Imidazoline adsorption on 1018 Steel: Angle dependence NEXAFS Study

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INTRODUCTION

CO_2 corrosion is a great concern in these C-steel pipelines, which leads to the formation of a weak carbonic acid (H_2CO_3) during the corrosion reaction.[1,2] Several factors, such as, flow type, fluid composition, pH, temperature influence CO_2 corrosion of C-steel.[4] Earlier research has demonstrated that corrosion rate increases with increase in Froude (Fr) number.[4,5] Corrosion of C-steel pipelines has prompted the consideration of a corrosion inhibitor program in various oil fields around the world. The importance and usefulness of oleic imidazoline inhibitors in oil and gas pipelines has been studied in detail by several researchers.[6-9] It is also important to know the adsorption angle of the inhibitor molecule. A completely flat molecule can cover the whole surface for better corrosion prevention. Ramachandran et al. has carried out computer simulation of molecular modeling of inhibitors/substrate interaction.[10,11] Edwards et al. have used the 2nd harmonic generation (SHG) laser to study the insitu imidazoline adsorption kinetics on the steel surface.[12] This communication presents a detailed angle dependent NEXAFS (Near Edge X-ray absorption fine structure) study to probe the orientation of imidazoline on selectively heat treated 1018 steel exposed to multiphase corrosion environment.

EXPERIMENTAL

1018 C-steel coupons of 0.437 inch in diameter and 0.126 inch in thickness were rough polished and cleaned in deionized water prior to the experiments. Some steels were converted to ferritio-pearlitic and martensitic structure. For unexposed samples, a drop of imidazoline was smeared on ferrito-pearlitic(A1), martensitic (A2) and plain C steels (as received - should be ferrito-pearlitic – A3) and kept for 24 hours. The microstructures of A1 and A3 should not change. Selected plain C-steels were exposed to multiphase corrosion environment (10-ppm imidazoline (OI), 100% water cut – no oil, full pipe flow) in a Corrosion Loop at the NSF/IUCRC, Ohio University. References spectra were also recorded on a plain Si wafer coated with imidazoline. NEXAFS measurements were carried out in a total electron yield mode at the Advanced Light Source (ALS) on a bend magnet beamline 7.3.1.1. Both C K and N K edge NEXAFS spectra were obtained for imidazoline on steel for normal (90^{o}), intermediate (60 and 45^{o}) and grazing (30^{o}) photon incidence angles with respect to (wrt.) the surface. All NEXAFS spectra have been ratioed to the incident photon flux and normalized to the largest spectral feature. Energy calibration of NEXAFS spectra was achieved by using the Fe L edge at 710 eV (iron oxide) as a reference.

RESULTS AND DISCUSSION

Changes in corrosion inhibitor chemistry can dramatically alter the corrosion prevention of steels in oil and gas lines. When corrosion inhibitors are brought close to the surface it is important to determine which functional groups bind to the metal and how they bind. It is also critical for a corrosion inhibitor to be able to displace water from the surface, bind preferentially to the surface and prevent water and corrosive ions from transporting to the surface. Oleic imidazoline (OI) has three components: a ring (five memebered ring with 2 N atoms) or head group, a tail composed of long hydrocarbon chain and pendant side chain (CH_2CH_2-NH_2) consisting of a short hydrocarbon chain with an active functional group at the end. The existing theory of OI adsorption on steels suggests that the lone pair of electrons on the amine group on the pendant side chain was determining the molecule adsorption and anchoring to the metal surface. Edwards et al[12] suggested that the OI ring is flat on the surface and bonding to the metal through the nitrogens in the ring and the pendant chain. A tilt angle of 32^o is predicted from their SHG experiments. In their report, the importance of the pendant chain is not highlighted. Ramachandran et al reported that the five memebered ring of a 1,2 dimethyl-2-imidazoline was inclined at 23^o angle with the Fe_3O_4 surface and the angle increases to 52^o with 11 water molecules. It is critical for corrosion inhibitors to be able to displace water from the surface, bind preferentially to the surface and prevent water and corrosive ions from transporting to the surface. In our report we perform angle dependence NEXAFS measurements to shed some light on the imidazoline molecule orientation on steels.

Figures 1 (x, y, z) illustrate NEXAFS spectra of OI on steels (A1, A2 and A3) with varying microstructures as a function of incidence angles (90, 60, 45, 30^o). 30^o is grazing incidence and hence one might see a strong C and N signal from the imidazoline, however that's not the case here as represented in various figures. In the all the spectra the adsorption at 350 eV is from the 2nd order Fe L edge. Taking the advantage of the polarization of synchrotron light, the orientation of an adsorbed molecule relative to the surface can be assessed because the photoabsoprtion process is governed by the dipole selection rule. Figure 1 shows a strong adsorption at 45^o for sample A1, whereas for the martensitic steel the strong π* resonances were found at 30^o. For sample A3, strong adsorption was measured only at 90^o. Although sample A1 and A3 should be the same, however, the prior heat treatment history of A3 is not known, since it is an "as received sample". From these results, it is evident that the orientation angle of imidazolines on steels is very much microstructure dependant, although exact orientation angles were not calculated in this report. This conclusion is drawn from the relative peak intensities (π* resonances) in both N and C K edges in the NEXAFS spectra.

