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*Effect of Water - Organic Solvent Mixtures on
Pitting Corrosion of Mild Steel*

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ABSTRACT

The pitting corrosion of mild steel was studied in 0.1 M NaCl + 0.015 M NaOH in water-glycerol, water-ethylene glycol, water-ethanol and water-dioxane solutions with various compositions (from 0.0 to 60 %v/v of the organic solvent component). The results obtained from the potentiodynamic and potentiostatic measurements show that the pitting corrosion is inhibited by the organic components in the medium. The inhibition percentage was increased with the increasing of the concentration of the organic solvent in the medium and reached about 80%.

It is suggested that the organic solvents inhibited the pitting corrosion of mild steel by (i) increasing the viscosity of the medium, which leads to a decrease in the diffusion coefficient of the corrosion products. It also decreases the dielectric constant of the medium, which lowers the basicity of the solution, and (ii) adsorption of solvent molecules on steel surface.

INTRODUCTION

Corrosion research in aqueous media has received most of the attention of corrosion scientists; little attention has been directed towards corrosion of metals in mixed solvents⁽¹⁻¹²⁾ or non-aqueous media, despite its importance in the chemical and fiber industries of processes employing non-aqueous environments. This also applies to the development of new technologies, especially the fuel formation and battery techniques.

Pitting corrosion is one of the most intensive forms of localized corrosion. The surface damage in pitting corrosion is usually much more severe than is indicated by the surface appearance.

The pitting corrosion of stainless steel caused by 0.1 M KCl was studied in water-methanol, water-isopropanol, water-2-ethoxyethanol, water-ethylene glycol and water-acetonitrile solutions with various compositions (from 0.0 to 80 %v/v of the organic solvent component). It was found that the pitting corrosion of stainless steel was inhibited by the organic component in the medium, and also the inhibition percentage (inh.%) was found to increase with increasing the concentration of the organic solvent in the medium⁽⁶⁾.

The object of the present work is to elucidate the corrosion behaviour of steel in water-glycerol, water-ethylene glycol, water-ethanol and water-dioxane solutions.

The effect of the nature and composition of the solvent on the corrosion of steel in 0.1 M NaCl + 0.015 M NaOH media was studied to obtain a clear understanding about the effect of some physical properties of the medium such as viscosity and dielectric constant on the corrosion of the steel.

EXPERIMENTAL

The experiments were performed with mild steel rods of cross sectional area 0.45 cm². The chemical composition of the material is given as follows.

Element	Fe	C	Si	Mn	P	S
Amount %	98.12	0.34	0.22	1.2	0.022	0.01

Prior each experiment the steel electrode was polished with a series of emery papers of variable grades, of 231 Q wetordry, Imperial, Papel Peso C. Starting with a coarse one, 3M(100) and proceeding in steps to the finest grade available, 3M(1000). The electrode was then washed several times with deionized water then with acetone and air dried.

Two types of electrochemical polarization measurements were conducted in deaerated 0.1 M NaCl + 0.015 M NaOH solutions using an AMEL potentiostat (Mod.555). These were: (i) Potentiodynamic polarization in the range (-0.1 to + 0.6V)^{*#} and (ii) potentiostatic polarization, at two constant values 0.0 and + 0.5V. All the electrode potentials were measured with reference to a saturated Ag/AgCl electrode ($E^0 = 0.1989$ V on the hydrogen scale). All experiments were thermostated at 30 °C ± 0.1, using freshly abraded clean electrode.

Deaeration was achieved by bubbling purified nitrogen into the solution for 30 min before each polarization study.

The composition of the bulk solution was changed by the addition of increasing amounts (0-60% v/v) of the organic solvent, i.e., glycerol, ethylene glycol, ethanol and dioxane. The used organic solvents were of pure grade (BDH) without further purification.

*The analysis was carried out at King Abdulaziz university, Jeddah Saudi Arabia

* * Potential changes were carried out manually.

