Salicylaldehyde and Furfuraldehyde as Corrosion Inhibitors for 3S Aluminum in Sodium Hydroxide

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THE inhibition of corrosion of 3S aluminium (Al-1.3% Mn) in caustic soda solutions containing furfuraldehyde, salicylaldehyde and their mixture has been studied w.r.t. the concentration of alkali, time of immersion and temperature. The efficiency of furfuraldehyde increases whereas that of salicylaldehyde and of the mixture decreases with increase in alkali concentration. A rise in temperature decreases the efficiency of furfuraldehyde but increases that of salicylaldehyde and of the mixture. Increase in the period of immersion also slightly improves the efficiency.

All the inhibitors increase the open circuit potential of 3S aluminium in 0.1M NaOH. Galvanostatic polarization data also show that the inhibitors are mixed type inhibitors with preponderant action on the local anodes.

CAUSTIC soda solutions are frequently employed for cleaning aluminium surfaces or to give an attractive matt finish. As the action of caustic alkali on aluminium is very rapid and severe the cleaning solutions need to be inhibited. Desai et al.[1,2] and Subramanyan et al.[3] have studied the use of various aldehydes in inhibiting the corrosion of 2S and 3S aluminium in sodium hydroxide. In an earlier paper[4] from this laboratory, various aldehydes have been reported as corrosion inhibitors for 3 S aluminium (Al–1·3% Mn alloy in potasium hydroxide solutions. It was observad that the behaviours of furfuraldehyde and salicyladehyde w.r.t. alkali concentration and temperature was quite different from one another. The inhibitive efficiency of salicylaldehyde decreased with alkali concentration but increased with temperature ; that of furfuraldehyde increased with alkali concentration but decreased with temperature. In the present paper the effect of both salicylaldehyde and furfuraldehyde individually and mixtures (1 : 1 by weight on the corrosion of 3S aluminium in sodium hydroxide solutions has beeen reported.

EXPERIMENTAL

Rectangular specimens of 3S aluminium (Indian Aluminium Co. Ltd., Bombay) of size 5 × 4 cm with a small hole of ~ 2 mm dia. near the upper edge of the specimen, were used for determining the corrosion rates. The percentage composition of the alloy was determined by the method of vogel[5] and found to be as follows :

Mn 1.3 ; Fe 0.54 ; Si 0.65 ; Cu 0.15 ; Zn ≤ 0.1% ; Al remainder.

The purity of aldehydes was checked by melting or boiling point measurements. The specimens were polished according to the method described earlier[6,7] using first the tripoli composition followed by jeweller's rouge. The specimens were exposed to caustic soda solutions (0.1–1.0M) containing controlled additions (1.0 or 2.0% by wt.) of the aldehydes. One specimen only was suspended by a glass hook in each beaker which contained 230 ml of the test solution at 30° ± 0.5°C. In order to check the depletion of alkali during weight loss measurements at 40 and 50°C, experiments were also performed with 500 ml of 0.1M alkali (plain as well as inhibited). Very little difference in inhibitive efficiency was noticed. After the tests the specimens were cleaned in a potassium dichromate-phosphoric acid mixture[8].

For polarization measurements, circular compons were used (dia.2.80 cm, handle 1.81 cm long and 0.5 cm wide). The handle and back of the coupon as well as the auxiliary Pt-electrode were coated with a mixture of perspex and wax from chloroform solution, leaving only the circular portion (~ 6.1E cm^2) exposed to the corrosive medium in an H-type cell with Luggin's capillary as close to the electrode surface as possible. The applied direct current varied from 1.63×10^{-5} to 1.63×10^{-3} A/cm^2. The potentials were recorded wirh an accuracy of ± 5 mV.

RESULTS AND DISUSSION

The results are given in Figures 1-3 and Table I-III.

The pH values of 1% aqueous solutions of salicylaldehyde and furfuraldehyde are found to be 7.4 and 6.3 respectively and the solutions are noncorrosive to aluminium. The pH values of 0.1M NaOH (pH 12.8) containing 1% inhibitor were found to be 11.6 and 12.3 respectively for salicylaldehyde and furfuraldehyde i.e., the inhibitors do not have much effect on the nature of the corrosive medium.

