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# MECHANISTIC STUDIES OF THE CORROSION INHIBITOR OLEIC IMIDAZOLINE

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**Abstract**—An investigation of the mode of action of the corrosion inhibitor oleic imidazoline has been carried out using corrosion testing, second harmonic generation at surfaces and molecular modelling techniques. Selected variations to the molecular structure have been made to elucidate the relevant roles of the constituent parts of the molecule. Results show that the molecule is primarily bonding through the five-membered nitrogen ring which is lying planar to the metal surface, that the long hydrocarbon chain is playing an important role in the mechanism of inhibition, and that varying the chemistry of the pendant side chain does not affect the performance of the molecule to a major extent.

## INTRODUCTION

INHIBITION still represents the most cost effective and flexible means of corrosion control and remains a major consideration in current and future design and operation of North Sea Oil fields. The need to produce and transport oil and gas under increasingly more severe operating conditions is, however, placing a major strain on the performance of conventional corrosion inhibitors used for this service. Furthermore, more severe environmental legislation may restrict the continuing use of such conventional inhibitors.

To improve the current chemistry of oilfield corrosion inhibitors a fundamental understanding of the mechanism of action of these molecules is required. A survey of the literature in this area has shown that there are few studies that relate molecular structure to performance in a systematic way.[1] To this end a mechanistic study of the performance of the corrosion inhibitor oleic imidazoline (OI) has been undertaken.

OI is widely used as an active component in commercial corrosion inhibitor packages. Imidazoline based corrosion inhibitors are well known to have high corrosion inhibitor activity in acidic medium and therefore are used to minimise carbon dioxide induced oil field corrosion.

Derivatives of OI have been synthesised to assist in the determination of the inhibitor mechanism. The performance of these derivatives has been evaluated electrochemically using the linear polarisation resistance method under both bubble test conditions and the more severe flow loop conditions. Second harmonic generation (SHG) laser light scattering has been used to study the adsorption of OI and its derivatives on to metal surfaces. Molecular modelling has been used to investigate the relative roles of the constituent parts of the molecules.

## BUBBLE TEST CORROSION APPARATUS. 1 LITRE CAPACITY OIL/BRINE:UP TO 50/50. TEST ELECTRODES: FLUSH - MOUNTED IN RESIN; SURFACE AREA 3.8CM²
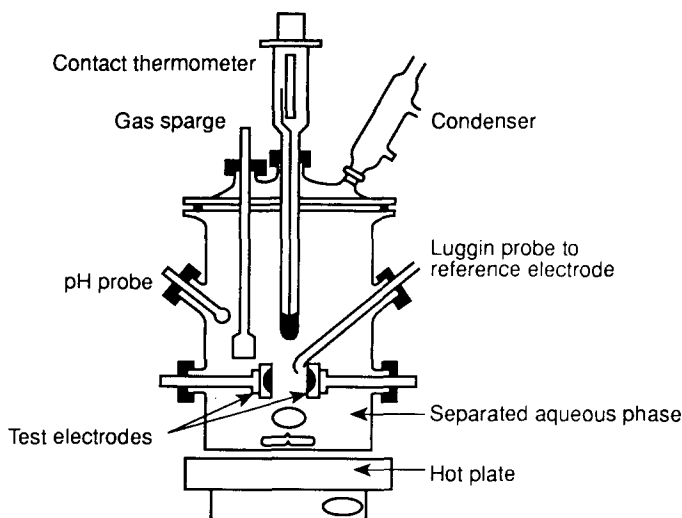


FIG. 1.   Bubble test corrosion apparatus.

### EXERIMENTAL TECHNIQUES

*Corrosion testing*

*Bubble tests.* All measurements were undertaken in a standard bubble test cell which is shown in Fig. 1. The corrosion rate measurements were undertaken using a standard three-electrode arrangement incorporating carbon steel test electrode, counter electrode and an SCE reference electrode. The cell design allows for continuous gas sparging for the duration of the test and also for gentle agitation of the solution. The carbon steel test electrodes were prepared by polishing to a 600 grit finish with silicon carbide paper, etching with concentrated HCl for 2 min before being thoroughly rinsed with de-ionised water and washed with acetone. The test solution was a simple 10% NaCl solution at room temperature $23 \pm 2°C$ which had been de-aerated with nitrogen for 90 min and then saturated with carbon dioxide prior to commencement of the experiment.