RESULTS AND DISCUSSION

a- Anodic Dissolution under Potentiodynamic Conditions

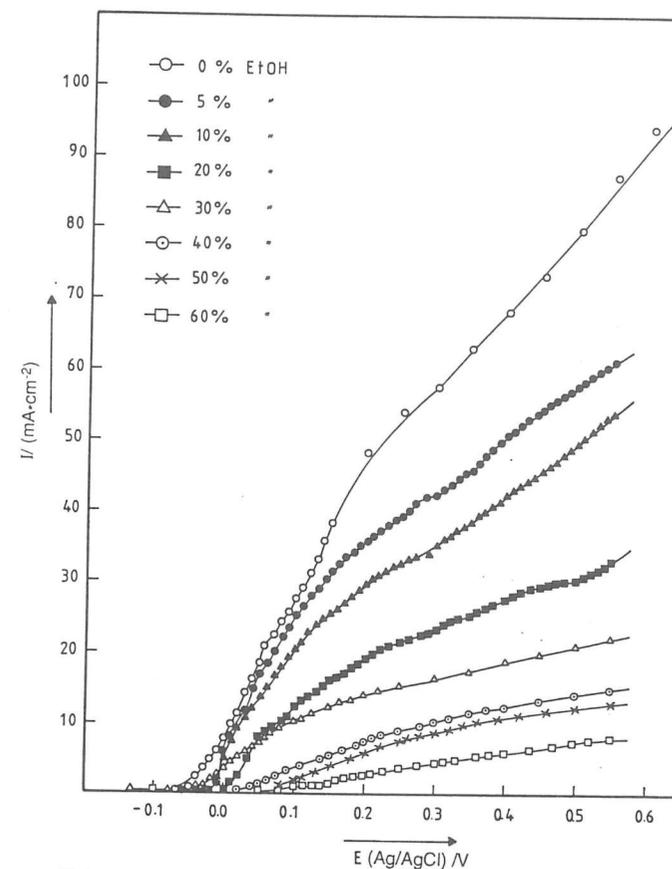
Potentiodynamic measurements show visible pits formed at the steel electrode when immersed in 0.1 M NaCl + 0.015 M NaOH. These pits gradually disappear by the addition of increasing amounts of the organic components in the medium, i.e. the pitting corrosion caused by Cl⁻ is inhibited.

Figure (1) shows the potentiodynamic polarization curves for steel in 0.1 M NaCl + 0.015 M NaOH in water-ethanol solutions. The composition of the water-ethanol solutions was varied from 0.0 to 60 %v/v ethanol. From the figure it can be seen that increasing the percentage of ethanol in the medium up to 60 %v/v has no pronounced effect on the critical pitting potential E_p of steel in these studied solutions. The obtained values of E_p are -0.05V for 0.0 vol % of Et OH and 0.0V for 60 %v/v.

The potentiodynamic polarization curves for steel in 0.1 M NaCl + 0.015 M NaOH in water-glycerol, water-ethylene glycol and water-dioxane solutions show similar behaviour to that of steel in 0.1M NaCl + 0.015 M NaOH in ethanol solutions, i.e., there is no significant change in the critical pitting potential of steel by the change in the nature and the composition of the solvents, as indicated in table (1). However, the increase in the percentage of the organic solvent in the medium causes a marked decrease in the dissolution current for the pit growth. This indicates that the dissolution process of the pit growth is greatly affected by the composition of the medium.

Table(1) Value of the Pitting Corrosion Potential In the Studied Solutions.

(by %v.v)	Solvent Mixture*			
	Et OH	D	EG	GI
0.0	-0.05	-0.05	-0.05	0.05
10.0	-0.03	-0.025	-0.04	-0.07
20.0	-0.03	-0.020	-0.04	-0.06
30.0	-0.02	-0.02	-0.03	-0.06
40.0	-0.02	-0.01	-0.03	-0.05
50.0	-0.01	-0.01	-0.02	-0.05
60.0	-0.00	-0.00	-0.00	-0.05



Fig(1) Potentiodynamic polarization curves for steel in 0.1 M NaCl + 0.015 M NaOH in water-ethanol solutions of various ethanol concentrations.

