Qatar Univ. Sci. J. (1993), 13(1): 40 - 45

THE INHIBITIVE ACTION OF SODIUM SOYA SULPHONATE TOWARDS THE CORROSION OF ALUMINIUM IN HYDROCHLORIC ACID

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التأثير التثبيطي لسلفونات صويا الصوديوم تجاه تآكل الألمونيوم في حمض الهيدروكلوريك

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تمت دراسة ذوبان الألمونيوم في محلول ٢ مولارى من حمض الهيدروكلوريك في وجود سلفونات صويا الصوديوم كمثبط للتآكل باستخدام طريقة التصاعد الهيدروجيني والطريقة الحرارية . وقد أعطيت الطريقتان نتائج متطابقة . وقد بينت النتائج أن التأثير التثبيطي للسلفونات يعود إلى ادمصاصها على سطح الفلز من خلال الكترونات الباي الموجودة في الروابط الزوجية في مركبات السلفونات .

Key Words: Sodium soya sulphonate, aluminium, corrosion, inhibition.

ABSTRACT

The dissolution of aluminium in 2M hydrochloric acid in the presence of sodium soya sulphonate (SSS) as corrosion inhibitor has been studied using hydrogen evolution and thermometric methods. The two methods gave consistent results. The results obtained indicate that the inhibitive effect of the sulphonated mixture relates to chemisorption mechanism on the metal surface via the π electrons in the double bonds.

INTRODUCTION

The wide use of aluminium in various industrial and constructional operations makes the study of its corrosion inhibition of great importance. Some corrosion inhibitors have been prepared through the ethoxylation of four commercially available unsaturated fatty acid mixtures; tall oil, soya bean, cotton seed and linseed oil. The produced compounds have been tested as steel corrosion inhibitors in HCl and H_2SO_4 acid solutions (Hana *et al.,* 1987). They provide adequate inhibition of steel in HCl and H_2SO_4 of different concentrations and at temperature up to 80°C and act as mixed inhibitors.

The present study aimed to investigate the effect of sulphonated soya bean oil as corrosion inhibitor for aluminium in 2M HCl solution and to relate the inhibition mechanism to the additive structure.

EXPERIMENTAL

1. Hydrogen Evolution Measurement

Reactions in which gases are given off or taken up can be monitored by studying the changing amount of gas over time. Since aluminium is readily soluble in aqueous acids with liberation of hydrogen, the hydrogen evolution method was used to measure the rate of dissolution of aluminium in HCl solutions (Thiel and Eckell, 1928; Urmanczy, 1937; Gonet 1939; Quartaroli and Belfiori, 1939; Fouda *et al.* 1986; Mourad *et al.* 1986; Mourad *et al.* 1990). The Reaction vessel used in this method and the procedure for determining the dissolution of aluminium in the acid solution were the same as described elsewhere (Deren *et al.,* 1963). The efficiency of a given inhibitor can be evaluated as the percentage reduction in reaction rate K, % inhibitor efficiency (% IE).

$$= \frac{K_{uninhibited} - K_{inhibited}}{K_{uninhibited}} \times 100$$

2. Thermometric Measurement

A simple and rapid method has been developed (Aziz and Shams El-Din, 1965) based on the thermometric corrosion test of Mylius (Mylius, 1922). This method has been successfully used for comparing the inhibition efficiency of different organic additives in reducing the rate of dissolution of aluminium (Ahmed *et al.* 1985; Darwish, 1978; Abd El-Wahab and Khedr, 1980). The procedure for the determination of metal dissolution rate by the thermometric method has been described previously (Aziz and Shams

El-Din, 1965). The reaction number RN is defined as (Mylius, 1924)

$$RN = (T_m - T_i) / t$$

where T_m and T_i are the maximum and initial temperature, respectively, and it is the time (in minute) required to reach the maximum temperature. The percent reduction in RN (Mourad *et al.*, 1990) is given as

$$= \frac{RN_{uninhibited} - RN_{inhibited}}{RN_{uninhibited}} \times 100$$

The chemical composition of aluminium sheet used (Riedel de Haen, West Germany) is given in Table 1.

Table 1
Chemical composition of aluminium

Element	Al	Fe	Cu	Si	Ti	Zn
Amount (%)	99	0.2	0.2	0.2	0.03	0.08

A stock solution of 2M HCl was used. Aluminium test pieces measuring 0.1 x 10 x 30 mm used for the hydrogen evolution method, while 0.1 x 10 x 100 mm test pieces were used for the thermometric method. These were degreased and etched as previously mentioned (Rawdon, 1930). Each experiment was carried out with 100 ml of the acid solution in hydrogen evolution method and 15 ml of the acid solution in thermometric method.

