The Influence of Temperature on Corrosion Inhibition of Carbon Steel in Air-Saturated 7N H_3Po_4 by Potassium Iodide

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ABSTRACT

The corrosion inhibition of carbon steel (ASTM 108) in 7N H_3PO_4 by KI has been investigated at the temperatures: 30, 40, 50, and 60 °C. Weight loss and polarization techniques were employed in this investigation. The weight loss data showed that corrosion rate in presence and absence of KI as inhibitor increased with temperature and that for a given inhibitor concentration an Arrhenius plot was obtained from which the activation energies were calculated. The corrosion rate decreased with increasing inhibitor concentration for a given temperature resulting in an efficiency as higher as 99.6% at 50 °C in presence of 10 g/L concentration. The fraction of surface covered calculated from corrosion rates followed Langmuir adsorption isotherm.

Potentiostatic polarization experiments showed that for a given temperature, the curves were shifted towards the potential axis, leading to lower the corrosion rates, as the inhibitor concentration increased. The influence of temperature and inhibitor concentration was found to be mixed, affecting both the anodic and cathodic reactions, but anodic more. KI as corrosion inhibitor was found to be very effective in retarding carbon steel corrosion in air-saturated 7N H_3PO_4 acid.

INTRODUCTION

Like most chemical reactions, the corrosion reactions are temperature dependent, Arrhenius equation expresses this dependency [1].

High acid concentrations are encountered in pickling processes, oil well acidizing and during the transportation of acids for use in chemical processes. Sulfuric and phosphoric acid concentrations up to 70% can be inhibited by methods similar to those used for HCl acid. Concentrations of H_2SO_4 higher than 70% attack steel slowly and do not require inhibition. Fertilizer grade, H_3PO_4 acid (73% black acid) attack steel readily and usually is inhibited with KI. Organic inhibitors are not effective in concentrated H_3PO_4, when used alone but it has been reported that a lower concentration of KI is required for inhibition if a fatty amine is also added [2]. Usually handling and transportation of H_3PO_4 are carried out at 35-40 °C, but in some cases temperature in the range of 50 °C are reached[3].

The 60 °C temperature, was used in this work, which is mainly aimed to describe the effect of KI as inhibitor on H_3PO_4 corrosion in the storage, transportation and pickling operations. It is clear that the adsorption of chemicals used as inhibitors may follow one of the four well known adsorption isotherms [4].

Is KI an inorganic additive to H_3PO_4 follow one of the mentioned isotherms? This is the question which must be answered later.

EXPERIMENTAL

Material and Solutions

The material used was low carbon steel (ASTM 108), obtained in sheet form which was cut into 3 cm long specimens x 1 cm wide x 0.1 cm thick with exposed surface area of about 6.8 cm^2 for weight loss and polarization experiments. They were grounded and degreased with analar benzene and acetone, annealed in a vacuum at 600 °C for 6 h's., and furnace cooled to room temperature, they were then stored over silica-gel. Emery papers of grade No. 220, 320, 400, and 600 were used to abraded the samples in sequences, washed by tap and distilled water, dried, degreased by analar benzene and acetone, then kept over silica-gel until use.

The solutions used were air saturated 7N H_3PO_4 prepared using distilled water containing non and various concentrations of KI as corrosion inhibitor.

Procedure

Weight loss experiments:

The tests were carried out in one liter round bottom glass flask, with two necks, one was used for immersing a thermometer to observe the test temperature, and the other to immerse the specimen hanging within on a glass hook in the test solution. Before each test the cell was washed with tap, distilled water, and test solution respectively, then filled with test solution and immersed in a constant temperature water bath, and allowed to reach thermal equilibrium before immersing the specimens. Tests were allowed to last for 3 h's, at temperatures of 30, 40, 50, and 60 °C.

After each test, specimens were washed with running tap water, scrubbed with a special brush to remove adherent corrosion products, washed with running and distilled water and dried; rinsed in analar acetone, dried and left on silica-gel before weighing them accurately.