Figure 2 represents a comparative N K edge NEXAFS data at normal and grazing incidence of imidazoline adsorbed on Si, plain carbon steel (steel - 30 and 90^o). NEXAFS spectra (sam - 30 and 90^o) of the same steels exposed to full pipe flow (100% water cut) in presence of 10-ppm imidazoline were also included for comparison. Nitrogen adsorption on Si was strongest as compared to rest of the samples. This is an important observation in a sense that the multiphase environment existing in oil and gas lines includes various sands and waxes. If sand adsorbs most of the imidazoline, then the steels will not be effectively protected from multiphase corrosion. In the π* resonance region, the two nitrogen peaks corresponds to N_1 (N in five memebered benzene ring) and N_{II} (N in the pendant chain). No significant changes in peak intensities of imidazoline on steel at 90 and 30^o were observed. However, the exposed samples do show changes in the relative peak intensities at 30 and 90^o. Not only the N_I peak position changes wrt to Si and steel, but also the peak intensity of N_{II} in the sample increases at 30^o angle of incidence. No significant changes in peak intensities of N_I suggests that the five memebered ring is primarily remaining flat, whereas the N in the C-N functional groups are oriented in between 30 – 35^o, and is close to the predicted values from molecular dynamics simulation by Ramachandran et al.[10,11]

CONCLUSIONS

Angle dependant NEXAFS spectra of imidazoline on steel are shown to be microstructure dependent. Orientation angle of imidazoline on ferrito-pearlitic steel is more than the martensitic steel, although the imidazoline adsorption on plain carbon steel (as received) has the highest intensity at 90^o angle of incidence. Adsorption of imidazoline on Si was higher than the steels with varying microstructures. Sample exposed to full pipe multiphase flow condition showed a high absorbance at 30^o angle of incidence, with the five remembered ring remaining parallel (or flat) on the surface.

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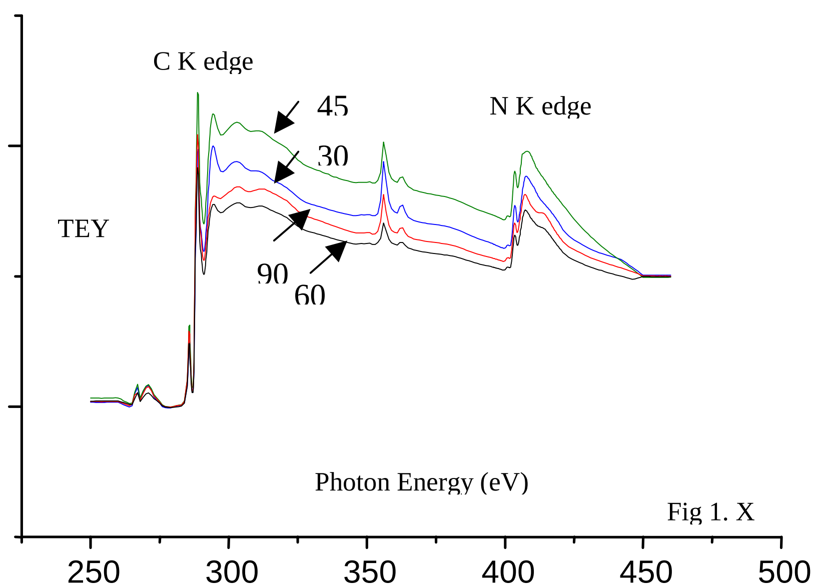

