53
x_{16}	[N]([C][C][C])	216.88
x_{17}	[N]([C][C][H])	679.95
x_2	[C]([C][C][C][H])	194.61
x_8	[C]([C][H][H][N])	–158.94
x_{12}	[C]([H][H][H][N])	–239.13
x_6	[C]([C][C][H][O])	113.48
x_{10}	[C]([C][N]=[O])	354.22
x_{18}	[N]([C][H][H])	–120.87
Constant	–	86.46

- A Signature describes the connectivity of an atom in a molecule to its neighbors with a distance from the "root" atom called "height".

- QSPR with Signature descriptors correlates the occurrences of each atomic Signature to a property of interest using a forward stepping multilinear regression. In this study the dependent variable was the pitting potential, and the independent variable was the occurrence of each atomic signature in the dataset.
- Utilizing this method, the model chooses [O](=[C]) as the most significant atomic Signature that impacts the pitting potential. This Signature encapsulates π–bond electrons, thus the modelling results corroborate the experimental results.

Conclusion

- Inhibitors possessing π– bond electrons have better anticorrosive properties.
- The QSPR model agrees with the experimental results, showing the importance of π–bond electrons in the inhibition process.

References

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