(i) *Effect of Alkali Concentration:* The effect of alkali concentration on inhibitive efficiency of the two aldehydes is shown in Fig. 1. From the

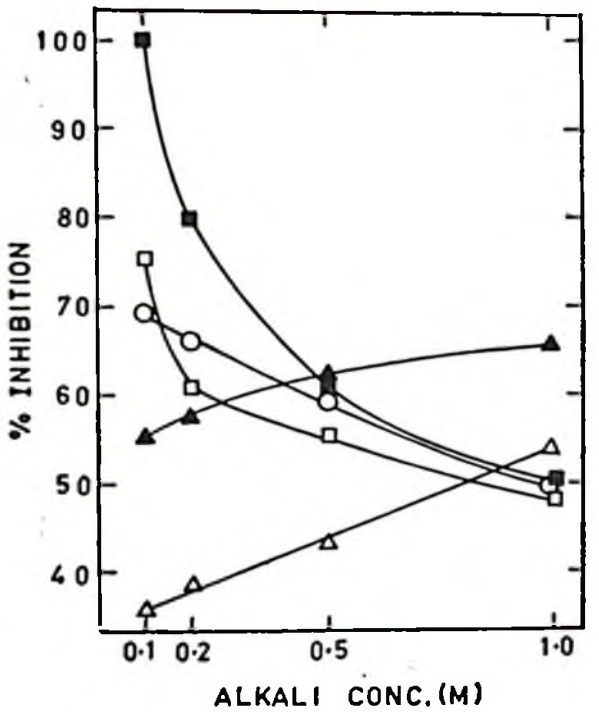


Fig. 1. Effect of concentration of NaOH on inhibitive efficiency of aldehydes for 3S aluminium (30°C, 1h.)

△—△ 1% furfuraldehyde
▲—▲ 2% Furfuraldehyde
○—○ 1% furfuraldehyde + 1% Salicylaldehyde
■—■ 2% Salicylaldehyde
□—□ 1% Salicylaldehyde

figure it is evident that at both the concentrations (1 and 2%) the inhibitive efficiency of furfuraldehyde increases with alkali concentration whereas that of salicylaldehyde and 1 : 1 furfural, salicylaldehyde mixture decreases. But at a given alkali concentration, the efficiency of the inhibitor increases with inhibitor concentration, the effect being more pronounced at lower concentrations of alkali. The inhibitor efficiency at different concentrations of alkali is given in Fig. 1.

(ii) *Effect of Immersion Period:* The effect of immersion period on inhibitive efficiency of the two aldehydes is shown in Fig. 2A. In all cases the inhibitor increases with the period of immersion, the effect being more evident in the case of 1% concentration of salicylaldehyde. The inhibitive efficiency of salicylaldehyde at 2% concentration was found to be ~ 100% during an immersion period of 10-60 min. This may be traced to a decrease in pH of the solution (viz., 9.3) in the noncorrosive range. In other cases the efficiency increased by ~ 5.6% when the period of immersion was increased from 10 min to 60 min.

In general, for an immersion period of 10-60 min, the order of efficiency of the inhibitors was found to be :

2% salicylaldehyde > 1 : 1 mixture > 1% salicylaldehyde > 2% furfuraldehyde. > 1% furfuraldehyde.

(iii) *Effect of Temperature:* To determine the effect of temperature on the inhibitive efficiency of aldehydes, weight losses were determined in 0.1 M NaOH, with and without inhibitor at solution temperatures of 20, 30, 40 and 50°C. The results are given in Table I & II, and Fig. 2B.

The corrosion of 3S aluminium in 0.1 M NaOH increased with tempurature in the range 20-50°C. However, the increase in the rate of corrosion was more at lower temperatures (20→30°C) than that for higher ranges of temperatures (40→50°C), (Table I). From Fig. 2B it is evident that the inhibitive efficiency of furfuraldehyde slightly decreases whereas that of 1% salicylaldehyde and the 1 : 1 mixture increases with a rise in temperature. 2% salicylaldehyde conferred complete protection to 3S aluminium in the range 20-50°C, probably because the pH (viz., 9.3) of the inhibited alkali was found to be in the noncorrosive range.

The values of the energy of activation calculated with the integrated form of the Arrhenius equation[4] are also given in Table I. From the Table it is evident the E values decrease for higher ranges of temperatures in inhibited as well as in uninhibited alkali. In the case of furfuraldehyde the E values are slightly lower, it being more so in the case of mixture in the range 30-40° and 40-50°C. It may also be noted that the behaviour of the mixture

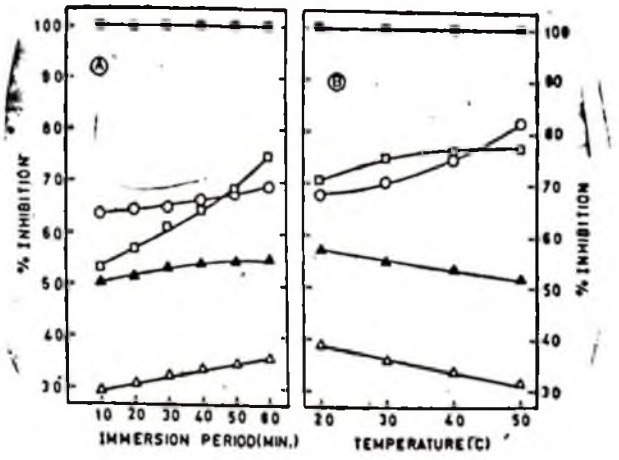


Fig. 2A Effect of time of immersion on inhibitive efficiency of aldehydes for 3S aluminium in 0.1M NaOH (30°C).

