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

By

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التأثير التثبيطي لسلفونات الخروع الصوديومية تجاه تآكل الألومنيوم في حمض الهيدروكلوريك

سمير عبد السلام سليمان و ممدوح يوسف مراد

تمت دراسة ذوبان فلز الألومنيوم في محلول ٢ مولاري من حمض الهيدروكلوريك في وجود سلفونات الخروع الصوديومية باستخدام الطريقة الحرارية وطريقة تصاعد غاز الهيدروجين

وقد أثبتت النتائج أن المادة المضافة تثبط عملية النوبان نتيجة لادمصاصها على سطح الفلز من خلال ألكترونات الباي في الروابط الزوجية . وقد وجد أن الادمصاص يتبع ايزوثرم فرومكين .

Key Words: Acid corrosion, Aluminium, sodium castor sulphonate, hydrogen evolution and thermometric methods, inhibition.

ABSTRACT

The dissolution of aluminium in 2M HCl solution in presence of sodium castor sulphonate (SCS) has been studied using thermometric and hydrogen evolution methods. The results showed that the additive retards the dissolution due to its chemisorption on the metal surface via π the electrons of the double bond. The inhibition object the Frumkin's isotherm.

INTRODUCTION

The study of corrosion inhibition of aluminium metal is of great importance because of its widespread use in various industrial and constructional operations. Organic compounds containing multiple bonds especially triple bonds have been widely used as corrosion inhibitors (Toshiharu *et al.*, 1969). It has been reported that ethoxylates of unsaturated fatty acids such as oleic, linoleic, linolenic, eleostearic and ricinoleic are quite effective compounds in retarding the dissolution of steel in hydrochloric acid. The inhibition efficiency also increases with the increase in number of double bonds, or due to presence of bifunctional moles in the structure as in ricinoleic acid (Hanna *et al.*, 1987). Also, ethoxylates of tail oil, soya bean, cotton seed and linseed oil provide adequate inhibition of steel in pickling acids (Hanna *et al.*, 1989) and act as mixed inhibitors.

The object of this work is to examine the effect of sodium castor sulphonate (SCS) as corrosion inhibitor for aluminium in 2M hydrochloric acid.

EXPERIMENTAL

The chemical composition of aluminium used is: Al 99%, Fe 0.2%, Cu 0.2%, Si 0.2%, Ti 0.3% and Zn 0.08% (Riedel de Haen, Germany). Stock solution of HCl (2M) was prepared.

The used sodium castor sulphonate (SCS), prepared in Egyptian Petroleum Research Institute (EPRI), Nasr City, Cairo, Egypt, has the general formula R-COO-SO₃Na, where R is mainly a mixture of C₁₇H₂₉, C₁₇H₃₁ and C₁₇H₃₃. Oleic linoleic and ricinoleic are the main constituents of the commercially used castor oil. The composition of commercial castor oil used is illustrated in Table 1.

Table 1
Composition of the commercial castor oil

Composition wt %	oleic	linoleic	ricinolic
	4 - 5	4 - 5	85 - 90

Two experimental techniques have been used in carrying out this work, namely:

1. The thermometric technique

It is a simple and rapid method based on the thermometric corrosion test of Mylius (Mylius, 1922). This method has been developed (Aziz et al., 1965) and successfully used for comparing the efficiency of different organic and organometallic additives in reducing the corrosion rate of aluminium (Darwish, 1978; Mourad et al., 1989). The reaction number (RN) is defined as (Mylius, 1924):

$$RN = \frac{T_m - T_i}{t}$$
 °C/min

where T_m and T_i are the maximum and initial temperature, respectively, and t is the time (in minutes) required to reach the maximum temperature. The percent reduction in reaction number (% RR) is given as Fouda *et al.*, 1987:

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

Aluminium test pieces measuring $0.1 \times 10 \times 100$ mm were used.

2. The hydrogen evolution technique

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 hydrochloric acid (Thiel et al., 1928; Urmanczy, 1937; Gonet, 1939; Quartaroli et al., 1939; Fouda et al., 1986; Mourad et al., 1990). The reaction vessel and the procedure for determining the dissolution of aluminium in the corroding media 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) (Mourad et al., 1989).

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

Aluminium test pieces measuring 0.1 x 10 x 30 mm were used. All test pieces used were degreased and etched before carrying out the experimental work (Rawdon, 1930).

The experimental data were analysed using a BEAM personal computer and curve fitting was carried out using a standard linear regression package.

RESULTS

1. Thermometric measurements

In this method the temperature change of the system involving Al in 2M HCl was followed in absence and in presence of different concentrations of sodium castor sulphonate SCS (Fig. 1). The maximum temperature measured in acid solution is 58.4° C, and is attained after 65 min. This corresponds to an RN of 0.668 °C/min. On increasing the concentration of SCS the time required to reach T_m increases. This indicates that the additive retards

the dissolution of aluminium, presumably by adsorption onto the surface of the metal. The extent of retardation for inhibition depends on the degree of coverage of the metal with the adsorbate, and the temperature - time curves provide a means of differentiating between weak and strong adsorption (Aziz et al., 1965). Weak adsorption is noted in the acid solution. This is produced mainly through a corresponding increase in t causing a remarkable decrease in the RN of the system. The results recorded in (Table 2) reveal that the efficiency of corrosion inhibition as determined from the percent reduction in RN increases with the concentration of SCS in 2M HCl solution.