The dissolution current density (mA/cm^2) of steel in 0.1 M NaCl + 0.015 M NaOH in water-organic solvent mixtures versus the mole fraction of the organic solvent in the medium at an applied positive potential + 0.4 V [to provide conditions for pit growth] is shown in figure (2). These plots show that the dissolution current for pit growth decreases rapidly with the increase in mole fraction of the organic solvent in the medium which confirms the effect of the composition of the medium on the pit growth in pitting corrosion of steel.

The dissolution current was also investigated at two applied positive potentials (+ 0.3 and 0.5 V); the behaviour of the dissolution currents at these potentials were similar to that at 0.4 V. This indicates that the organic solvents inhibit the corrosion of steel in the studied media.

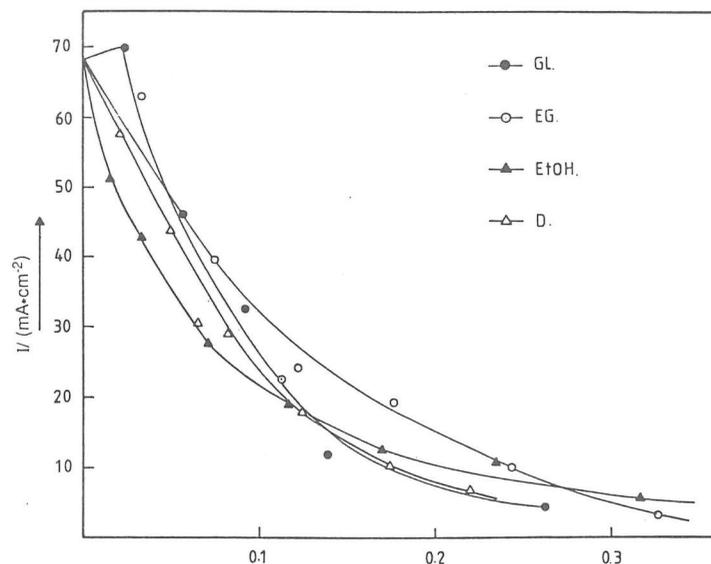


Fig.(2) Relation between the dissolution current density for steel in 0.1 M NaCl + 0.015 M NaOH in water-organic solvent mixtures at 0.4 (Ag/AgCl) /V and the mole fraction of the organic solvent in medium.

b) Anodic Dissolution Under Potentiostatic Conditions

To study the anodic dissolution of steel at the early stages of pit growth, the steel is polarized potentiostatically at the pitting potential [$E_p = -0.05$ V] in 0.1 M NaCl + 0.015 M NaOH in water organic solvent mixtures with various composition. It was found that, after a period of continuous dissolution, the anodic polarization curves are characterized by limiting values of the dissolution current density I_l . These findings are illustrated in figures (3) and (4) for water-glycerol and water - dioxane solutions, respectively. From the relation between I_l and the mole fraction (X) of the organic solvent in the medium (figure 5), it appears that the limiting dissolution current density of the pit growth for steel decreases with the increase in the percentage of the organic solvent, in agreement with the data obtained from the potentiodynamic studies (figure 2).

