

Investigation of Cyclohexylidencyclohexanon Steel Corrosion Inhibitor as Surfactant

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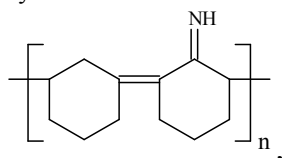
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The waste products of the caprolactam production (POD – oil) are inhibitor of steel acid corrosion in hydrochloric acid solutions (1). The efficiency of the investigated inhibitor reaches 85 - 88% at 1 mass % concentration.

The basic inhibiting component of the POD-oil is dimer of hexanon (2). The more effective inhibitor is produced under POD-oil condensation with formalin at the presence of the alkaline catalytic agent and at amination of the product (3). The inhibition efficiency such inhibitor reaches 92 ... 93 % at 1 mass % concentration. The special investigations have shown that the basic inhibiting component in such modified POD – oil is cyclohexylidencyclohexanon



where $n = 2 \dots 3$.

All effective inhibitors are strong surfactants. Generally a surface activity of the nonionic surfactants can be determined by the interaction of surfactant molecules with metal or the interaction of these molecules with a solution. However overwhelming majority of works about the adsorption mechanism relates the adsorption just to interaction of the surfactant and metal.

Here the adsorption mechanism of modified POD – oil surfactant on steel – hydrochloric acid and air – hydrochloric acid interfaces is investigated.

Adsorption on the steel – solution interface by Electrochemical Impedance Spectroscopy technique is investigated (2). The Maximum Bubble Pressure technique for the surface tension investigation on air – solution interface is applied. On these interfaces usually take place monomolecular Langmuir adsorption which is described by the equation:

$$\Gamma = \Gamma_{\infty} \frac{K_{ad}C}{1 + K_{ad}C} \quad \text{or} \quad \frac{1}{\Gamma} = \frac{1}{\Gamma_{\infty} K_{ad}C} + \frac{1}{\Gamma_{\infty}}, \quad [1]$$

where C is the surfactant concentration, Γ is the adsorption value, Γ_{∞} is the limiting adsorption, K_{ad} is the adsorption constant.

If the inhibitor adsorption is described by the Langmuir adsorption isotherm, the surface coverage θ

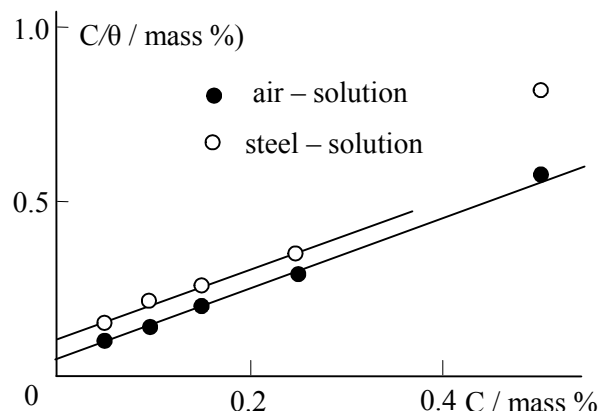
$$\frac{C}{\theta} = \frac{1}{K_{ad}} + C. \quad [2]$$

For air – solution interface $\theta = \Gamma/\Gamma_{\infty}$ and for steel – solution interface

$$(1 - \theta) = \frac{R_{corr}}{R_{corr(inh)}},$$

where R_{corr} is the corrosion resistance without inhibitor presence and $R_{corr(inh)}$ is the corrosion resistance at the inhibitor presence.

Inhibitor adsorption isotherms at air – solution and steel – solution interfaces closely correspond to Eq. [2] at low concentrations (Figure). Slopes of straight lines (1.00 and 1.04) closely correspond to the theoretical (unit) slope. Therefore the Langmuir adsorption takes place for both interfaces at small concentrations.



From Figure using Eq. [2], K_{ad} values is calculated for the air – solution $\{(1.7 \pm 0.4) \times 10^3 \text{ M}^{-1}\}$ and steel – solution $\{(4.0 \pm 0.8) \times 10^3 \text{ M}^{-1}\}$ interfaces. Free adsorption energy ΔG_{ad}^0 from the equation

$$K_{ad} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ad}^0}{RT}\right)$$

was estimated as $(-28 \pm 0.5) \text{ kJ mol}^{-1}$ and $(-30 \pm 0.6) \text{ kJ mol}^{-1}$ respectively. The closeness of adsorption constant and free adsorption energy values suggests that the inhibitor adsorption on steel is caused basically by the hydrophobic interaction of the inhibitor with the solution components and less depends on the interaction with steel.

Conclusions

1. The modified POD – oil adsorption on the air – solution and the steel – solution interfaces follows to the Langmuir adsorption isotherm.

2. The modified POD – oil adsorption on the steel – solution interface is determined by interaction of the surfactant with solution components, but does not depend on interaction of the surfactant with steel.

References

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