

An experimental and theoretical study of the inhibition mechanism of organic substances in concrete

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ABSTRACT

Corrosion inhibitors are used to prevent chloride-induced corrosion in reinforced concrete structures. Several commercial inhibitors are available, but their efficiency and their inhibitive mechanism are not well understood. In this paper the inhibiting behaviour of five organic substances in delaying chloride-induced corrosion was evaluated in alkaline solution using EIS and potentiodynamic tests. The studied substances were sodium tartrate, sodium benzoate, sodium glutamate, DMEA and TETA. Theoretical calculations based on molecular mechanics and molecular dynamics were used to establish which functional groups bind to the passive film, the strength of their binding, the functional groups contributing to their filming, and their evolution with time.

Keywords: inhibitor, concrete, chloride, mechanism, efficiency.

1 INTRODUCTION

Steel reinforcements in concrete are normally passivated due to concrete's high alkalinity. However, this passive film can be destroyed mainly by two specific conditions: concrete carbonation and chlorides presence at the metal surface. The former causes a decrease in concrete pH, changing the steel condition from passive to active, whereas the latter provokes local breakdown of the passive film, originating pits on the metal surface. In most cases, the use of high quality concrete and adequate cover are enough to prevent corrosion [1]. Corrosion inhibitors are a very attractive prevention method, due to their low cost and easy handling. They can be added to the concrete mix as additives, or applied to the concrete surface and migrate towards the reinforcement. So far, most researches have focused on determining the efficiency of some organic substances as corrosion inhibitors, either in solution or in concrete; however, little has been done to determine the interaction mechanism between these substances and the passive film [2-7]. In this research, five organic substances were studied by theoretical and experimental methodologies in order to establish how their interaction with the passive film delayed corrosion initiation.

2 EXPERIMENTAL SET-UP

Tests and simulations were performed on five organic substances: sodium tartrate, sodium benzoate, sodium glutamate, dimethylethanolamine (DMEA) and triethylenetetramine (TETA). High purity commercial products, except for TETA, with a 70% purity, were used. Computer simulations using Molecular Mechanics (MM) and Molecular Dynamics (MD) techniques were used to establish which functional groups bind to the passive film, the strength of their binding, the functional groups contributing to their filming, and their evolution with time. Electrochemical test results from electrochemical impedance spectroscopy (EIS) and potentiodynamic tests (obtained from previous research) were used to confirm the proposed mechanism.

2.1 MM and MD simulation protocol

The interaction between the inhibitors and the passive film was studied using a simulation protocol [8]. Calculations were performed with Materials Studio Modeling v.3.2.0.0 software, using the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field. A force field simply gives the potential energy of the system as a function of the coordinates of all constituent atoms. In practice, it is expressed through appropriate bonded and non-bonded energy contributions. The solvent was modeled as a dielectric medium with a distance-dependent dielectric constant. The monolayers were composed of 16, 25 and 36 molecules distributed on the surface. They were disposed as close as possible to one another to check whether the intermolecular interactions affect the adsorption energy. Only the systems containing a monolayer of 36 molecules were then subjected to MD simulations. Energy minimizations with respect to all of the variables (the atomic coordinates) were done with the conjugate gradient algorithm. MD simulations were carried out at a constant temperature (300 K), controlled by the Berendsen thermostat. The integration of the dynamic equations was performed with the Verlet algorithm using a time-step of 1 fs (10^{-15} s), and the instantaneous coordinates (or frames) were periodically saved for further analysis or geometry optimization.