Potentiostatic Polarization Measurements

Test were carried out in an ASTM cell. Platinum electrodes were used as counters, SCE as reference electrode, fitted with spherical ground joint for manipulating the luggin capillary prob. Using a potentiostat model 551 supplied by Amel (Italy), measurements of this investigation were carried out. The specimens were placed in position and the initial E_{corr} was measured; after which the potential was adjusted at different values in the cathodic and anodic directions (i.e., -700 to 300 mV). Potential against log current was recorded. Each test was made twice, any doubt in reproducibility of the results a third test was carried out.

RESULTS AND DISCUSSION

Weight Loss Experiments

Temperature Effect:

Arrhenius equation expresses the temperature dependence of corrosion reactions as [1]:

$$\text{Corrosion Rate} = A\exp(-E/RT) \qquad \ldots(1)$$

where: E is the activation energy (kcal/mole).

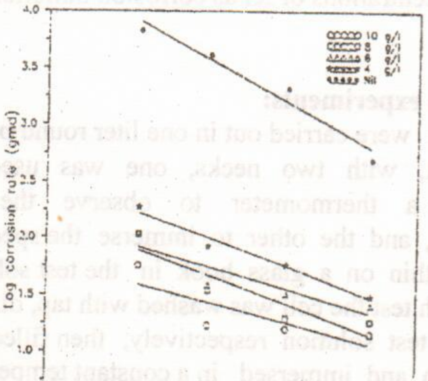
T is the absolute temperature (K).

A is a constant.

R is the universal gas constant. (8.314 J/mole.K).

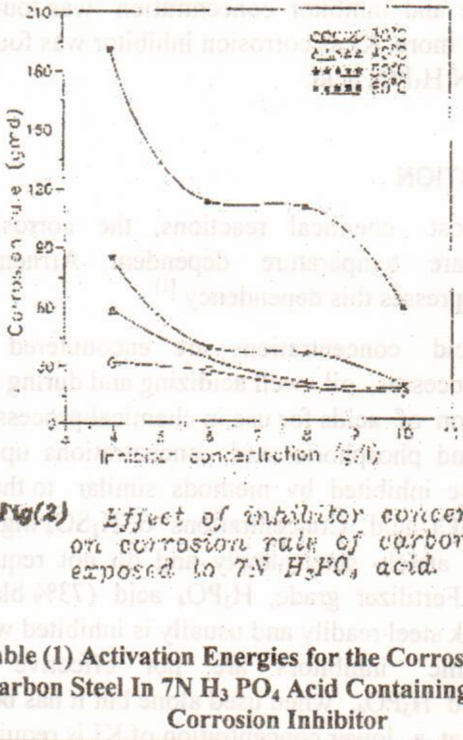
A plot of log (corrosion rate) against (1/T) represents graphically the above relation, giving a straight line with slope equal to (-E/2.303R) from which the activation energy can be calculated.

In the present study, Arrhenius plots were drawn in presence of various concentrations of KI as shown in Fig. (1). From these plots the activation energies were calculated as shown in Table (1).



Fig(1) *Arrhenius plot of carbon steel in 7N H_3PO_4 containing various concentrations of KI in temperature range of (30-60°C).*

Corrosion rates were found to increase with temperature, increase for both inhibited and uninhibited acid solutions, while they decrease with inhibitor concentration increase for a given temperature as shown in Fig. (2). From the activation energy values of low carbon steel in 7N H_3PO_4 in the presence and absence of different inhibitor concentrations of KI shown in Table (1), it is concluded that: in uninhibited 7N H_3PO_4 solutions, the activation energy of the dissolution process is 17 kcal/mol. For low carbon steel in H_3PO_4 acid solution, very few values given in the literature for the activation energy ranging from (15-20 kcal/mole) with the majority grouped at about (16 kcal/mole) [5]. The activation energies in presence of KI are lower generally than that in uninhibited 7N H_3PO_4, showing that this reduction is associated with an improvement in inhibitor efficiency with an increase in its concentration.