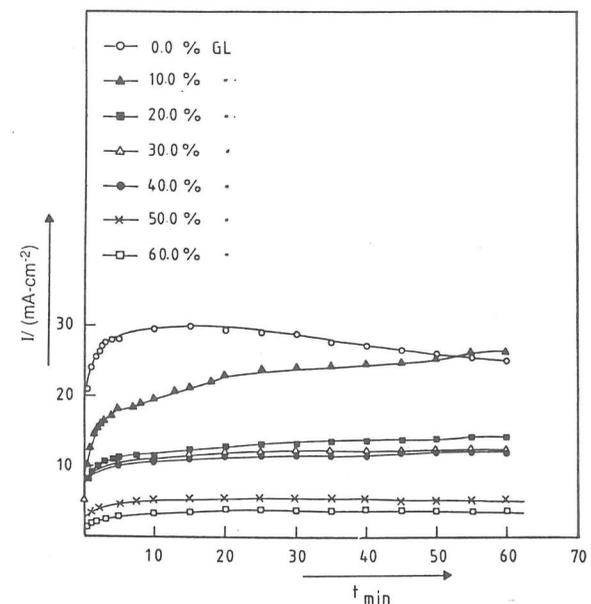


Fig.(3) Potentiostatic polarization curves for steel in 0.1 M NaCl + 0.015 M NaOH in water-glycerol solutions of various glycerol compositions at the pitting potential, [$E_p = -0.05$ (Ag/AgCl)/ v] .

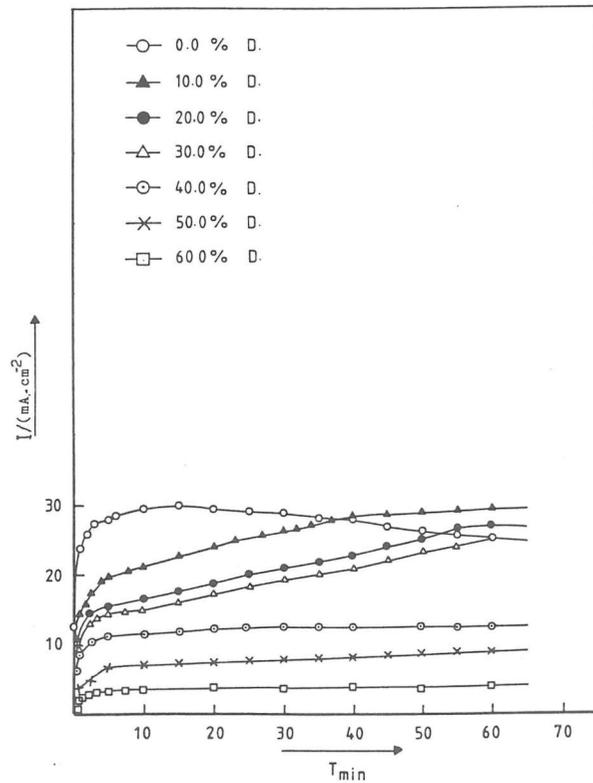


Fig.(4) Potentiostatic polarization curves for steel in 0.1 M NaCl + 0.05 M NaOH in water-dioxane solutions of various dioxane compositions at the pitting potential, [$E_p = -0.02$ (Ag/AgCl) /v.]

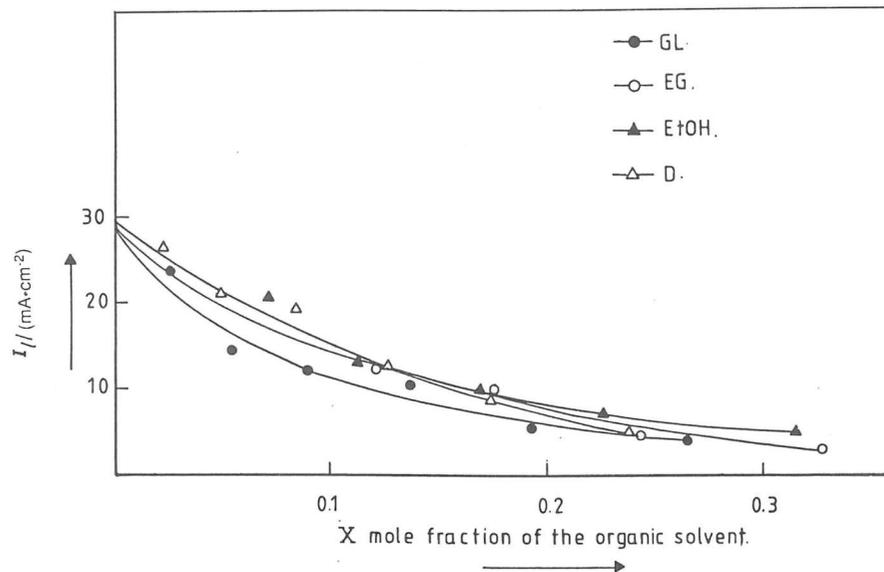


Fig.(5) Relation between the limiting dissolution current of steel of the studied media, at the pitting potential and the mole fraction of the organic component.