The performance of the corrosion inhibitors was measured at a range of concentrations (0, 1, 2, 5, 10, 20 and 50 ppm). For each corrosion inhibitor concentration a fresh solution and electrodes were used. The performance of the corrosion inhibitors were then compared at a concentration of 10 ppm. This gave good corrosion efficiency (90%) for OI in the bubble test to which the derivatives were compared.

*Flow loop tests.* Comparative corrosion assessment was undertaken in a standard recirculating corrosion flow loop, details of which have been described previously.[2] The loop is shown schematically in Fig. 2. Again the performance of the corrosion inhibitors were compared in a simple 10% NaCl brine under flowing conditions ($2 \text{ m s}^{-1}$) at 35°C. The test solution was fully de-aerated with nitrogen and then saturated with carbon dioxide prior to any corrosion rate measurements being undertaken. The corrosion rate measurements were made on carbon steel test electrodes the design of which has been described previously.[2] The corrosion inhibitor performance for the best performing corrosion inhibitors from the bubble tests were compared at a corrosion inhibitor concentration of 10 ppm. Results showed that 10 ppm is an optimum concentration.

*Second harmonic generation*

Second harmonic generation (SHG) at surfaces is an optical laser technique, by which molecular adsorption from solution on to a solid surface can be probed.[3] The second harmonic response, whereby a fraction of the incident fundamental beam is converted into a spatially coincident beam at twice the
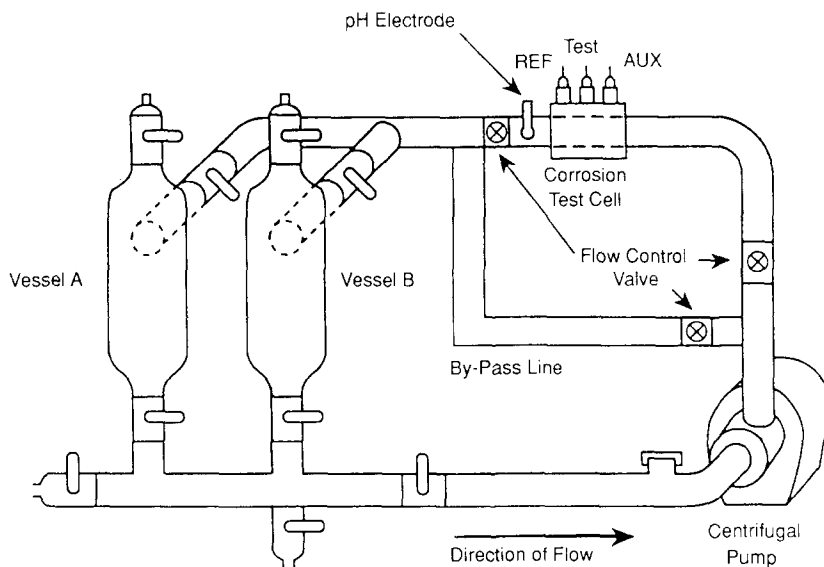
FIG. 2. Schematic of flow loop.

original frequency, depends on the nature of the surface and any species adsorbed at it. Second harmonic generation is extremely surface specific because it is governed by symmetry selection rules such that it only occurs in non-centrosymmetric media. This condition is met at the interface between two centrosymmetric media, such as a metal immersed in an electrolyte. Consequently, the second harmonic signal is generated by only the top few atomic layers of the metal and any overlayer present. This technique is sub-monolayer sensitive. However, the conversion efficiency is very low, so a high peak power, short pulse laser is required.

An active corrosion inhibitor such as OI can be adsorbed on to a metal surface in an electrochemical cell and followed in real time by SHG.[4,5] Green laser light at 532 nm is used as the input beam, with the second harmonic signal being detected at 266 nm in the ultraviolet (see Fig. 1 in the previous paper[6]). The mild steel electrodes are ground and polished with diamond suspension to $1 \mu m$ providing good reflectivity. They are then cycled electrochemically to produce a clean oxide-free metal surface. The observed increase in the SHG signal as the corrosion inhibitor is added to the system corresponds to a change in the open circuit potential of the electrochemical cell, indicating that the molecule has adsorbed on the metal surface. The magnitude of the SHG signal gives an indication of the coverage and interaction strength. The speed of change of the signal gives a measure of the rate of adsorption. These can be qualitatively compared between different inhibitor molecules. For OI the SHG signal intensity reaches a plateau at 10 ppm bulk concentration. This supports previous work[7] on the adsorption of radioactive OI on to iron powder, which showed that a monolayer would form at a concentration of approximately 10 ppm in the bulk electrolyte. These results correspond well with the good corrosion efficiency found for OI at 10 ppm.

