J. Chem. Research (S), 1999, 408–409
J. Chem. Research (M), 1999, 1701–1726

Kinetics of Substituted Bis- and Mono-azo Dyes as Corrosion Inhibitors for Aluminium in Hydrochloric Acid and Sodium Hydroxide Solutions

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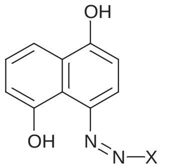
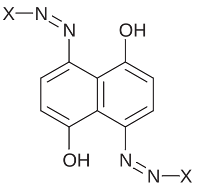
This investigation is designed to apply an advanced kinetic–thermodynamic model on the data obtained from acidic and alkaline corrosion of aluminium using bis- and mono-azo dyes as corrosion inhibitors.

A number of organic compounds have been introduced as aluminium corrosion inhibitors in acidic and alkaline media.[6–10,15–17] Their inhibitory action is connected with several factors: (i) the structure of molecules, (ii) the number and type absorption sites, (iii) the distribution of charge in the molecules, and (iv) the type of interaction between the organic molecules and the metallic surface. This work is aimed to investigate the inhibitory effect of some bis- and mono-azo dye derivatives on corrosion of aluminium in 2 M HCl and 2 M NaOH solutions by weight-loss, thermometric and polarization measurements. In general, the role of the inhibitor has both kinetic as well as thermodynamic implications.

The investigated mono- and bis-azo dye compounds (**I**–**X**) are shown below:



X	
C_6H_4OMe-*p*	**I**
C_6H_4Me-*p*	**II**
C_6H_4Me-*o*	**III**
α-Naphthyl	**IV**
β-Naphthyl	**V**



X	
C_6H_4OMe-*p*	**VI**
C_6H_4Me-*o*	**VII**
C_6H_4Me-*m*	**VIII**
α-Naphthyl	**IX**
β-Naphthyl	**X**

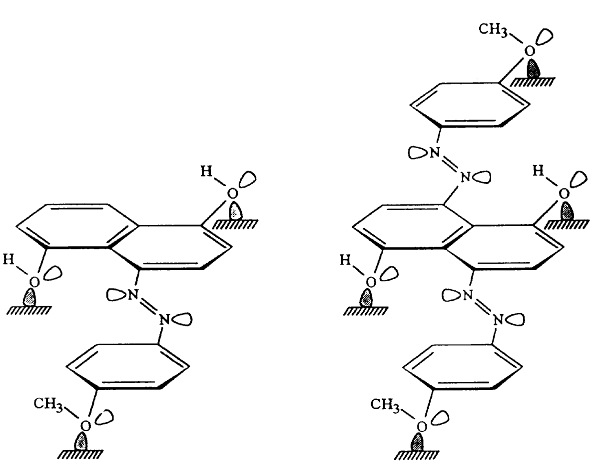
On increasing the concentration of the inhibitor the time (t) required to reach maximum temperature (T_{max}) increases, and both factors cause a large decrease in the reaction number[25] (RN) of the system. This indicates that the azo dye additives retard the dissolution of aluminium in both acidic and basic solutions by strong adsorption. Plots of %reduction in RN and the degree of surface coverage (θ) *versus* molar concentration of the additives are invariably sigmoidal in nature. The relation between RN, time delay (Δt) and/or log (Δt) *versus* molar concentration of the additives confirms a two-step adsorption process.

Weight-loss of aluminium depends on the type of inhibitor, and generally decreases as the concentration of the additives is increased. This inhibitive effect may be explained by considering the adsorption of the azo dye molecules through oxygen atom centers (OH and OMe) and/or complex formation (surface chelation) on the corroding Al surface.[31]

Polarization curves, Tafel plots and electrochemical corrosion parameters, of aluminium in both acidic and alkaline media in the absence and presence of inhibitors were investigated. The decrease in corrosion rate associated with an increase in the cathodic overvoltage and a positive shift in the corrosion potential, in the presence of the investigated azo dyes, indicates inhibition of a mixed type but predominantly anodic.[34] This behaviour indicates that the adsorbed molecules mechanically screen the coated part of the aluminium surface and therefore protect it from the action of the corrosion medium, and their adsorption in the double layer does not affect the mechanism of hydrogen evolution. The higher inhibition efficiency of the azo dye additives in acidic than in alkaline media may be due to the less negative potential of Al in HCl, favouring adsorption of the additive. The presence of chloride ions (2 M HCl) has been proposed to facilitate the adsorption of organic cations, due to the fact that they form intermediate bridges in which the negative charge of the Al–Cl dipoles may be oriented towards the solution. Formation of such dipoles also increases with increase of chloride concentration.