Fig(2) *Effect of inhibitor concentration on corrosion rate of carbon steel exposed to 7N H_3PO_4 acid.*

Table (1) Activation Energies for the Corrosion of Low Carbon Steel In 7N H_3PO_4 Acid Containing KI as the Corrosion Inhibitor

Inhibitor concentration (g/l)	Activation energy (kcal/mole)
4	11.41
6	8.795
8	11.343
10	8.024

It can be concluded that the decrease in activation energy at high levels of inhibitor arises from a shift of the net corrosion reaction from that on the uncovered surface to one involving adsorbed sites directly [1]. The fraction of surface covered by inhibitor is equal to the corrosion inhibition efficiency and can be expressed mathematically as:

$$\theta = \mathit{Inhibition\ Efficiency} = \left(1 - \frac{R_i}{R_u}\right) x100 \qquad \ldots(2)$$

where R_u and R_i are the uninhibited and inhibited corrosion rates respectively. It is very clear the improvement with the increase in temperatures shown in Table (2).

Table (2) Corrosion inhibition efficiency of carbon steel in 7N H_3PO_4 acid by KI at different temperature levels.

Inhibitor Concentration (g/L)	Corrosion Inhibition Efficiency (% θ)			
	30 °C	40 °C	50 °C	60 °C
4	93.71	97.2	97.98	97.2
6	94.73	98.43	99.07	98.32
8	96.24	99.05	99.16	98.37
10	97.14	99.59	99.56	99.14

Potentiostatic Polarization

Table (3) shows the corrosion potential obtained from the polarization curves. It is observed the influence of both the temperature and inhibitor concentration on it clearly.

Table (3) Corrosion Potential Values at Different Conditions

Run No.	Temperature °C	Inh. Conc. (g/l)	E_{corr} (mV)
1	30	Nil	-495
2	40	Nil	-497
3	50	Nil	-515
4	60	Nil	-522
5	30	4	-418
6	40	4	-462
7	50	4	-440
8	60	4	-463
9	30	6	-460
10	40	6	-450
11	50	6	-465
12	60	6	-466
13	30	8	-425
14	40	8	-442
15	50	8	10-448
16	60	8	-485
17	30	10	-405
18	40	10	-480
19	50	10	-469
20	60	10	-474

The higher the temperature, the more the shifting the $E_{corr.}$ of uninhibited acid to negative values, i.e., the increase of temperature affects both anodic and cathodic reactions with the anodic is being more depolarize.

The same behavior can be observed at 8 g/L inhibitor concentration where $E_{corr.}$ was shifted to more negative values as the temperature was increased from 30-60 °C and as compared with uninhibited acid, i.e., the inhibitor mechanism possibly changed strongly leading to a big extent of effect on both anodic and cathodic reactions.

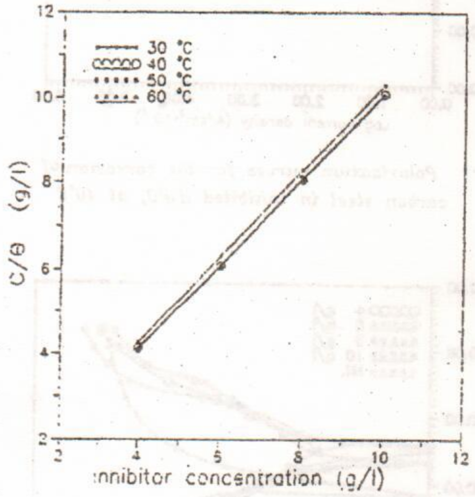
Corrosion inhibition by KI was found to follow Langmuir adsorption isotherm expressed mathematically [6].

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad \cdots(3)$$

where K: is the adsorption constant which indicates the degree of adsorption i.e., the higher the value of K (L/g), the higher the indication that the inhibitor strongly adsorbed on the metal surface [7].

C: is the concentration of the inhibitor (g/L).

The results are plotted according to above equation (i.e., C/θ vs. C) as shown in Fig. (3). The equilibrium constant (K) for KI is the highest in 7N H_3PO_4 acid at 50 °C (i.e., 99.6% inhibition) and the lowest value is in 30 °C (i.e., 93% inhibition). Fig. (3) shows the dependence of C/θ on C (inhibitor concentration). The rectilinear nature of the plots indicate increased adsorption occurred in accordance with Langmuir adsorption equation. Thus the data stresses the powerful action of KI in 7N H_3PO_4 concentration at elevated temperature manifested by the Kvalues.