The SHG technique can also be used to provide information about orientation of adsorbed species if the dipole moment is known or can be calculated.[5,8] The input laser beam is polarised at 45° with respect to the electrode surface and the emitted SHG signal is measured as a function of polarisation.

*Molecular modelling*

The Quanta/Charmm suite of programs was used to investigate molecular properties of OI and its derivatives for correlation with experimental data. The properties that were examined were: the electronic configuration of the molecule, the partial atomic charges of the atoms in the molecule; the molecular electronic energy levels; the molecules' conformational preferences (planarity and orientation of pendant groups); the flexibility or swept volume and radius of gyration of the tail group. Also the mean packing area, and fractional free volume of the molecules when packed as a Langmuir plane were investigated.
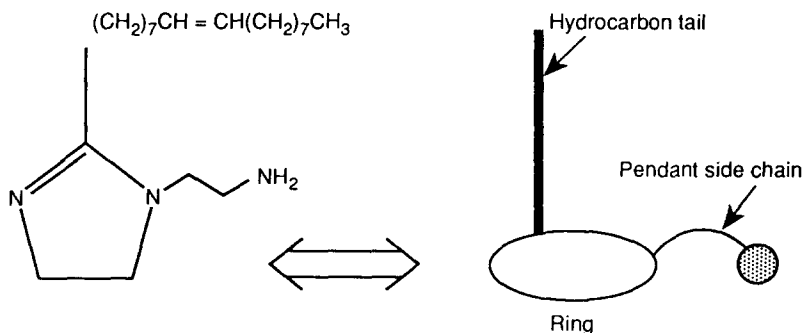
$(CH_2)_7CH = CH(CH_2)_7CH_3$

N

N

$NH_2$

Hydrocarbon tail

Pendant side chain

Ring

FIG. 3.    Representation of oleic imidazoline.

## EXPERIMENTAL RESULTS AND DISCUSSION

OI can be considered as being comprised of three components: a ring or head group, a tail composed of a long hydrocarbon chain and a pendant side chain consisting of a short hydrocarbon chain with an active functional group on the end (see Fig. 3). OI itself is composed of a five membered ring containing two nitrogen atoms, an oleyl hydrocarbon tail and a $CH_2CH_2-NH_2$ pendant group. Potentially, changes can be made to the ring, tail or pendant group.

The prevalent theory on the mechanism of OI as a corrosion inhibitor proposed that the lone pair of electrons on the amine group on the pendant side chain was determining the molecule adsorption and anchoring it to the metal surface. A possible precedent for this is the fact that many aliphatic amines also act as corrosion inhibitors. The ring structure was potentially opening to provide a second amine to bond with the surface thereby explaining the better corrosion inhibition over the single amine inhibitor. The long hydrocarbon chain was interpreted as being hydrophobic in nature and driving the molecule to the surface as well as acting as barrier to water and corrosion products. Changes have been made to OI to investigate these concepts, elucidate the mechanism of action of OI for corrosion protection, and to suggest improvements to the molecule (see Table 1).
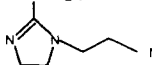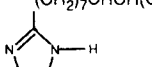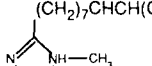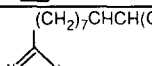
An initial baseline corrosion test against concentration for OI was undertaken. Figure 4 shows a corrosion calibration curve for pure OI in 10% NaCl de-aerated with nitrogen and saturated with carbon dioxide. The corrosion rates were determined for carbon steel by the linear polarisation resistance method. As can be seen on the addition of 2 ppm corrosion inhibitor the corrosion rate falls to below 10 mpy (70% efficient) and at concentrations in excess of 5 ppm corrosion rates below 3 mpy (90% efficient) were observed. Very little variation in corrosion inhibitor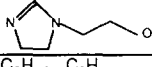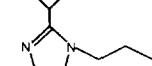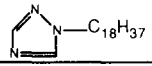 performance was observed on increasing the inhibitor concentration in excess of 100 ppm. At 10 ppm OI gave a corrosion rate of 2.5 mpy (92% efficient). Full corrosion rate calibration curves have been obtained for each compound. For comparison, however, data are presented for a dosing rate of 10 ppm (see Table 1).

