Simplified approach to performance evaluation of selected organic compounds for corrosion inhibitor application in petrochemical plants

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Abstract
Corrosion inhibitors have been researched into, studied and applied in numerous industries worldwide to mitigate the electrochemical deterioration of carbon steels in contact with aggressive medium. Effective and sustainable application of corrosion inhibitors in the oil and gas industry necessitates compatibility with the corrosive environment, non-toxicity and must be economical. Corrosion coupon measurement is the oldest and most widely used corrosion monitoring technique. The traditional approach to evaluate the viability of corrosion inhibitor focuses on inhibitor efficiency. Prevailing industry conditions shows this factor alone is insufficient for evaluation of organic chemical inhibitor compounds. This manuscript focuses on the importance and effect of inhibitor concentration, exposure time and Gibbs free energy in evaluating inhibitor performance and on the selection and suitability of organic chemical compounds for corrosion inhibitors.

Keywords: corrosion; coupon measurement, inhibitor; adsorption; carbon steel

1. Introduction
The consequences of corrosion have been a major focus of scientific, industrial and economic concern [1]. Corrosion costs in oil and gas exploration and production amounts to $1.372 billion yearly according to a study in the United States of which $589 million is the cost incurred from corrosion in surface pipelines and structures, $463 million from downhole tubing corrosion, and $320 million in asset expenses related to corrosion [2, 3] Another study indicates corrosion control in petroleum refining costs $3.7 billion of which petrochemical/chemical manufacturing contributes $1.7 billion. Most of these expenses results from plant shutdowns and process interruptions [4]. The composition and chemistry of crude oil is the single most important causative factor responsible for corrosion in the petrochemical industry. Crude oil is a mixture of specific fluid hydrocarbons consisting dissolved gases, H₂O, and salts. The H₂O composition varies from slightly fresh to saturated salts solutions, which is majorly responsible for crude corrosiveness [5]. Oilfield corrosion occurs in different forms amongst which the most prevalent corrosion types includes pitting corrosion, stress corrosion cracking, crevice corrosion, microbial corrosion, sour corrosion, O₂ corrosion, sweet corrosion and microbial corrosion. Application of corrosion inhibitors is the most economical technique of controlling losses due to corrosion in the oil and gas industry. Corrosion inhibitors vary in composition, toxicity, performance, interaction with metallic surfaces and modification of the environment. There are different corrosion inhibitor chemicals on the market today for specific applications such as phosphate for concrete, ammonia and morpholine for boilers; propargyl alcohol for the acid pickling of metal etc. Research has shown that application of corrosion inhibitors in the United States climbed to 4.1% in 2017 (USD$ 2.5 billion) [6]. Consequently the process of selecting a corrosion inhibitor is often overwhelming. Appropriate evaluation of their inhibition performance is paramount in terms of selection for corrosive
environments where they are most effective. This manuscript focuses on cost effective performance evaluation method of admixed chemical inhibitor compounds through coupon measurement for application in petrochemical industry.

1.1 Carbon steels
The cost of carbon steels coupled with their desirable mechanical and physical properties is responsible for their extensive industrial application worldwide [7, 8]. The oil industry consumes about 8% of all metals worldwide with carbon steel making up about 90%. Carbon steels have very low resistance to corrosion which hinders their versatility and thus limits application to specific environments. The inability of carbon steels to passivate in corrosive conditions is a serious setback lifespan and service life. Corrosive wears of these steels determines the viability and operational service life of equipment, extent of overhaul periods and cost due to repairs.

1.2 Application of corrosion inhibitors
Corrosion control in the oil and gas industry is of utmost importance due to the resulting huge economic losses. Application of corrosion inhibitors is one of the most effective and economical technique in mitigating corrosion-induced problems, aggravated by hugely differing processing variables in the oil and gas production processes. Factors influencing the efficiency of corrosion inhibitors include inhibitor concentration, exposure period, temperature and effect of inhibitor structure. Their mode of action involves (a) chemical absorption onto the surface of a metal, (b) oxidation in the environment to create a protective layer and (c) reaction with a corrosive chemical within water. Corrosion inhibitors currently used in the oil industry are multicomponent mixtures due to their unique physical, physiochemical and chemical properties and successful application in the corrosion protection of downhole equipment, loop lines, gathering systems, intra- and interfield pipelines, tanks vessels and pumps [9]. Selection of appropriate corrosion inhibitor for specific industrial applications is an extremely complex issue as there is no universal set of corrosion inhibitors. Laboratory and field-testing are often required before selection. The most important factors to consider before using a corrosion inhibitor include its toxicity, environment friendliness, availability and cost. Corrosion inhibitors can be classified into, film inhibitors, passivating inhibitors, anodic inhibitors, cathodic inhibitors, anodic-cathodic (mixed) inhibitors, vapor phase, neutralizing and reactive. Most corrosion inhibitors used in oil gas industry consist of reactive organic materials such as amines and organic acids. The specific chemical structure of their molecules will determine the properties the inhibitor have (solubility, film persistency, etc.) and its ability to control corrosion.