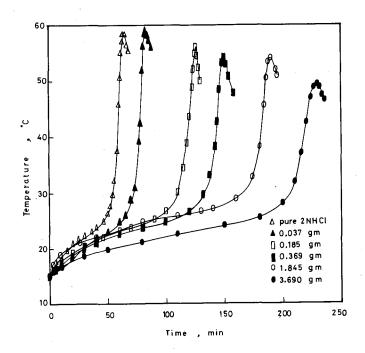


Fig. 1: Effect of SCS concentration on thermometric curves of Al in 2M HCl solution.

Table 2
Effect of SCS concentration on the parameters of the thermometric curves for Al in 2M HCl solution.

SCS Concentratio gm/L	Ti ℃	T _m °C	t min	RN °C/min	% RR	Δt min
0.0	15	58.4	65	0.668	0.0	0.0
0.037	15	58.8	83	0.528	20.96	18
0.185	15	56.0	126	0.325	51.35	61
0.369	15	53.8	151	0.257	61.53	86
1.845	15	54.1	190	0.206	69.16	125
3.690	15	49.4	230	0.150	77.54	165
18.450	15	41	363	0.072	89.22	289

Fig. 2 represents the logarithm of the reaction number to the logarithm of the concentration of SCS. The curve is invariably sigmoid in nature, substantiating the idea that SCS reduces the corrosion rate by way of adsorption. The associated with the formation of a monolayer of the adsorpate on the surface of the corroding metal, in accordance with Frumkin's isotherm (Frumkin, 1925).

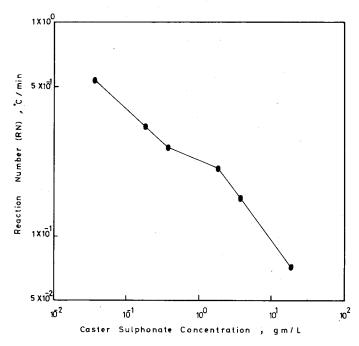
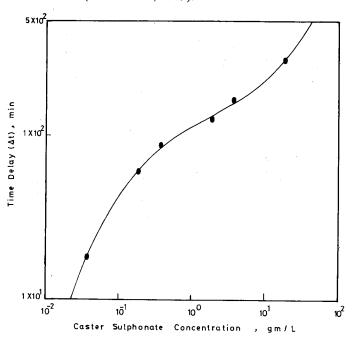


Fig. 2: Variation of reaction number with the concentration of SCS.

Fig. 3 relates to the logarithm of the time delay, Δt with logarithm of SCS concentration. The turn in the curve observed indicates the formation of a monolayer of the adsorpate on the surface of the metal (Aziz *et al.*, 1965).

Accordingly, one can safely verify that the inhibition mechanism is due to chemical adsorption. The effect can also be related to chemisorption mechanism on the metal surface via π electron in the double bonds of the sulphonated fatty acids mixture (Hanna *et al.*, 1989).



2. Hydrogen evolution measurements

Fig. 4 shows the volume of hydrogen evolved as a function of time for dissolution of Al in 2M HCl at 27° C in evolution increases linearly with time after a certain time interval which increases with an increase of SCS concentration. This initial time interval was attributed to an incubation period (Muller et al., 1936) representing the breakdown of the oxide film on the metal surface and the start of attack (Aronson et al., 1940). Accordingly, it can be stated that the dissolution of aluminium itself is linearly related to the reaction time. This behaviour is characteristic of zero - order reactions (Smrcek et al., 1958), generally given by (Mourad et al., 1989).

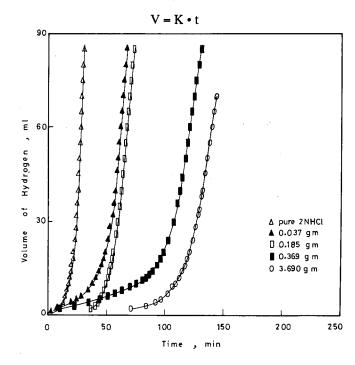


Fig. 4: Effect of SCS concentration on volume-time curves of Al in 2M HCl solution at 27° C.

where V is the volume of hydrogen evolved and this is proportional to the fraction of the reactant converted into reaction product at time t, K is the specific reaction rate. The data in (Table 3) indicate that the specific reaction rate decreases with an increase in SCS concentration. The % IE, determined by the hydrogen evolution technique, increase with an increase in the concentration of the additive. Fig. 5 shows the plot of logarithm of % IE as a function of logarithm of the concentration of SCS which has the characteristic S-shape, indicating that SCS forms a monolayer on the surface of aluminium and that its adsorption takes place according to the Frumkin's isotherm (Frumkin, 1925).

Table 3
Effect of SCS concentration on the dissolution rate of aluminium in 2M HCl at 27° C

SCS concentration (gm/L)	0.0	0.037	0.185	0.369	0.690
Corrosion rate K (cm ³ /min)	10.50	4.72	4.37	2.56	2.50
% IE	0.0	55	58.4	75.7	76.1

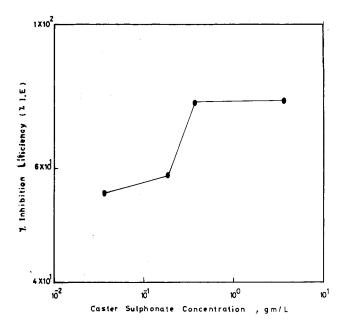


Fig. 5: Relation between % IE and concentration of SCS.

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 in 2M HCl solution. 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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