

Retrospective and Developing Concepts of Passivity and Passivity Breakdown of Metallic Materials in Organic Solutions

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Different studies have offered various explanations for the passivity of metals in organic solvents and the effect of water on passivation processes. This has often assumed that organic solvents were inert to metals and alloys. Some explanations have related passivity to adsorption characteristics of the solvent. One investigator suggested that corrosion of metals in organic solvents depended primarily on solution conductivity and acidity. Kelly and Moran [1] reviewed the literature and summarized two observations: (1) most metals were not passive in highly acidified, anhydrous organic solutions, but small water additions led to passivity; and (2) most alloys passivated in neutral or weakly acidic anhydrous organic solvents, but small amounts of water tended to interfere with passivity.

Organic solvents have been classified into three general groups. The first of these groups are nonpolar, aprotic solvents that includes aromatic and aliphatic hydrocarbons and symmetrical halogenated hydrocarbons. Solvation in these systems occurs by relatively weak van der Waals-London forces. The second of these organic groups are dipolar aprotic solvents that display electrostatic forces due to ion-dipole and dipole-dipole interactions. The last group of organic solvents are protic solvents that include organic acids, alcohols, amines, amides, and water. Solvation in protic solvents occurs through dipole-dipole interaction, ion-dipole interaction, and hydrogen bonding. The protic or aprotic character of the solvent is determined by the ability to provide protons. Protic media contains active hydrogen protons; aprotic solvents do not.

The specific type, structure, and reactions of an organic functional group influence the reactivity of metals in organic solvents. An organic solvent may transport the aggressive reactants and the products formed during the corrosion process. The

genus of solvents in use and their solvation properties affect the solubility of these reactants; many different physical and chemical interactive forces occur during solvation. These different interactive forces play a significant part on the mechanistic paths that, in turn, can affect the passivity of different alloys in a given organic solvent or mixtures of two or more organic solvents.

This paper will summarize early investigations of different alloys in aprotic organic solutions and mixtures by exploring various mechanistic pathways available for passivation. The character of the passive films on metals and alloys and the environmental contributions that influence possible mechanistic paths and the potential regions where passivity is effective will be reviewed. Rather than alloys being inert in organic solvents, the passivity of alloys in organic solutions is complex; water increases this complexity by its influence of organic passivation mechanisms and/or by its enhancement of oxide/oxyhydroxide formation. Factors that may contribute to passivity in these solutions will be discussed.

[1] R.G. Kelly, P.J. Moran, *Corrosion Science*, v. 30, 495 (1990).