2. Selected chemical compounds
The synergistic effect of admixed chemical compounds usually results in higher inhibition performance though this is not always the case as single component compounds have also proven effective [10-13]. Evaluation of corrosion inhibitors must identifies the following; (a) compounds with high inhibition efficiency at the lowest possible concentration, (b) compounds capable of acting instantaneously in the corrosive medium, (c) compounds whose inhibition efficiency increase and remain stable with time, (d) compounds capable of chemical or physical adsorption through effective surface coverage and (e) compounds capable of withstanding metallic oxidation in strong oxidizing environments. Table 1 identifies some organic and green chemical compounds, including their class and name which has been previously evaluated for their inhibition performance on carbon steel in dilute H_2SO_4 and HCl solution while Table 2 shows the abbreviations of the organic chemical compounds and their admixtures.
Table 1: Some types of chemical compounds studied

| Compound         | Class of compound           | Name of compound                                                                 |
|------------------|-----------------------------|----------------------------------------------------------------------------------|
| Organic          | Aromatic amine              | Aniline                                                                         |
|                  | Thiadiazole aromatic        | 2-Amino-5-ethyl-1,3,4-thiadiazole                                               |
|                  | amine                       |                                                                                 |
|                  | Amino alcohol               | N,N-dimethylaminoethanol                                                        |
|                  | Aromatic amine derivative   | P-phenyldiamine                                                                 |
|                  | Organosulphur               | Thiocarbanilide                                                                 |
|                  | Aromatic nitrile            | Benzonitrile                                                                    |
|                  | Primary alcohol             | Butan-1-ol                                                                      |
|                  | Phenolic aldehyde           | 4-hydroxy-3-methoxybenzaldehyde                                                 |
|                  | Quaternary ammonium surfactant | Hexadecyltrimethylammoniumbromide                                             |
| Inorganic        | Inorganic salt              | Sodium molybdate                                                                |
| Green            | Essential amino acid        | l-leucine                                                                        |
|                  | Plant extracts              | Carica Papaya, Camellia Sinensis Leaves, Tobacco and Kola Tree Extracts, Manihot Esculenta, Dextrin, Camelia sinensis, Allium Sativum- Garlic, Allium Cepa extracts-Onion, Vernonia amygdalina, Neem leaf (Azadirachita indica) extract |
|                  | Essential oil extracts      | Salvia officinalis, Simmondsia chinensis, Rosmarinus officinalis, Lavendulan officinalis, Ricinus communis |

Table 2: Abbreviation of compounds and admixed compounds studied [14-32].

| Abbreviation | Organic Chemical Compound                                                                 |
|--------------|------------------------------------------------------------------------------------------|
| CBH          | 4-Hydroxy-3-methoxybenzaldehyde and hexadecyltrimethylammoniumbromide                     |
| HTH          | Thiocarbanilide and hexadecyltrimethylammoniumbromide                                      |
| LCN          | 2-Amino-4-methylpentanoic acid                                                             |
| LTC          | l-leucine and trypsin complex                                                              |
| ROTC         | Rosmarinus officinalis and trypsin complex                                                |
| SYG          | 4-Hydroxy-3-methoxybenzaldehyde and l, 4-diaminobenzene                                    |
| TCB          | Thiocarbanilide                                                                           |
| VAL          | Vanillin                                                                                  |
| VTU          | 1, 3-Diphenyl-2-thiourea and 4-Hydroxy-3-methoxybenzaldehyde                              |
| LASO         | Salvia officinalis and lavendulan officinalis                                              |
| SASC         | Salvia officinalis and simmondsia chinensis                                                |
| ROSV         | Rosmarinus officinalis and 5-bromovanillin                                                |
| SMV          | Sodium molybdate and vanillin                                                             |
BNV  |  Benzenecarbonitrile and 5-bromovanillin
TTD  |  2-Amino-5-ethyl-1,3,4-thiadiazole
NNDT |  N, N’-diphenylthiourea
MDMEA|  N, N’-Dimethylaminoethanol

2.1 Effect of inhibitor concentration and exposure time on inhibition performance

Fig. 1(a) to (e) shows the plots of inhibition efficiency versus exposure time, i.e. depicting the different forms of inhibitor performance. Fig. 2(a) and (b) shows the comparison of CBH compound inhibition performance in H$_2$SO$_4$ and HCl solution. The TTD compound [Fig. 1(a)] shows an optimal inhibition performance value of 80% at 0.75% TTD concentration. However, TTD performance is heavily dependent on its concentration. The performance of NNDT compound [Fig. 1(b)] decreased from an average value of 86.6% at 72 h to inhibition efficiency values generally below 60% and 20% at all concentrations (432 h exposure time). Fig. 1(c) shows the inhibition efficiency of MPPD compound whose performance is unreliable and risky for application in petrochemical plants. Despite its performance being independent of time and concentration, its inhibition efficiency values are significantly disproportionate to time and concentration. Fig. 1(d) and (e) shows the performance of TTD inhibitor with inhibition efficiency values above 97% at all concentrations. The values are independent of concentration and exposure time, yet follows a define plot symmetry which can be relied upon compared to the plot in Fig. 1(c).