***Fig(3)** Langmuir adsorption isotherm of potassium iodide on carbon steel in 7N H_3PO_4 acid.*

Figures (4, 5, 6, and 7) show that the current density decreases as the inhibitor concentration increases, (i.e., the increase in inhibitor concentration shifts the anodic and cathodic curves in the direction of less current density indicating that KI inhibits both anodic and cathodic reactions to different extents.

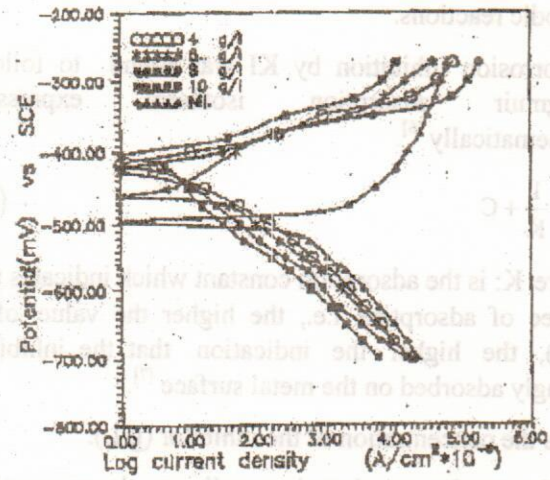


Fig.(4) Polarization curves for the corrosion of low carbon steel in inhibited H_3PO_4 at 30°C.

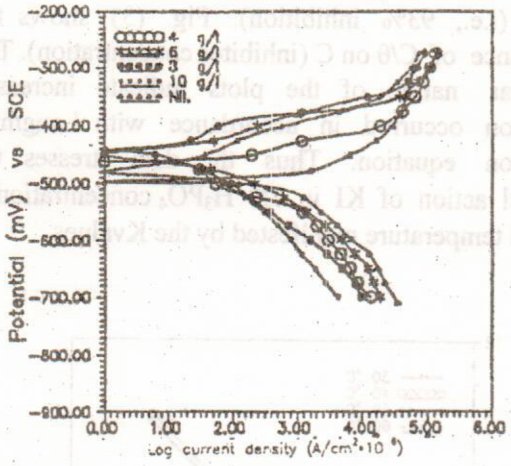


Fig.(5) Polarization curves for the corrosion of l carbon steel in inhibited H_3PO_4 at 40°C

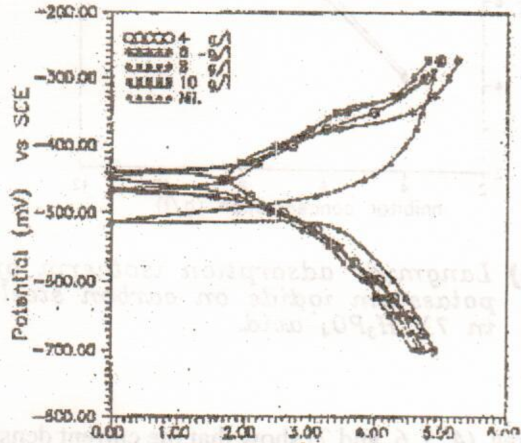


Fig.(6) Polarization curves for the corrosion of low carbon steel in inhibited H_3PO_4 at 50°C.