The percentage of inhibition efficiencies (Inh.%) of the studied solutions were calculated by applying the following relationship :

$$\text{Inh. \%} = 100 \left(1 - \frac{I}{I_0} \right) \quad (1)$$

where I_0 and I are the corrosion currents measured in absence and presence of the organic component at a given potential, respectively.

Figure (6) shows that the percentage of inhibition efficiency increases non-linearly with increasing the mole fraction of the organic solvent in the medium. The effectiveness of the solvents in inhibiting the corrosion of steel in 0.1 M NaCl+ 0.015 M NaOH was found to be glycerol > ethylene glycol \approx dioxane > ethanol.

The obtained results can be explained on the following two bases: (i) effect of medium properties i.e. viscosity and dielectric constant, (ii) effect of solvent adsorption on the steel surface.

(I) Effect of Medium Properties

The validity of the following Stokes -Ilkovic relation ⁽¹³⁾ is used to study the effect of the viscosity on the corrosion inhibition.

$$I_l \eta^{1/2} = \text{constant} \quad (2)$$

The variation of the viscosity (η) was previously studied by Sadek and Hafez ^(14,15) and later by Abd. El-Nabey et al. ⁽⁶⁾ for water-glycerol, water-ethylene glycol, water-ethanol and water-dioxane solutions with the mole fraction of the organic component.

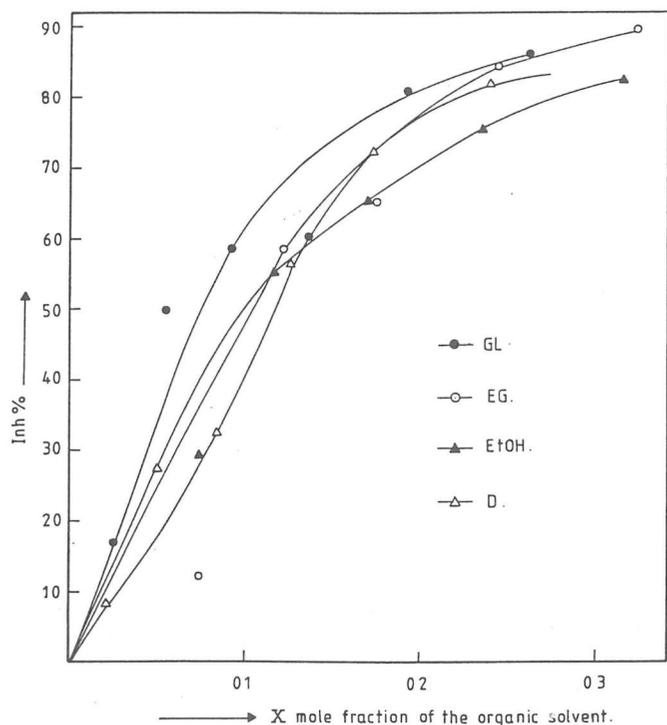


Fig.(6) Variation of the inhibition percentage with the mole fraction of the organic component, at positive [E=0.4 (Ag/AgCl) v.]