SHG experiments showed that 10 ppm was required to give a full monolayer coverage on a polished steel electrode for this class of molecules.

*Changes to the pendant side chain*

The pendant side chain was thought to be anchoring the molecule to the metal

TABLE 1.

## MOLECULES SYNTHESISED AND TESTED

| Molecule | Structure | | Corrosion rate mpy | Corrosion rate mpy |
|---|---|---|---|---|
| | | | Bubble test | Flow loop |
| | Baseline Corrosion | | 30.0 | 50.0 |
| OI | $(CH_2)_7CHCH(CH_2)_7CH_3$ [imidazoline structure with $NH_2$ pendant] | | 2.5 | 5.0 |
| CI - 1 | $(CH_2)_7CHCH(CH_2)_7CH_3$ [imidazoline structure with N—H] | | 7.0 | |
| CI - 2 | $(CH_2)_7CHCH(CH_2)_7CH_3$ [imidazoline structure with $NH$—$CH_3$] | | 3.0 | 6.5 |
| CI - 3 | $(CH_2)_7CHCH(CH_2)_7CH_3$ [imidazoline structure with OH pendant] | | 3.0 | 6.5 |
| CI - 4 | $(CH_2)_7CHCH(CH_2)_7CH_3$ [imidazoline structure with $NH_2$ pendant] | | 3.0 | |
| CI - 5 | $(CH_2)_3CHCH(CH_2)CH_3$ [amide structure with two $NH_2$] | 50:50 OI:Uncylised | 12.0 | |
| CI - 6 | $(CH_2)_3CHCH(CH_2)CH_3$ [amide structure with two $NH_2$] | 24:76 OI:Uncylised | 12.0 | |
| CI - 7 | $CH_2CH_3$ [imidazoline structure with OH pendant] | | 26.0 | |
| CI - 8 | $C_9H_{19}$  $C_8H_{17}$ [imidazoline structure with OH pendant] | | 2.5 | 6.0 |
| CI - 9 | [triazole structure]—$C_{18}H_{37}$ | | 12.0 | |
| CI - 10 | [bicyclic structure] $C_{18}H_{37}$ | | 5.0 | 15.0 |
| CI - 11 | [bicyclic structure] $CH_3$ | | 12.0 | 28.0 |

surface through the lone electron pair on the nitrogen in the amine group and was therefore thought to be integral to the mechanism of adsorption of the molecule.

The pendant side chain in oleic imidazoline consists of a C2 chain with an amine group on the end (see Fig. 3). Several changes were made to the pendant group to
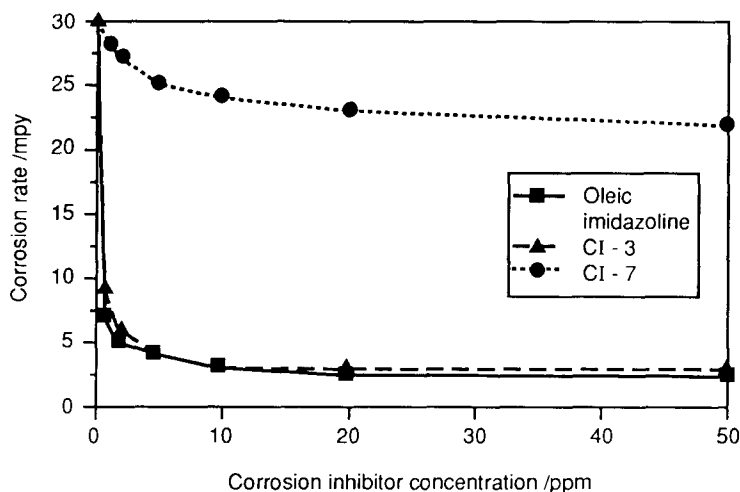
FIG. 4.   Corrosion calibration curve for oleic imidazoline, CI-3 and CI-7.

elucidate its role in the corrosion inhibition effectiveness of OI. In molecule CI-1 the chain was removed completely. The corrosion rate for this molecule rose from 2.5 mpy for OI to 7 mpy showing that the molecule was still acting as a corrosion inhibitor but that it was not as effective. On adding a single CH3 group to the ring the corrosion rate dropped to 3.0 mpy, close to that of OI itself. From this it can be concluded that a pendant side chain is required to improve the effectiveness of the molecule although it would not appear that an electronegative moiety is required.