Fig 1. X

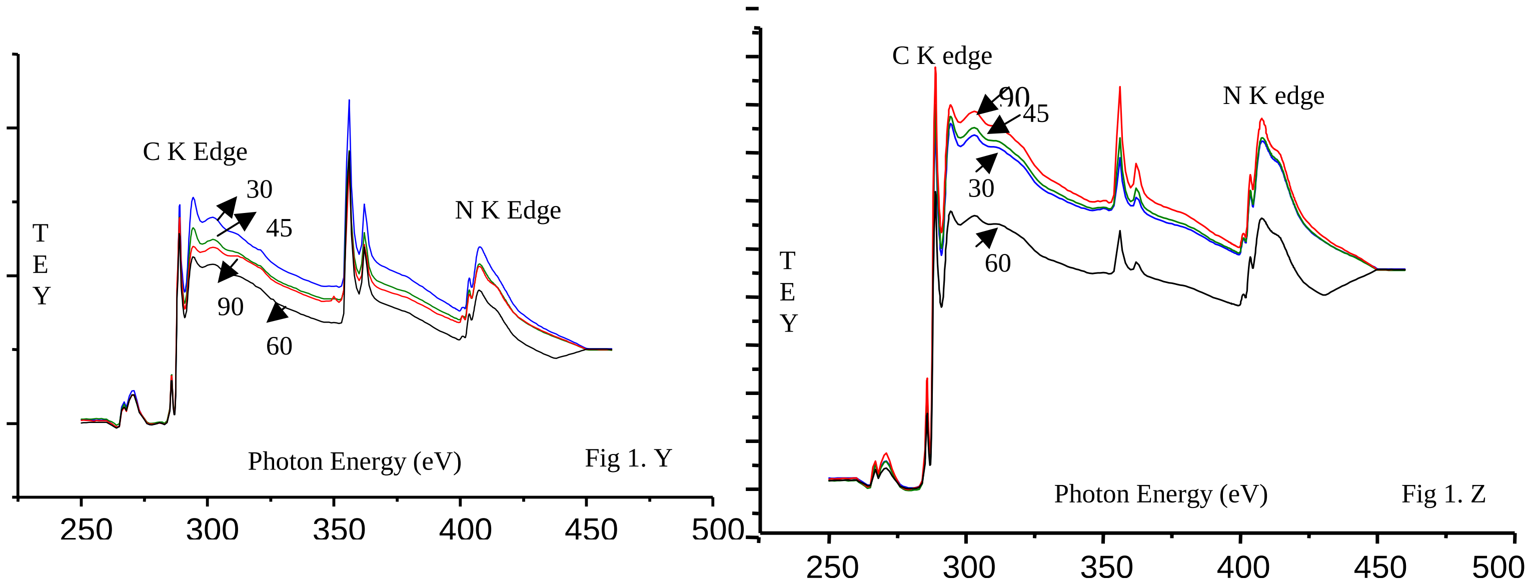

Figure 1: NEXAFS Carbon K and Nitrogen K edge of imidazoline on 1018 C-steel at 30, 45, 60 and 90^o incidence angele: (X) ferrito-pearlitic, (Y) martensitic and (Z) as received condition. Peak at 350 eV is from the Fe 2nd order.

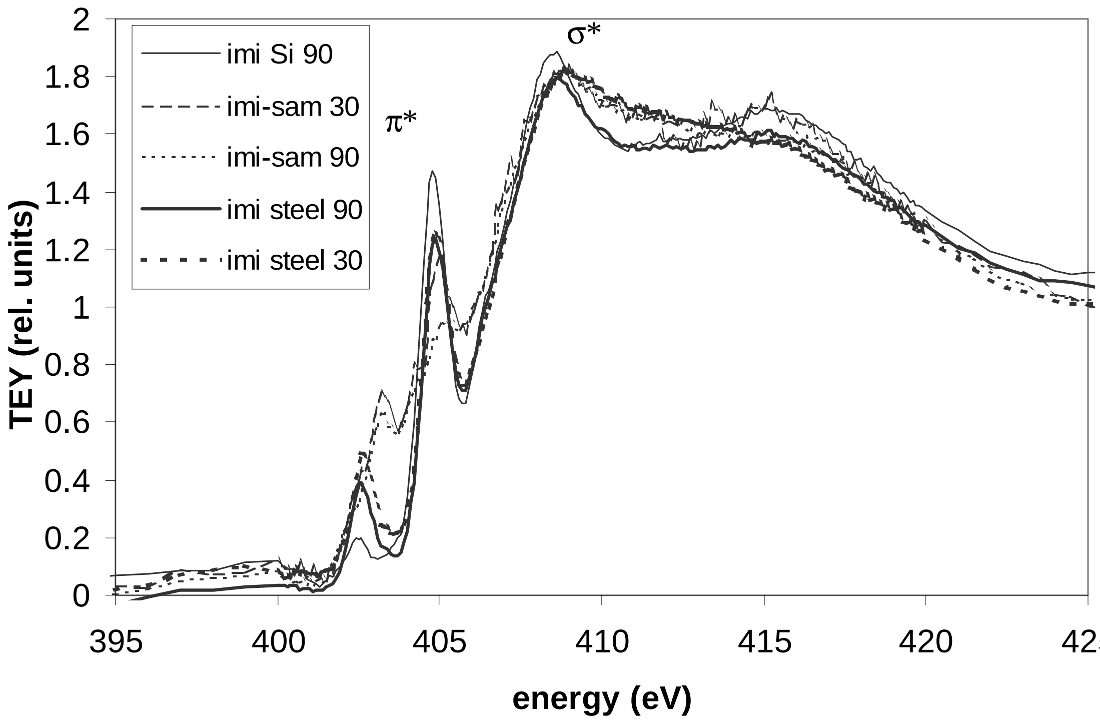

Figure 2: NEXAFS Nitrogen K edge of imidazoline on Si wafer and 1018 plain C steel at various conditions described in the report. Sam – means exposed to multiphase conditions, steel – means no-exposure.