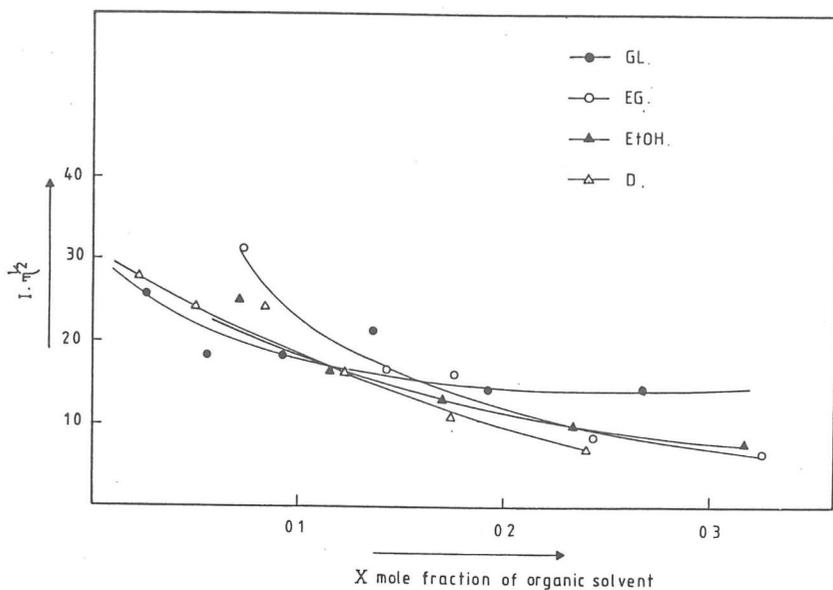


Fig.(7) Test of the Stokes-Ilkovic relation $I_p \eta^{1/2}$ vs. the mole fraction of the organic component for the steel dissolution at the pitting potential in the studied media.

The data show that when the concentration of the organic solvent increases (X), the viscosity (η) of the studied medium increases, so steel dissolution will be inhibited due to the decrease in the diffusion coefficient of the corrosion products in the studied medium.

Figure (7) shows that $I_p \eta^{1/2}$ for various studied solutions is not constant, which indicates that the Stokes - Ilkovic relation is not valid for these media, i.e., the variation of viscosity is not the only controlling factor in the dissolution process of the steel in the studied solutions.

Accordingly, in addition to the viscosity effect, the dielectric constant seems to lower the basicity of the solution, so the degree of NaOH association will increase, also the diffusion coefficient and the saturation concentration of the dissolving cations should decrease. The change in the dielectric constant as a function of the mole fraction of the organic component was studied before (6,16,17).

The data show that the increase in the mole fraction of the organic component leads to a decrease in the dielectric constant of the medium, which consequently causes increase in the inhibition percentage in each of the studied media. The study also shows that the dielectric constant of the water-organic solvent mixture decreases in the order water-glycerol > water-ethylene glycol > water-ethanol > water-dioxane.

On comparing this order of decreases in the dielectric constant of the medium with the inhibition order, it will not be the same. Accordingly, one may suggest that in the case of water-glycerol, water-ethylene glycol and water-ethanol the inhibition of steel corrosion is effected mainly by viscosity and to less extent by the dielectric constant, while the higher inhibition in water-dioxane solutions than that in water-ethanol solutions (having nearly the same viscosity) , indicated that the effecting factor in these solutions

is the value of the dielectric constant and the viscosity is of minor effect. The major decrease in the dielectric constant of dioxane solutions will lead to a decrease in the saturation concentration of the corrosion products, i.e., higher inhibition.

From the previous picture, viscosity and dielectric constants play an important role to explain the inhibition of pitting corrosion of steel in the studied media; in addition the effect of organic solvent adsorption may be also considered.

(II) Effect of Solvent Adsorption

The addition of the studied organic solvents (up to 40 %v/v) to the aqueous medium produces a marked decrease in the inhibition efficiency, but above this level (40-60 %v/v) the composition of the medium has only little effect on it (Figure 6) despite of the increased value of η (mixture). These results indicate that the studied solvents are specifically adsorbed at the steel-solution interface. The solvents adsorption at the steel solution interface was reported before ^(10,18,20).