△—△ 1% furfuraldehyde
▲—▲ 2% furfuraldehyde
○—○ 1% furfuraldehyde + 1% Salicylaldehyde
■—■ 2% Salicylaldehyde
□—□ 1% Salicylaldehyde

Fig. 2B Influence of temperature on inhibitive efficiency of aldehydes for 3S aluminium in 0.1M NaOH (1h)

△—△ 1% furfuraldehyde
▲—▲ 2% furfuraldeoyde
○—○ 1% furfuraldehyde + 1% Salicylaldehyde
■—■ 2% Salicylaldehyde
□—□ 1% Salicylaldehyde

TABLE I

Effect of Temperature on Inhibitive Efficincy of Aldehydes for 3S Aluminium in Sodium Hydroxide
(Surface area of specimen, 40 sq. cm ; Immersion period, 1 hr.)

Inhibitor	E, Kcal/mole, for the temperature range 20—30°C	30—40°C	40—50°C
Nil	15.5	11.9 (12 3)	9.3 (10.3)
1% furfuraldehyde	16.7	12.4 (12.9)	10.0 (10.8)
2% furfuraldehyde	16.9	12.0 (12.3)	10.2 (11.1)
1% Salicylaldehyde	14.5	9.4 (12.5)	8.0 (10.0)
2% Salicylaldehyde	—	—	—
1% furfuraldehyde + 1% Salicylaldehyde	13.9	8 6 (9.8)	5.8 (7.1)

Figures in brackets show values for 500 ml of the test solution

towards the increase in alkali concentration or the period of immersion or temperature is almost the same as that observed with 1% salicylaldehyd.

If it is assumed that the inhibitors function by adsorption in the form of a monomolecular film on the metal surface, covering at any instant a frection $\theta = \left(\frac{W_u - W_i}{W_u}\right)$, of the total metal surface in a uniform manner, then the heat of adsorption, Q, can be calculated with the help of the equation ;

$$Q = 4.576 \left(\log \frac{\theta_2}{1-\theta_2} - \log \frac{\theta_1}{1-\theta_1} \right) \left(\frac{T_1 \times T_2}{T_2 - T_1} \right) \quad (1)$$

where θ_1 and θ_2 are the fractions of the metal surface covered by the inhibitor at temperatures T_1 and T_2 (°K) respectively. The values of Q are given in table II. From the Table, it is evident that

TABLE II

Values of the Heat of Adsorption (Q) for corrosion of 3S Aluminium in 0.1M NaOH containing Aldehydes

Inhibitor	Q, kcal/mole, for the temperature range 20—30°C	30—40°C	40—50°C
Nil	—	—	—
1% furfuraldehye	33.9	38.8 (38.5)	41.8 (43.5)
2% furfuraldehyde	24.0	41.6 (42.9)	42.6 (43.4)
1% Salicylaldehyde	50.9	45.2 (42.5)	48.9 (47 3)
2% Salicylaldehyde	—	—	—
1% furfuraldehyde + 1% Salicylaldehyde	46.4	53.5 (51.8)	56.4 (57.2)

Values in brackets are for 500 ml of the test solution.

in all the cases except salicylaldehyde in the range 20-30°C, the heat of adsorption increases for higher temperature ranges. However, no specific generalizations can be drawn regarding the relation between inhibitor efficiency and heat of adsorption.