On substituting the $NH_2$ in OI group for an OH the corrosion rate was similar to that of OI in both the bubble and flow loop tests. This showed that the nature of the group on the end of the side chain was not critical to the mode of action of the inhibitor. This did show, however, that the ring was not breaking during the adsorption on to the metal surface thereby allowing two amines to bond. The SHG signal for CI-3 showed that the energy of adsorbtion was similar to that of OI. It did, however, require slightly less concentration to form a monolayer, 7–8 ppm. The presence of the two lone pairs of electrons on the oxygen might lead to the expectation that the hydroxyl derivative would adsorb more strongly than the OI. This was not found to be the case in the SHG experiments where a similar signal was found for both OI and CI-3, or in the flow loop tests where a more loosely bound molecule would be removed from the metal surface due to the increase in surface shear stress decreasing the corrosion efficiency.

Molecular modelling showed that an odd even effect in the number of carbons in the pendant side chain might be taking place (see Fig. 5). It was proposed that this might affect the ability of the lone pairs on the oxygen or nitrogen to interact with the metal surface. A minimum energy conformation of the molecule showed that inserting another $CH_2$ in the pendant side chain would allow the lone pair to be directed towards the surface. Molecule CI-4 was synthesised and tested and gave a similar performance to both OI and CI-3, proving that this effect is insignificant.

From the change made to the side chain it has been shown that although a pendant chain is necessary, its size, in terms of the number of carbons, and the actual chemistry of the end group does not play a critical role in the effectiveness of the
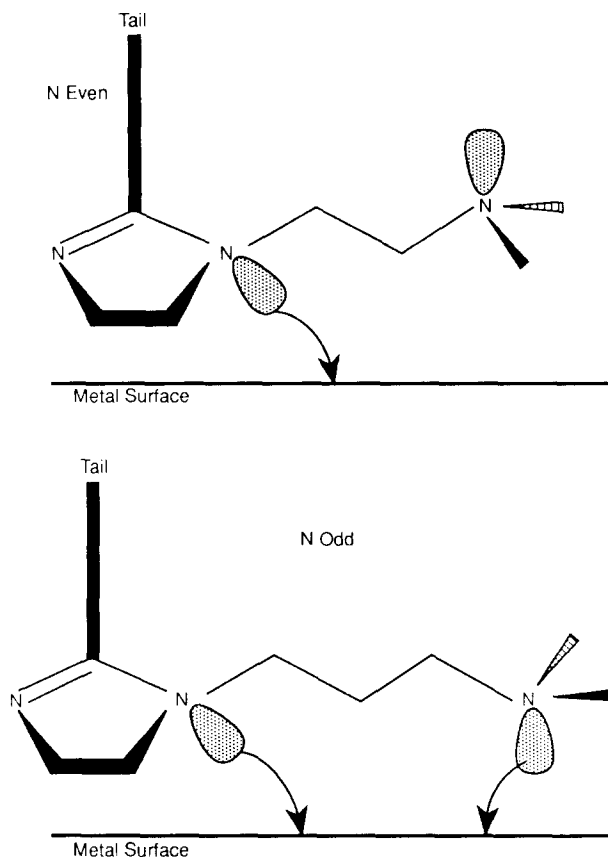
FIG. 5.   The effect of the number of methylene spacers on the pendants arm's ability to interact with the surface.

inhibitor. From this it can be inferred that the five membered ring is playing a major part in the adsorption of the molecule to the surface.

### The effect of the hydrophobic chain length

Removal of the C17 chain and replacement by a C2 (CI-7) chain drastically reduced the effectiveness of the corrosion inhibitor. The corrosion rate increased from 2.5 mpy for OI to 26 mpy for CI-17. The hydrophobic chain is therefore playing a major role in the action of OI as an inhibitor. SHG experiments of CI-7 showed that it adsorbed just as strongly, and that the rate of adsorption was similar, as CI-3 or OI indicating that the hydrophobic chain is playing little part in driving the molecule to the surface.