Figure (8) shows the inhibition efficiency for a given inhibitor concentration at different temperature levels which was calculated as follows:

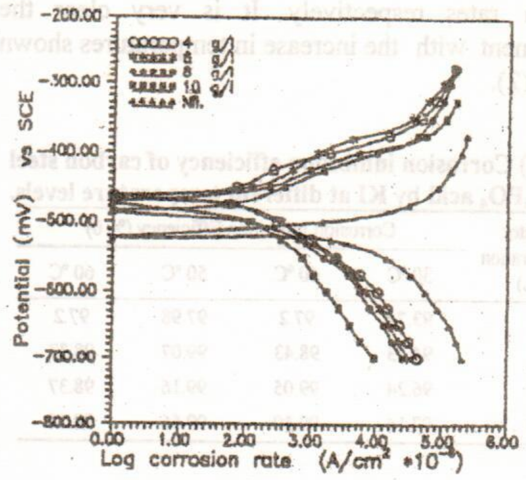


Fig.(7) Polarization curves for the corrosion of low carbon steel in inhibited H_3PO_4 at 60°C.

$$\%\text{Inhibition} = \left(1 - \frac{i_{in}}{i_{un}}\right) x100 \qquad \cdots(4)$$

where i_{un} and i_{in} are the uninhibited and inhibited current densities respectively. This figure shows that inhibition efficiency is concentration dependent, i.e., the higher the inhibitor concentration the higher the inhibition efficiency, this behavior confirms that the surface coverage of metal is function of inhibitor concentration as was shown in the weight loss experiments. Table (4) shows the fraction of surface covered by inhibitor, θ, at potentials taken on the anodic and cathodic curves respectively i.e., -375 mV and –600 mV (SCE) and indicate that the inhibition efficiency as well as the fraction of surface covered are inhibitor concentration dependent, but in the same time are potential independent for the cathodic reaction as it is clear from the behavior of cathodic polarization curve (i.e., they seem to be parallel). For the anodic reaction it was found that θ is potential dependent.

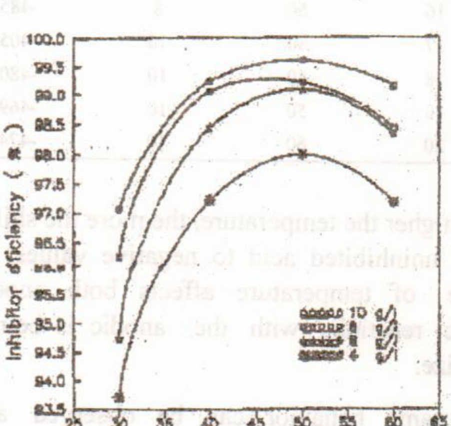


Fig.(8) Effect of temperature on inhibitive efficiency of KI for carbon steel in 7N H_3PO_4 acid.

Table (4) Cathodic and Anaodic Inhibition Efficiency at Different Operating Conditions

Inh. Conc. (g/l)	Temperature (°C)	Cathodic (θ_c) at – 600 mV	Anodic (θ_a) at – 375 mV
4	30	0.39	0.9915
6	30	0.53	0.9912
8	30	0.74	0.9922
10	30	0.82	0.9980
4	40	0.56	0.75
6	40	0.396	0.973
8	40	0.76	0.968
10	40	0.88	0.983
4	50	0.394	0.956
6	50	0.498	0.93
8	50	0.648	0.973
10	50	0.661	0.974
4	60	0.89	0.926
6	60	0.97	0.979
8	60	0.81	0.951
10	60	0.87	0.959

Finally, it can be concluded that KI as an inorganic inhibitor adsorbed due to the Langmuir adsorption isotherm, it inhibits both anodic and cathodic reactions to different extent with the $E_{corr.}$ shifting to more or less negative values depending on inhibitor concentration and acid temperature.

References

1. Riggs, O. L., JR and Hurd, R. M., "*Corrosion*", 23, 8, 252 (1967).
2. Norman, H., and Snavely, E. S., NACE, Houston, Texas, P. 9-8 (1975).
3. Barraco, P., Chiaro, G., and Farina, C. A., 11th International Corrosion Congress, Florece, Italy, P. 2-539, Vol. 2 (1990).
4. Smialowska, S. Z., and Weizorek, G., "*Corrosion Science*", 11, 843, (1971).
5. Riggs, O. L., "*Corrosion*", 24, 1, P. 125-126 (1968).
6. Moore, W. J., "Physical Chemistry", 5th edition, P. 500, Longman (1972).
7. Chain, R. J., and Nobe, K., J. Electrochem. Soc., 118, 4 (1971)