(iv) *Galvanostatic Polarization Behaviour :* A specimen of 3S aluminium when immersed in 0.1M NaOH developed a steady state potential of-1520 mV vs SCE. In the presence of inhibitor the open circuit potentials were observed to be higher (Table III)

TABLE III

Tafel Parameters and Inhibitor efficiency of Aldehydes for 3S Aluminium in 0.1M NaOH
(Surface area of specimen ; 6.15 sq cm ; Temperature 30° ±0.5°C)

Inhibitor	Open circuit potential vs S.C.E. (mV)	Tafel slope, mV/decade		Energy Transfer Coefficient (cathodic)	Corrosion current A/cm² from extrapolation of		Inhibitor efficiency(%) calculated from		
		Cathodic	Anodic		cathodic Tafel line	anodic Tafel line	extrapolation of Cathodic Tafel line	extrapolation of Anodic Tafel line	weight loss data
nil	—1520	50	150	1.20	3.25×10^{-4}	4.87×10^{-4}	—	—	—
1% furfuraidehyde	—1270	100	875	0.60	1.91×10^{-4}	1.13×10^{-5}	41.2	83.3	35.8
2% furfuraldehyde	—1250	120	750	0.50	1.72×10^{-4}	4.25×10^{-5}	47.1	91.3	55.1
1% Salicylaldehyde	—1460	63	660	0.89	9.75×10^{-5}	4.25×10^{-5}	70.0	90.3	75.1
2% Salicylaldehyde	— 840	71	—	0.79	9.55×10^{-7}	—	99.7	—	100
1% Surfuraldehyde + 1% Salicylaldehyde	-1380	170	230	0.35	1.46×10^{-4}	9.75×10^{-5}	58.2	80.0	69.2

and thus the compounds appeared to be functioning as anodic inhibitors.

Anodic and cathodic galvanostatic polarization curves for 3S aluminium in 0.1M NaOH, alone and containing 1 or 2% concentrations of the various inhibitors are shown in Fig. 3. The figure shows both anodic and cathodic polarization, anodic polarization being more pronounced than the cathodic

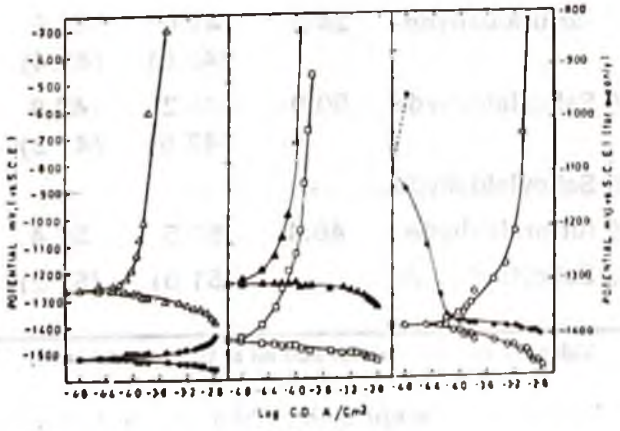


Fig. 3 Effect of current density on cathode and anode potentials of 3S aluminium in 0.1M NaOH (30°C)

● — ● 0.1M NaOH
△ — △ 1% furfuraldehyde
▲ — ▲ 2% furfuraldehyde
○ — ○ 1% furfuraldehyde + 1% Salicylaldehyde
■ — ■ 2% Salicylaldehyde
□ — □ 1% salicylaldehyde

especially in solutions containing inhibitors. The inhibitors thus appear to be mixed type inhibitors with preponderant action on the local anodes.

When the inhibitor efficiencies were calculated by extrapolating the cathodic as well as the anodic Tafel lines it was found that the efficiency obtained from cathodic Tafel line almost agreed with the weight loss efficiency. The efficiencies calculated from anodic Tafel lines were however somewhat higher (Table III).

It is also interesting to note that on addition of 2% salicylaldehyde the pH of 0.1N NaOH (viz., 12.8) drops down to 9.3 which is in the noncorrosive pH range for aluminium. This must be the reason for 100% inhibition in this solution even upto 50°C. During cathodic polarization, the polarization increases rapidly up to a c. d. of 6.48×10^{-5} A/cm² and then it increases slowly. However, at a c. d. of 3.25×10^{-4} A/cm² there is an evolution of bubbles from the metal surface which is now dull in appearance due to etching on some parts and indicates the onset of corrosion. The polarization curve with 2% salicylaldehyde also appears to be quite different from the rest of the plots which are almost similar in nature.

CONCLUSIONS

The inhibitive efficiency of furfuraldehyde increases whereas that of salicylaldehyde and of their 1:1

mixture decreases with alkali concentration. However, with a rise in temperature, the efficiency of furfuraldehyde decreases while that of salicylaldehyde and the 1 : 1 mixture increases. With increase in immersion period all the inhibitors show an increase in efficiency.

The increase in the open circuit potential in inhibited alkali and also the galvanostatic polarization data suggested that the inhibitors are mixed type inhibitors with preponderant action on local anodes.

Acknowledgement

The authors are thankful to the Uttar-Purva Gujarat Uchcha Kelavani Mandal, Pilvai, for laboratory facilities, and to Gujarat University, Ahmedabad, for the award of a research scholarship to one of them (N.H.H.).

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