The experimental data were analysed using a Beam Professional Computer and curve fitting was carried out using a standard regression package.

3. Composition of Sodium Soya Sulphonate (SSS)

Sodium soya sulphonate (SSS) was prepared in laboratories of Egyptian Petroleum Research Institute (Nasr City - Cairo, A.R.E.) by sulphonation of Soya bean oil. The product has the general formula R. $COO.SO_3N_a$, where R is mainly a mixture of $C_{17}H_{29}$, $C_{17}H_{31}$ and $C_{17}H_{33}$. Sulphonates of oleic, linoleic and linolenic acids are the main constituents of the product. The composition of sulphonated soya bean oil is given in Table 2.

Table 2
Composition* of sulphonated product (SSS)

	Composition Wt %
Oleic (one double bond)	20 - 30
Linoleic (two double bonds)	43 - 56
Linoleni (three double bonds)	8 - 14
Palmetic (single bonds)	9

*The main constituents are given.

RESULTS AND DISCUSSION

1. Hydrogen Evolution Measurements.

Figure 1 shows the volume of hydrogen evolved as a function of time for dissolution of aluminium in 2M HCl at 30°C in the absence and presence of SSS over concentration rang (0.1 - 150) x 10^2 mg / L. It was found that the hydrogen evolution increases linearly with time after a certain time interval which increases with an increase of SSS concentration. The initial time interval was attributed to an incubation period (Muller and Low, 1936) representing the breakdown of the oxide film on the metal surface and the start of the attack (Aronson and Yoffe, 1940). Accordingly, it can be stated that the dissolution of aluminium itself is linearly related to the reaction time, as seem from Fig. 2. This behavior is characteristic of zero - order reactions (Smrcek *et al.*, 1958), generally given by:

$$V = K t$$

where V is the volume of hydrogen evolved, which is proportional to the fraction of the reactant converted into reaction product at time t, and K is the specific reaction rate.

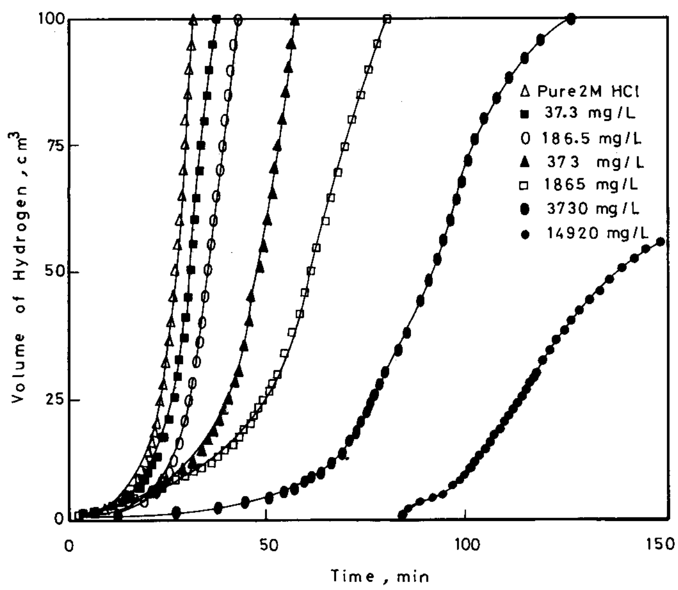

Fig. 1: Effect of SSS concentration on volume - time curves for Al in 2M HCl at 30°C.

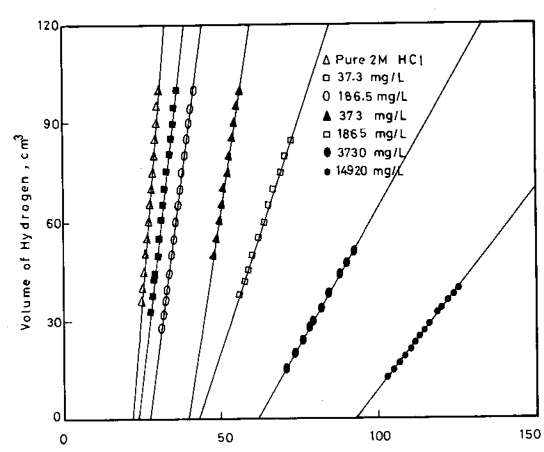

Fig. 2: Effect of SSS concentration on volume - time curves for for free dissolution of Al in 2M HCl at 30°C.