In H$_2$SO$_4$ solution [Fig. 2(a)], the performance of the CBH compound is above 90% at all concentrations. However, in HCl [Fig. 2(b)], its performance is concentration and time dependent which is quite disadvantageous in petrochemical conditions. Concentration dependence has the problem of aggravating corrosion when the concentration of the inhibitor decreases in process conditions. Time dependent inhibitors are disadvantageous in aggressive environments where the corrosive anions would have cause substantial damage before the inhibition action of the chemical compounds take effect. Recommended compounds must be concentration dependent to a large degree and must react instantaneously with respect to time. It must be noted that differences in performance of CBH in H$_2$SO$_4$ and HCl solution is due to the specific inhibiting action of corrosion inhibitors with respect to environment. Fig. 3(a) and (b) shows the summary of the peak inhibition performance of 11 admixed inhibitor compounds in H$_2$SO$_4$ and HCl solution. Observation of the plots shows the differences in inhibition behaviour of the admixed compounds with respect to time, concentration and corrosive media. Some compounds displays good inhibition performance which increased with time while for some others there was visible decrease. In H$_2$SO$_4$, SASC displays the highest corrosion inhibition performance, maintaining inhibition efficiency value above 99% throughout the exposure period. The performance of CBH in both acid solutions varied with time, shifting from 68.6% and 63.1% at 24 h to 94.8% and 93% at 168 h. In H$_2$SO$_4$, the performance of ROSV decreased from 84.5% at 24 h to 66.17% at 168 h. Its performance in HCl was significantly impressive with inhibition efficiency value of 95% at 24 h and 95.6% at 168 h. While TCB performed poorly in H$_2$SO$_4$ with optimal value of 51.17%, its performance in HCl was quite different increasing from 55.5% at 24 h to 86.2% at 168 h.
Figure 1: Corrosion inhibition results from weight loss measurement (a) Compound with concentration dependent high inhibition efficiency, (b) Compound whose inhibition efficiency decreases with time from high efficiency values, (c) Chemical compound whose inhibition performance is unreliable, (d) High performance inhibitor suitable for petrochemical plants and (e) Corrosion rate versus time for a high performance inhibitor
2.2 Observation of Gibbs free energy of inhibitor compounds

The plot Gibbs free energy versus inhibitor concentration in H$_2$SO$_4$ and HCl solutions is shown in Fig. 4(a) and (b). Inhibitors with Gibbs free energy value below 25 KJ/mol are known to physically adsorb on steel surfaces. The intermolecular interaction between the inhibitor molecule and the steel surface tends to be weak and can easily be removed from the steel surface. Inhibitors with Gibbs free energy value between 28 KJ/mol and 35 KJ/mol physiochemically adsorbs on steel surfaces. The intermolecular interaction between the inhibitor molecule and the steel surface is partly strong. Inhibitors with Gibbs free energy value of 40 KJ/mol and above chemically adsorbs on steel surfaces. The intermolecular interaction between them is generally strong. The most effective inhibitors are in this category [33]. VTU inhibitor has the highest Gibbs free energy value in H$_2$SO$_4$ and HCl solution indicating chemisorption molecular interaction value of 49.1 KJ/Mol and 49.54 KJ/Mol at 1M acid conc., and 45.63 KJ/mol and 46.04 KJ/Mol at 6M acid conc. RSZ displayed the lowest Gibbs free energy value in H$_2$SO$_4$ and HCl solution at 27.96 KJ/Mol and 24.95 KJ/Mol (1M conc.), and 24.92 KJ/Mol and 22.87 KJ/Mol at 6M conc. The Gibbs free energy value of LASO increased from -30.95 KJ/Mol at 1M to 43.28 KJ/Mol at 6M in H$_2$SO$_4$ solution. The Gibbs free energy value is an important indicator of the adsorption strength of the inhibitor.
compound and the intermolecular reaction (lateral interaction) of inhibitor molecules especially admixed compounds. Changes in Gibbs free energy value with respect to inhibition concentration in both acid solution gives information on the optimum concentration for effective inhibition performance and synergism of admixed inhibitor compounds. In most cases the plots of Gibbs free energy versus exposure time shows higher Gibbs value at lower concentration than the values at higher concentrations indicating intermolecular instability due to lateral interaction as earlier mentioned. The plots shows higher concentration/application of inhibitor compound to the corrosive solution does not necessarily imply effective protection of carbon steels. There are certain concentrations where lateral repulsive effect defeats the whole purpose of corrosion inhibition.

![Figure 4: Comparison of adsorption strength of inhibitor compounds (a) in H₂SO₄ solution and (b) in HCl solution](image)

3. Conclusion
Inhibitor concentration and exposure time are equally important as percentage inhibition efficiency in determining the viability and industrial application of organic corrosion inhibitors through coupon measurement. Performance evaluation of corrosion inhibitors was discussed in view of the detrimental effect of high inhibition efficiency heavily dependent on inhibitor concentration and the transient corrosion that occurs in time for slow acting chemical compounds.

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