The effect of packing of the molecule was investigated by branching the chain (CI-8) whilst keeping the total carbon content at C17. It had been proposed that this molecule would not be effective as OI with its straight chain, since the branched chain version could not pack as efficiently on the surface. In both bubble and flow loop tests CI-8 was just as effective as OI and its hydroxy substituted derivative CI-3.

The molecular dynamics showed that the presence of the two short chains (CI-8)

caused, through mutual repulsion, a large swept volume to be occluded by the chains when compared to the single chain on OI. From this it can be inferred that the larger swept volume of the branched chain causes more of a barrier per head group than the straight chain version. From this it can be predicted that a marginally lower concentration would be required to form a monolayer.

### The effect of cyclisation

The effect of hydrolysis and ring opening on the performance of oleic imidazoline were investigated by preparing mixtures of OI and the uncyclised precursor. Sample CI-5 consisted of a 50:50 mix of the two and gave a corrosion rate of 12 mpy compared to 2.5 mpy for a pure sample of fully cyclised OI. A 76:24 sample of uncyclised to OI (CI-6) also gave a corrosion rate of 12 mpy. From this it can be shown that the cyclised version is a better performer than the uncyclised. The ring structure is obviously playing an important part in mechanism/adsorption of OI.

### Changing the head group chemistry

Molecules with variations on the head group chemistry (CI-9-11) were synthesised and tested. Two different heterocyclic head groups containing nitrogen were chosen on the premise that it was the nature of the ring structure and the nitrogen atoms in them that was causing the strong adsorption to the metal surface. These molecules were synthesised and tested to see if the corrosion protection and adsorption to the metal surface could be improved. Both head groups were synthesised with long (C18) hydrophobic chains which, from the previous work, were found to be effective corrosion barriers.

A five-membered ring containing three nitrogen atoms (CI-9) was tested giving a corrosion rate of 12 mpy. Clearly not as good as OI or its derivatives. CI-10 contained a double ring with three nitrogen atoms and a C18 tail. This molecule gave a corrosion rate of 5 mpy which compares well with OI in the bubble test. In the flow loop test however the corrosion rate for CI-10 increased to 12 mpy compared to 6 mpy for OI. Either the double ring is not adsorbing on the metal surface as strongly as OI and is more easily removed from the metal surface in flowing conditions or else is adsorbing as strongly but is more easily removed. Removing the tail from this molecule (CI-11) increased the corrosion rate to 12 mpy in the bubble test. A similar increase in corrosion rate for molecule CI-11 when compared to OI was found from the flow loop tests.

### OI orientation

The dipole moment of the molecule OI was calculated using the PM-3 Hamiltonian in the semi-empirical package MOPAC-6. Results from the SHG experiments indicated that the dipole moment of adsorbed OI was 32° with respect to the metal surface. Two possible orientations of the molecule can be deduced from these results: first, that the imidazoline ring resides sharply tilted towards the normal, or, secondly, that the ring lies parallel to the surface. The latter interpretation is the more likely with the ring flat on the surface and bonding to the metal through the nitrogens in the ring. This is supported by the fact that the removal or substitution of the pendant side group does not affect the adsorption process or corrosion efficiency to a significant extent.

*Molecular modelling*

Calculation of the partial atomic charges (using the MOPAC-6 semi-empirical program) of each of the atoms in the molecules showed no correlation with corrosion efficiency. This is probably due to the change in the partial charges when the molecule adsorbs, due to the donation of charge to and from the electronic bands in the metal. The molecular orbital energies were then calculated. In these, the two most commonly used descriptors of molecular interactions are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Unfortunately, no correlation was found for either the HOMO, LUMO or the magnitude of the HOMO–LUMO energy gap with the corrosion efficiency of each of the molecules. Analysis of the dipole moments and polarisability showed no clear trends with inhibitor efficiency. Clearly a more sophisticated model of the inter-actions between the metal and the molecule is required.

The minimum energy conformations of the molecules synthesised did show how variations in the tail shape and therefore the packing of the molecule on the surface might effect the corrosion efficiency.