The experimental data, given in Table 3, indicate that the specific reaction rate decreases with increase in SSS concentration. Fig. 3 shows that addition of increasing amounts of SSS lead to a marked decrease in the reaction rate of aluminium in the tested solution. The % IE increases with an increase in the additive concentration. Figure 4 shows the plot of % IE as a function of log Csss which is invariably sigmoid in nature, indicating that SSS exhibits its inhibitive effect through its adsorption on the metal surface. Figure 5 indicates that the incubation period (τ) increases with the additive concentration.

Table 3
Effect of SSS concentration on the dissolution rate of aluminium in 2M HCl solution at 30°C.

SSS concentration (mg/L)	0.0	37.3	186.5	373	1865	3730	14920
Corrosion rate K (cm^3 / min)	10.82	7.79	6.80	5.90	2.85	1.67	1.22
Incubation period (min)	13.85	15	18.83	21.75	28.75	43.67	82.88
% IE	0.0	28	37.15	45.47	73.66	84.57	88.72

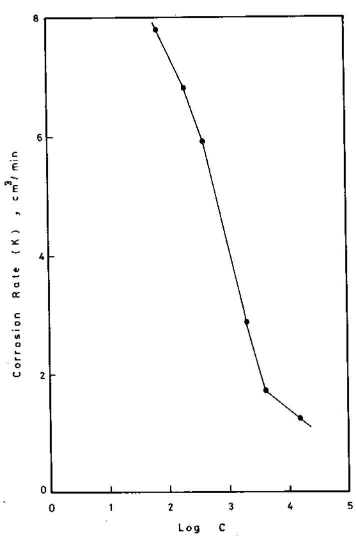

Fig. 3: Effect of SSS concentration on corrosion rate of Al in 2M HCl at 30°C.

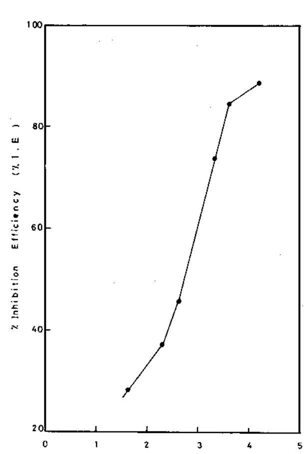

Fig. 4: Relation between % IE and concentration of SSS.

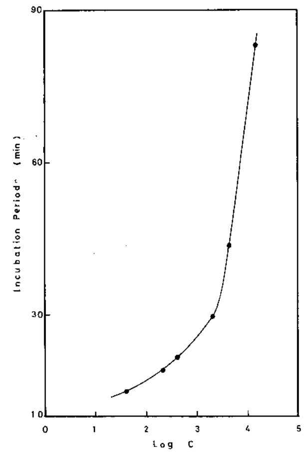

Fig. 5: Effect of SSS concentration on incubation period of Al in 2M HCl at 30°C.

The effect of temperature on the rate of dissolution of aluminium in 2M HCl was studied between 35°C and 60°C in the presence of 3730 mg/L sodium soya sulphonate (Fig. 6). The corrosion rates and incubation periods are listed in Table 4. The results indicates that the corrosion rate increases with increasing temperature (Fig. 7). The activation energy for the corrosion process was evaluated and found to be 5.49 Kcals. Accordingly, the corrosion process is controlled by the surface reaction, since the activation energy for the corrosion process is above 5 Kcals (Mourad *et al.*, 1989).

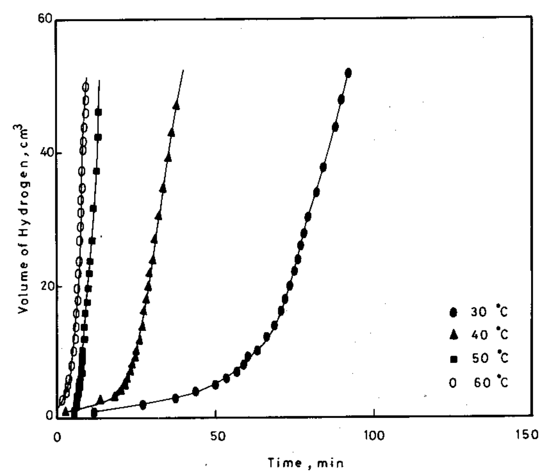

Fig. 6: Effect of temperature on volume - time curves of Al 2M HCl containing 3730 mg / L SSS.