2.2 Electrochemical tests

Three electrochemical tests were carried out: potentiodynamic tests (PT) to determine pitting potential at increasing chloride content and increasing inhibitor dosage; free corrosion tests (FC tests) to establish time-to-pitting initiation at increasing chloride content and increasing inhibitor dosage; electrochemical impedance spectroscopy (EIS) tests to determine adsorption parameters. Specimens were machined from commercial reinforcing carbon steel: exposed surface area was 18 cm². Tests were carried out in simulated concrete pore solution (SPS), consisting of saturated Ca(OH)₂ at pH 13.0 by addition of Na(OH) 0.06 M, at room temperature (25°C). Potentiodynamic curves were recorded with an Autolab Potentiostat (PGSTAT 30). FC tests were performed at increasing inhibitor dosage: from 10⁻⁴ M up to 0.1 M. Specimens were passivated for 168 hours in SPS. Free corrosion potential was monitored daily from the immersion of specimens. When passivation condition were reached, 0.1 M NaCl was added to the solution. Potential measurements continued till initiation of corrosion. Potentiodynamic Tests (PT) were performed in a 0.1 M NaCl solution containing 0.1 M of inhibitor, starting from -1.2 V vs SCE, increasing the potential with a scan rate of 1 V/h. Pitting potential was evaluated as the potential corresponding to a sudden increase of anodic current density. EIS spectra were recorded after 48 hours of immersion of specimens in SPS, at progressive inhibitor concentrations from 10⁻⁴ M up to 0.1 M, every 48 hours. EIS spectra were obtained at corrosion potential (E_{corr}), using a signal amplitude of ±10 mV in a frequency range 100 kHz to 5 mHz. Experiment and data collection were carried out under computer control using FRA v4.8 software. Data were analyzed with ZSimpWin v3.10.

3 RESULTS

3.1 MD & MM Results

Table 1 reports the energy calculated for the adsorption of a single inhibitor molecule on the substrate at its most stable conformation after MM and MD calculations. The adsorption energy E_{ads} was calculated as following:

$$E_{ads} = E_{tot} - E_s - E_{mol} \quad (1)$$

where E_{tot} is the total energy of the system, E_s accounts for the energy of the γ -FeOOH slab and E_{mol} refers to the energy of the isolated inhibitor. The E_{mol} values reported in Table 1 gives the energy of each molecule due to stretching, bending, deformations with respect to the ideal values, and to the non-bonded interactions within the molecule. In the present context the values of E_{mol} must simply be taken as reference values for the isolated molecule to be used in equation (1) for calculating the adsorption energy of the inhibitor molecules subject to the surface interaction

through the total energy E_{tot} of the composite system. In fact, E_{tot} is calculated for the slab with the adsorbed inhibitor molecules through the same terms as before in their optimized, i.e., energy-minimized, geometry. Moreover, following standard procedures for MM and MD simulations, the whole slab was kept fixed at a given position in the numerical minimization of the potential energy, so that its contribution to the total energy of the system, E_s , is equal to zero, even though all of its surface atoms (slightly more than 11500) correctly interact with the adsorbate molecules and their pairwise interactions with all inhibitors atoms are taken into account. The optimized values of E_{tot} and the corresponding adsorption energies calculated with equation (1) are reported in Table 1. By comparing the resulting adsorption energies, it is possible to establish an adsorption ranking for the studied substances, where glutamate shows the strongest adsorption and DMEA the weakest one.

Table 1 – Energy for a single molecule of the inhibitors

	E_{tot} (kJ/mol)	E_{mol} (kJ/mol)	E_{ads} (kJ/mol)
Tartrate	-114	-16.39	-97
Benzoate	-111	-44.04	-67
Glutamate	-134	-34.18	-100
TETA	-323	-229.35	-94
DMEA	-122	-68.08	-54

In order to ascertain how the inhibitor molecules interact among themselves and with the substrate, monolayers containing 16, 25 and 36 molecules of inhibitor were regularly placed on the surface as close as possible to one another. Their energy was then minimized considering only isolated islands of molecules without periodic boundary conditions. Placing the molecules in a regular way allowed determining the presence of intermolecular interactions, and to check whether their overall effect is repulsive or attractive. To establish the differences in the average adsorption energy per molecule between the monolayer and the single molecule, the total energy of the system was divided by the number of molecules forming the monolayer. This value was introduced in equation (1) to obtain the adsorption energy per molecule, which is shown in Table 2. MD calculations were also performed in order to see the time evolution of the monolayer. Figure 1 shows an optimized snapshot of typical instantaneous conformations obtained. Detailed results are reported in [9].