*Packing analyses of corrosion inhibitors on Langmuir surfaces using molecular modelling*
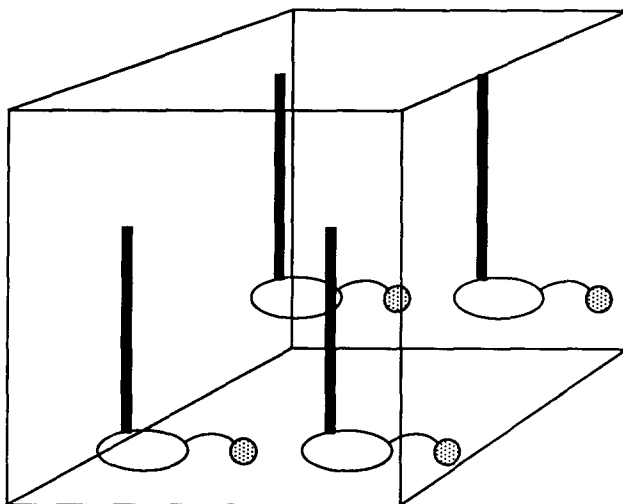
OI and CI-8, representing straight and branched chain molecules, were packed in 2-D hexagoinal close packed layers (in hexagonal primitive unit cells with one molecule per unit cell). The hexagonal cell was chosen as being representative of the packing on the surface. The cell dimensions were then optimised using molecular mechanics calculations.[8]

The results showed a stable configuration for the packed structures with an in the plane repeat of 10.5 Å for the straight chain and 11.7 Å for the branched chain molecule. To investigate the permeability of these monolayers, molecular dynamics calculations were performed at 293 K at the 10.5 Å spacing. The ring atoms of the inhibitor molecules were fixed in order to simulate their interaction with the surface, and the simulation was run for 3000 fs. The radius of gyration (the mean mass weighted radius of a cylinder that would encompass the molecule, see Fig. 6) and the free volume were calculated for the individual time steps in the simulations. The free volume (see Fig. 6) is the space left in a box, encompassing the simulation, when the van der Waals volumes of the atoms have been removed. The constraints on the rings were then removed and the simulations run for another 300 fs.

The results showed that the mutual chain repulsions caused an increase in the free space between the chains for both molecules, and that the radii of the gyration chains increased towards a limiting value throughout the simulation. It was also interesting to note that the di-aliphatic or Y-shaped molecule (CI-8) had a lower free volume, i.e. had less free space to allow permeation of gas molecules than the straight imidazoline.

For comparison with the experimental program, an imidazoline with two tails (CI-8) was simulated. The molecular dynamics showed that the presence of the two short chains caused, through mutual repulsion, a large swept volume to be occluded by the chains. This result correlated directly with the experimental observations that the corrosion inhibition performance of the molecule was nearly as good as that of OI.

Free volume is defined as the maximum volume encompased by the system in cubic angstroms minus the van der Waals volume of the atoms that make up the system.



The existance of free volume in structure can be associated with greater permeability to ion migration

FIG. 6.   Definition of free volume.

## CONCLUSIONS

(1) The pendant side chain is not the primary means of anchoring the molecule to the metal surface. The presence of a pendant side chain increases the corrosion inhibition performance but it appears that the chemistry of the active group or the number of carbons in the chain is not critical to that function. Changing the $NH_2$ to an OH has little effect on performance.

(2) The long hydrocarbon chain is critical to the effectiveness of OI as an inhibitor. It is not, however, playing an important role in driving the molecule to the surface. Molecules with and without the chain adsorbed at a similar rate and equally strongly. Branching the chain had little effect on the corrosion rate.

(3) The effect of cyclisation was investigated. It was found that OI performed better than its uncyclised precursor. From this it can be concluded that the imidazoline ring is not opening on adsorption to the metal surface and that it is playing a critical role in bonding to the metal. SHG and molecular modelling techniques used in concert showed that the ring lies flat on the surface of the metal.

(4) Changing the head group chemistry showed no significant improvement in performance over OI. Both changes in the number of nitrogens in the ring and the size of the ring gave molecules which gave good corrosion protection.

(5) Calculation of the electronic properties of OI and its derivatives showed little or no correlation with experimental results. More sophisticated models are needed to model the interaction of the molecule with the metal surface.

(6) Packing calculations using molecular mechanics and dynamics techniques show a relationship between fractional free volume and inhibition efficiency. It

should be possible using these techniques to design optimum tail size and geometries for specific head group chemistries.

(7) OI is a good inhibitor. Improving on the performance within this class of molecule may be difficult.

(8) A combination of synthesis, analytical techniques and molecular modelling provides a powerful way of investigating systems such as OI. Ultimately this will lead to the ability to design new improved and environmentally friendly inhibitor chemistries.

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