



Synergistic corrosion inhibition effect of metal cations and mixtures of organic compounds: A Review



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ABSTRACT

The devastating effect of corrosion on the structural integrity of metals surfaces has been of great concern for some time. However, the challenge is to develop a benign and cost effective inhibitor that is highly effective. Addition of substances that exert synergistic influence and blending of different metals inhibitors had been employed. This review article delineates the effect of addition of metals cations and blending on the inhibition efficiency of metals corrosion inhibitors. The mechanisms proposed for the synergistic inhibition resulting from either addition of metals cations or blending are also discuss based on reported experimental data.

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1. Introduction

Considerable attention has been given to the use of corrosion inhibitors in reducing metals loss in areas deploy in service due to the ease of being manipulated, effectiveness and the fact that the

technique is affordable [1]. Metal corrosion inhibitors are substances that when added in small amount to corrosive environment suppress the rate of metal dissolution. These substances functioned by either oxidizing the metal to form an impervious layer (inorganic inhibitors) or adsorbing on the metal surface through their heteroatoms and/or double bond (organic inhibitors) to form an hydrophobic layer which hinder the aggressive agents present in the environment from gaining access into the metal surface. However, it is not all substances that are qualify as metal corrosion inhibitor. Certain criteria abound for

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selecting metal corrosion inhibitor. Fundamentally, a substance to be used as metal corrosion inhibitor should be able to induce the formation of protective film on the metal surface which is not impermeable but rigid and compact enough to obstruct corrosive ions from gaining access into the metal surface [2]. Aside this, small quantity of the compound should effect an appreciable inhibitory action; it should be cost effective and harmless to the ecosystem. Unfortunately, most substances which have been found to possess good inhibitory ability have come under severe criticism either for environmental issues or for exorbitant prices. Eco-friendly inhibitors are those inhibitors which, when use do not interrupt ecological balance or have negative impact on human health. Ivusic et al. [3] divided this class of inhibitors on *ad hoc* basis into three groups: inorganic substances such as rare-earth metal (REM) salts, borates, silicates, molybdates; organic compounds such as thioglycollates, phosphonates, sulfonates, carboxylic acids and their salts (amino acids, fatty acids, gluconates), vitamins, pigments, antibiotic or antifungal drugs (e.g. imidazole compounds), alkaloids (nicotine, caffeine); and true “green” inhibitors such as various herbal extracts (water, alcohol or acid extracts). However, interest on the use of metals corrosion inhibitors has gone beyond mere inhibition to how effective is an inhibitor. Based on percentage inhibition efficiency (%I), corrosion inhibitors may be grouped into three: poor (those with %I < 40); moderate (those with %I between 40 and 69); and excellent inhibitors (those with %I > 70).

One of the steps taken by corrosion scientists to address the challenges of poor or moderate inhibiting ability of an inhibitor and that of exorbitant price in recent times has been finding substances that can exert synergistic effect when combined with inhibitor such that the quantity of an expensive inhibitor could be decrease or the efficiency of a moderately performed inhibitor enhanced. Synergism is described as a tendency in which the combined action of compounds is greater than the sum of the individual effects of the compounds. For corrosion inhibitor systems, synergism arises either as a result of interaction between components of the inhibitor formulation or due to interaction between the inhibitor and one of the species present in the aqueous medium. Synergism can be regarded as an effective method to improve the inhibitive force of inhibitor, to decrease the amount of usage, to diversify the application of inhibitor in corrosive media. It plays an important role not only in theoretical research on corrosion inhibitors but also in practical work. This effect is often assessed in terms of synergism parameter (S_1) as follows [4]:

$$S_1 = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}}$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$, θ_1 is the surface coverage (θ) of inhibitor, θ_2 is the surface coverage (θ) of additive and θ'_{1+2} is the combined surface coverage (θ) of inhibitor and additive. Value of S_1 greater than unity implies the existence of inhibition synergism between the two substances whereas S_1 less than unity points toward antagonistic effect.