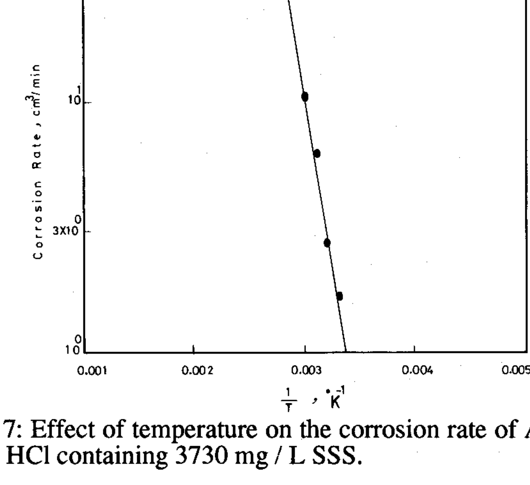

Fig. 7: Effect of temperature on the corrosion rate of Al in 2M HCl containing 3730 mg / L SSS.

It was found that the incubation period decreases with increase in temperature according to a linear relationship (Fig. 8), which satisfies the equation

$$\log \tau = 6.95 - 3.6 \log T$$

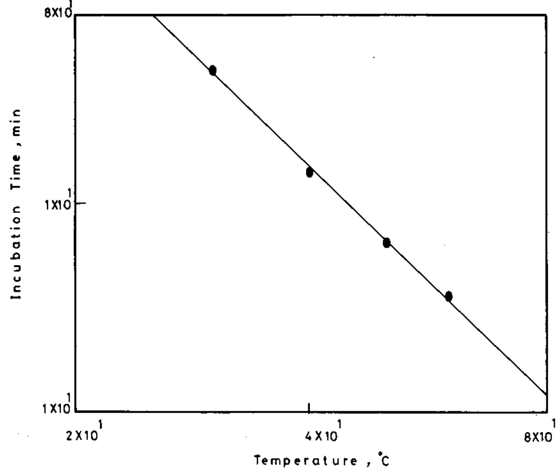

Fig. 8: Effect of temperature on incubation period for Al in 2M HCl containing 3730 mg / L SSS.

Table 4
Effect of temperature on corrosion of Al in HCl containing 3730 mg / L SSS

Temperature °C	30	40	50	60
Corrosion rate K (cm^3 / min)	1.67	2.71	6.17	10.36
Incubation period	43.67	14.42	6.5	3.62

Table 5
Effect of SSS concentration on parameters of thermometric curves for Al in 2M HCl

[SSS] mg / L	TI °C	Tm °C	t min	RN °C/min	%RR	t min	min
0.0	15	58.4	65	0.67	0.0	0.0	44
186.5	15	56.2	74	0.56	16.42	9	64
373	15	55.8	87	0.47	29.85	22	76
3730	15	45.6	137	0.22	67.16	72	127
14920	15	44.2	242	0.12	82.09	177	190

2. Thermometric Measurements.

The dissolution of aluminium in 2M HCl was accompanied by temperature change. The maximum temperature is 58.4°C, and is attained within 65 min, corresponding to an RN of 0.668°C/min. To this solution increasing amounts of sodium soya sulphonate are added. The recorded thermometric curves are shown in Fig. 9. One recognizes at first an incubation period, after which the temperature rises gradually with time. The rate of temperature rise increases progressively with time. Sodium soya sulphonate interferes with the dissolution of aluminium and lowers the RN. This is produced mainly through a lowering in T_m and a corresponding increase in t. This suggests strong adsorption of the additive (Aziz and Shams El-Din, 1965) as indicated from the thermometric curves. Table 5 represents the effect of the additive concentration on the parameters of the thermometric curves. Fig. 10 shows the variation of percentage reduction in reaction number (%RR) as a function of log C_{SSS} for aluminium in 2M HCl. One inflection point was observed indicating perhaps that sodium soya sulphonate reduces the corrosion rate by way of adsorption leading to the formation of a monolayer of the inhibitor on the aluminium surface, in accordance with Frumkin's isotherm (Frumkin, 1925). In a plot of the time delay (Δt) vs log C_{SSS}, the turn in the curve observed (Fig. 11) indicates the formation of a monolayer of the inhibitor on the metal surface (Aziz and Shams El-Din, 1965). Fig. 12 indicates that the incubation period (τ) is related to the SSS concentration by a straight line relationship which satisfies the equation