Table 2 – Energy for a monolayer of 36 inhibitor molecules

	E_{tot} (kJ/mol)	E_{ads} (kJ/mol)
Tartrate	-111	-94
Benzoate	-117	-73
Glutamate	-133	-98
TETA	-304	-75
DMEA	-125	-57

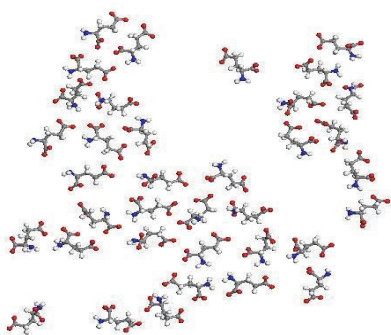


Figure 1 – Optimized snapshot of the monomolecular layer conformation for TETA

3.2 Electrochemical test results

Pitting potential around -0.25 V SCE was measured in the SPS without inhibitors. Tartrate and benzoate showed a significant inhibitive effect, since pitting potential increased up to +0.4 V SCE. TETA and DMEA increased pitting potential to +0.2 V SCE. Glutamate performances resulted to be worse than in the other cases. These results were confirmed by free corrosion tests through the measurement of time-to-pitting initiation, as reported in Figure 2: tartrate and benzoate showed best inhibition effect, while TETA and DMEA showed the worst inhibition, even at the highest inhibitor concentration. For carboxylate compounds time-to-corrosion increased with concentration.

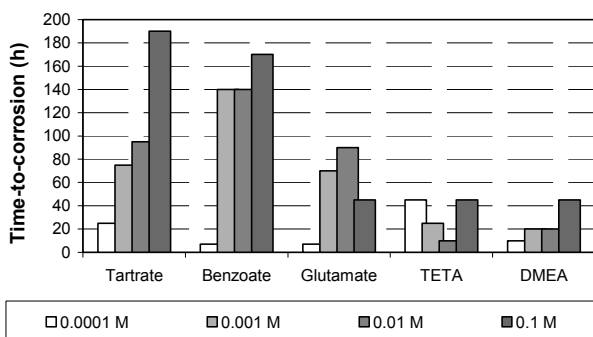


Figure 2 – Time-to-corrosion in SPS with NaCl 0.1 M

EIS spectra were used to derive adsorption parameters. Impedance response of the case study was investigated through the following equivalent electric: $R_s(Q_1R_1)(Q_2R_2)$, where R_s is solution resistance, Q_1 and R_1 represent processes occurring at high frequencies, thus corresponding to double layer capacitance and charge transfer resistance, respectively, Q_2 and R_2 are capacitance and resistance at low frequency range, describing redox processes occurring at the passive layer. The electric model adopted implies that R_1 and Q_1 describe the evolution of the interaction between substrate and inhibitor. A constant phase elements replacing

the pure capacitor was considered, in order to allow a non-ideal response of the system. The capacitance is therefore expressed in [$S \cdot s^p / cm^2$].

Figure 3 reports the evolution of R_1 and Q_1 at increasing inhibitor concentration. As expected, the charge transfer resistance, R_1 , increases as inhibitor concentration increases (i.e., with decreasing corrosion rate). Double layer capacitance, Q_1 , decreases as inhibitor concentration increases, indicating the formation of a homogeneous film ($n = 0.97$: the double layer is considered as pure capacitor).

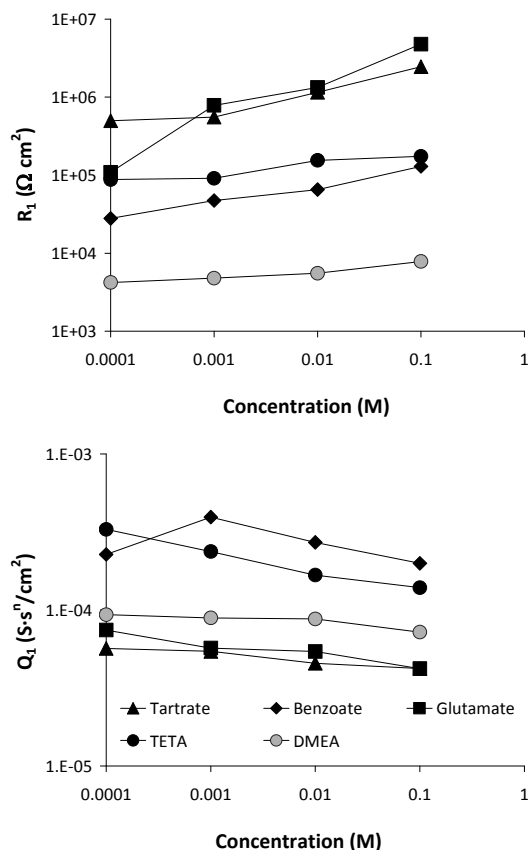


Figure 3 – Evolution of charge transfer resistance and double layer capacitance ($n = 0.97$)