Cations and anions have been extensively investigated for their possible synergistic effect with metal corrosion inhibitors [5–13]. In the category of anions, halide ions have received considerable attention and we have given a comprehensive review on the effect of addition of halide ions on the efficiency of metal corrosion inhibitors [14]. In this present report, the effect of addition of cation species to organic and inorganic inhibitors including polymers, naturally occurring substances and surfactants in aqueous corrosive environments as well as the effect of mixing two inhibitors on the inhibition efficiency is reviewed.

2. Effect of metal cations on the corrosion inhibiting action of organic compounds

2.1. Effect on inhibitive action of surfactants

Surfactants are surface active compounds with both hydrophilic (head) and hydrophobic (tail) regions. This rare feature makes surfactant very versatile as they could be useful in both polar and non-polar environments. Based on the nature of the head region, surfactants are grouped into four; cationic, anionic, amphoteric, and nonionic surfactants. The cationic surfactants are group of surfactants having positively charged hydrophilic region. An example is dimethyl dioctadecyl ammonium chloride. The anionic surfactants have negatively charged head region and sodium stearate is a typical example. Amphoteric surfactants such as β -N-alkyl amino propionic acid have a head region with both positive and negative charges. The nonionic surfactants, in the other hand, are those surfactants with neutral head region. Solubility of this class of surfactants is brought about by solvation. An example is the nonyl phenol ethoxylate.

There are numerous reports in the corrosion literature on surfactants as metals corrosion inhibitor [15–30] and interest on them stem from their ability to associate with one another at interfaces and in solution to aggregate [31]. According to some authors [14,31], in corrosive aqueous environment, surfactant molecules assembled to form micelles in a way that the hydrophobic ends huddle in the core of the micelle while the hydrophilic regions project outward into the polar bulk solution and locate at the micelle-water interface such that the hydrophobic tails are shielded from the water. This micelle aggregates substitute water molecules on metal surface and by so doing protect the metal surface from corrosive agents present in the aggressive environment. It has been reported [17,32–41] that addition of metal cations to surfactant influenced the inhibition efficiency (IE) of surfactant. For instance, Migahed et al. [33] reported synergistic inhibition of downhole tubing steel in produced water from old oil wells by Cu^{2+} and cationic gemini surfactant namely; 1,2-ethane bis(N,N-dimethyl hexadecyl ammonium bromide). The authors noted that the addition of Cu^{2+} to the inhibitor containing solution increased the inhibition efficiency and the degree of surface coverage. It has been reported [34] that the inhibition and biocidal efficiency of sodium dodecyl sulphate (SDS) and calcium propionate (CP) in controlling corrosion of carbon steel immersed in an aqueous solution had been significantly enhanced by Zn^{2+} . The formulation consisting of 125 ppm CP and 50 ppm Zn^{2+} was found to offer inhibition efficiency of 66%. However, the authors noticed that reduction in the quantity of CP to 50 ppm and addition of 200 ppm SDS synergistically increased the inhibition efficiency to 99% and 100% biocidal efficiency. This seems to suggest an efficient CP- Zn^{2+} -SDS complex formation. Li et al. [32] investigated the synergistic inhibition effect of rare earth cerium(IV) ion (Ce^{4+}) and sodium oleate (SO) on the corrosion of cold rolled steel (CRS) in 3.0M phosphoric acid (H_3PO_4) by means of weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM) methods. It was found from the report that SO has a moderate inhibitive effect while Ce^{4+} has a very poor effect. However, incorporation of Ce^{4+} with SO is seen to remarkably improve the inhibition performance. For example, at 20 °C the inhibition efficiency values of 2.0 mM SO and 2.0 mM Ce^{4+} are 64.4% and 17.3%, respectively, while that of SO + Ce^{4+} mixture reaches 96.7%. This observation is not surprising. Ce^{4+} belongs to lanthanide group in the periodic table and has a lot of vacant orbitals (4f, 5d and 6s). SO contains oxygen atoms with lone-pair electrons. So, when SO and Ce^{4+} are mixed, there is that possibility of Ce^{4+} -SO complex formation whereby SO sends in lone-pairs of

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