The Frumkin[30] adsorption isotherm (θ_{org} *vs.* log C) is found to be ideally obeyed in both acidic and alkaline solutions, suggesting that multilayer adsorption takes place. This behaviour is in agreement with the three applied methods. The order of increase of inhibition efficiency of the tested azo dyes (**I**–**X**) in both acidic and alkaline media appears to be: **IV** > **V** > **I** > **II** > **III** and **IX** > **X** > **VI** > **VII** > **VIII**. The three studied methods gave consistent results. The interpretation of the above series can be rationalized as discussed below. The absorbed species will lie flat on the surface of the metal resulting in a higher inhibitive effect (Fig. 9).

It is evident that the inhibition efficiency of the tested azo dyes depends on the number of adsorption oxygen sites (OH and OMe groups), their charge density, and π-electron clouds. Substituted phenyl rings in the α-position for compounds **IV** and **IX** lead to an increase in the longitudinal



I **VI**

Fig. 9 Representation of the proposed mode of adsorption of mono-*p*-anisidine **I** and bis-*p*-anisidine **VI**

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polarization of the π-electron clouds, where those at β-position (**V** and **X**) cause transverse polarization and consequently their adsorption is weaker on the aluminium surface.

The kinetic parameters and their correlation with the corrosion inhibition mechanism can be evaluated from a kinetic–thermodynamic model from the standpoint of the generalized mechanistic scheme proposed by El-Awady *et al.*[43,44] and using Frumkin adsorption isotherms.[30] The large observed values of the change in the standard free energy of adsorption, ($\Delta G^{\circ}_{\mathrm{ads}}$) for additives indicates that the reactions proceed spontaneously and result in highly efficient adsorption of the azo dye inhibitors. Also, large values of K (equilibrium constant) and B (binding constant) mean higher inhibition efficiency, *i.e.*, stronger electrical interaction between the double layer existing at the phase boundary and the adsorbing molecules. In general, the equilibrium constant of adsorption was found to become higher with increasing inhibition efficiency of the inhibitor tested.

Techniques used: potentiostatic polarization, thermometry, weight-loss in an open system, IR, UV, ^{1}H NMR

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Tables 1,2: Thermometric data for Al in 2 M HCl and 2 M NaOH containing **II** and **X**

Table 3: Electrochemical corrosion parameters for Al in 2 M HCl and 2 M NaOH containing **IX**

Table 4: Comparison between %inhibition efficiency by the three different applied techniques

Table 5: Curve fitting of Al data to kinetic–thermodynamic model and Frumkin isotherm for mono- and bis-azo dye inhibitors in HCl and NaOH solutions at 30 °C

Figs. 1,2: Temperature–time curves for Al in 2 M HCl containing **II** and in 2 M NaOH containing **X**

Fig. 3: %Reduction in RN *versus* C for Al in 2 M HCl and 2 M NaOH containing azo dye inhibitors

Figs. 4,5: Weight-loss *versus* time for Al in 2 M HCl containing **III** and in 2 M NaOH containing **VII**

Fig. 6: Polarization curves for Al in 2 M HCl and 2 M NaOH, containing **IX**

Fig. 7: Application of a kinetic–thermodynamic model on azo dye derivatives of Al in 2 M HCl and 2 M NaOH

Fig. 8: Surface coverage θ *versus* log C for Al in 2 M HCl and 2 M NaOH, containing **X**

Received, 20th July 1998; Accepted, 23rd March 1999
Paper E/8/05608K

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