$$\log \tau = 2.6 + 0.24 \log C_{SSS}$$

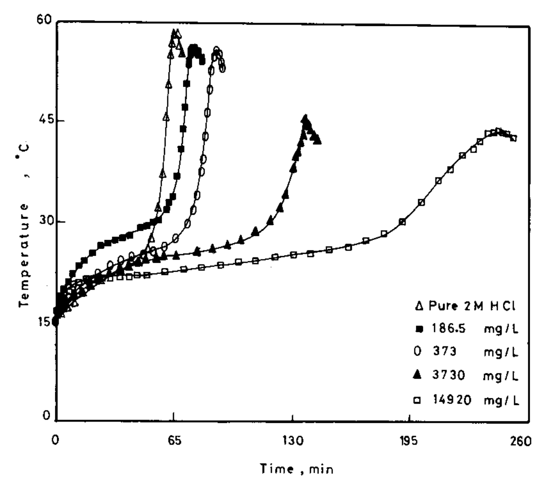

Fig. 9: Effect of SSS concentration on temperature - time curves of Al in 2M HCl solution.

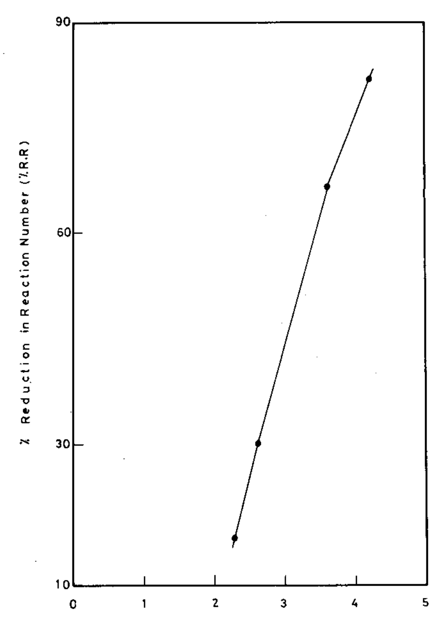

Fig. 10: % RR - log C_{SSS} relation.

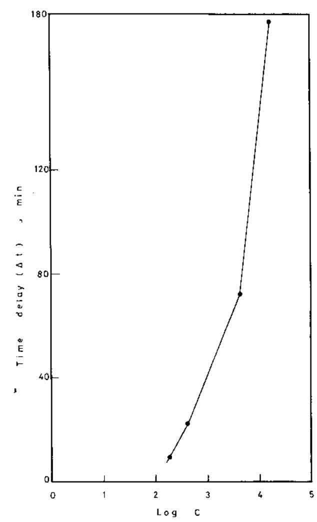

Fig. 11: t - log C_{SSS} relation.

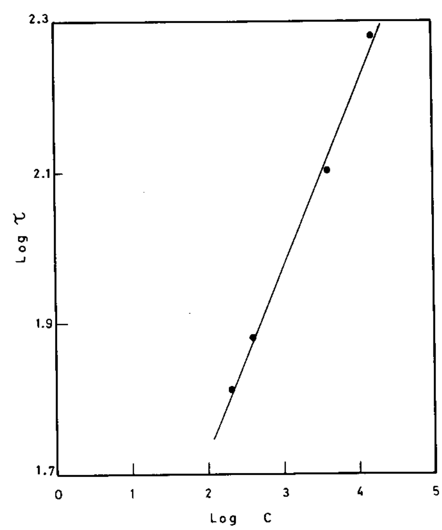

Fig. 12: Effect of SSS concentration on incubation time.

The experimental results suggest adsorption mechanism through monolayer formation of sodium soya sulphonate on the metal surface. As seen from the chemical composition of the additive, its main constituent is the sulphonate salt of linoleic acid which contains two double bonds. This substantiates the idea that the inhibitive effect of SSS can related to chemisorption mechanism on the metal surface via the electrons in the double bonds.

It should be noted that the two different techniques demonstrated the agreement and conformity of the experimental results as to the type of inhibition of the corrosion of aluminium. Nevertheless, they showed small differences in absolute values for the inhibition efficiency. However, this observed discrepancy could be attributed to the different experimental conditions under which each technique was carried out.

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