4 DISCUSSION

Comparing the values in Tables 1 and 2, it is possible to notice that the adsorption energy tends to become slightly less negative, indicating the presence of repulsive forces between the molecules. The related change of position of the molecules (see detail in [9]) present on the substrate is due to the intermolecular interactions, either attractive or repulsive, in the presence of the attractive interactions with the surface. In fact, the presence of delocalized charges on the functional groups of different molecules may result in a repulsive force, which makes them drift apart. This is more evident in the case of the carboxylate groups present in

tartrate. Conversely, the presence of groups such as hydroxyls which form hydrogen bonds with either the carboxylate or the amino groups, may produce attractive interactions among the molecules and allow them to rearrange in different ways. This is more evident in the case of TETA, but it is also clear in tartrate. These findings apply to the monolayers of glutamate and DMEA, whereas the only inhibitor where no clear trend can be discerned is benzoate. Upon comparison of Tables 1 and 2, most inhibitors present more negative adsorption energies for the isolated molecules than for the monolayer. An increase in the number of molecules forming the monolayer could imply an increase in the adsorption strength: in fact, intermolecular attractive interactions, such as the formation of hydrogen bonds, may stabilize the film, with an energy drop. On the other hand, the outcome was the opposite one: more molecules produce a slightly less stable film due to enhanced repulsive interactions. However, it should be noticed that these results may be affected by the limitations inherent to these calculations, such as the use of a dielectric medium instead of the explicit solvent and the lack of periodic boundary conditions.

The MD runs carried out starting from the initial optimized monolayers with an implicit solvent suggest a different behavior among the different inhibitors. An even surface coverage is observed with tartrate and benzoate with only some random local clustering of molecules. A significant clustering of the glutamate anions can clearly be noticed due to the intermolecular dipolar interactions and hydrogen bonds: it shows a strong surface adsorption, but unlike tartrate and benzoate it tends to form isolated clusters, leaving many exposed surface areas. DMEA shows an even surface coverage, but a weaker adsorption, whereas TETA shows strong hints of a significant molecular clustering leaving exposed surface area.

The results of molecular simulations contributed to confirm the electrochemical test results. Glutamate and tartrate showed the highest charge transfer resistance (R_1), i.e. the lowest corrosion rate. In the absence of inhibitor values close to $10^3 \Omega\text{cm}^2$ are reported as charge transfer resistance for carbon steel in alkaline environment [1]. Glutamate and tartrate showed the lowest double layer capacitance (Q_1), which means the highest homogeneity of the adsorbed organic layer (Figure 3). As reported in [1], capacitance values lower than 10^{-3} S/cm^2 are typical of homogeneous adsorbed monolayers.

A possible mechanism of the inhibition effect produced by the organic substances tested as inhibitors can be based on the following feature: an inhibitor molecule must include a free electron pair to enhance adsorption on passive film. From this viewpoint, aminic and carboxylic groups show this characteristic as potential inhibitive substances. On the other hand, once a molecule is adsorbed on the substrate, it must cover as much as possible the whole exposed surface. As a final requirement, such adsorbed molecules have to compete with the polar molecules, or charged ions, present in solution, such as

water and chloride ions, since both can induce the detachment of the inhibitors. Therefore, an ideal inhibitor should show two basic requirements: 1) it must strongly adsorb to the surface; 2) it must cover the whole surface.

Electrochemical tests, namely FC tests and PT, have the important feature to give the final behavior as a result of the combination of the two above-discussed requirements. Tartrate and benzoate showed the highest pitting potential. The inhibition effect of these two organic compounds was also confirmed by the increase of time-to-corrosion: with the higher concentration of tartrate and benzoate corrosion occurred more than 160 h after chloride addition. This electrochemical results confirmed what obtained from MM and MD simulations.

5 CONCLUSION

The following can be concluded:

- / a favorable interaction energy with the surface of the adsorbed molecules, with repulsive intermolecular interactions, mainly among the anions, was confirmed. The presence of repulsive lateral interactions between the inhibitors' molecules was confirmed. Different cluster-type patterns were obtained for inhibitor molecules
- / glutamate showed the strongest adsorption energy and an enhanced tendency to clustering
- / tartrate and benzoate showed less negative adsorption free energy and uniform distributed pattern, leading to more efficient inhibiting effect
- / amines showed an intermediate behavior, most likely because of a balance between adsorption and clustering with respect to other substances

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