The studied solvents glycerol, ethylene glycol, ethanol and dioxane possess an expected adsorption center: OH for the first three and -O- on dioxane. The obtained results of inhibition and the solvent concentration are tested for adsorption and the experimental data of water-ethanol, water-dioxane and water-glycerol fits Frumkin's adsorption isotherm, ^(21,22) which is given as:

$$\left(\frac{\Theta}{1-\Theta}\right) \exp f\Theta = KC \tag{3}$$

or

$$\ln \left(\frac{\Theta}{1-\Theta}\right) - f\Theta = \ln K + \ln c \tag{4}$$

where K is the equilibrium constant of the adsorption process, Θ is the surface coverage (effective of the organic solvent, $\Theta = \left(1 - \frac{I}{I_0}\right)$), c is the concentration of the organic solvent in the bulk solution and (f) is a parameter connected with the variation of adsorption energy with coverage and equal to -2a, where (a) is a quantity characterizing the interaction between the adsorbed particles. The equilibrium constant K is related to the standard free energy of adsorption ΔG_{ads}^0 by: ⁽²²⁾.

$$K = \frac{1}{55.5} \exp. \left(\frac{-\Delta G_{ads}^0}{RT}\right) \tag{5}$$

The value 55.5 in equation (5) is the concentration of water in the solution in mol/L.

Figure (8) shows the test of the experimental results obtained from pitting corrosion inhibition of steel in ethanol, dioxane and glycerol mixture solutions. Table (2) also shows the thermodynamic data obtained from figure (8). As it can be seen ΔG_{ads}^0 values are nearly the same, which indicates that the difference in inhibition of steel corrosion in these media should not be attributed to a difference in adsorption but due to the variation in viscosity.

Figure (9) shows that for water-ethylene glycol mixture a Langmuir's adsorption isotherm is followed according to the relation ⁽²³⁾.

$$\left(\frac{\Theta}{1-\Theta}\right) = KC \tag{6}$$

in which the parameters have the same meanings. The obtained values for ΔG_{ads}^0 and K in this mixture are -12.8 KJ mol⁻¹ and 20.07 M⁻¹, respectively.

On conclusion, the obtained values of ΔG_{ads}^0 for water-ethylene glycol mixture is the lowest, while the other three mixtures have nearly

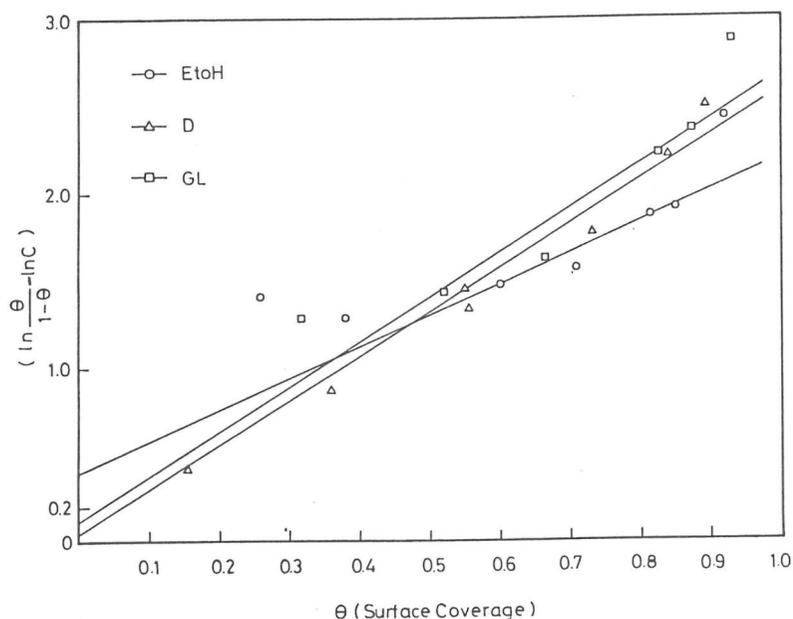


Fig.(8) Fitting Frumkin's adsorption isotherm for: water-glycerol, water-dioxane and water-ethanol solutions.

* EtOH: ethanol, D : dioxane , EG: ethylene glycol , and GL: glycerol.

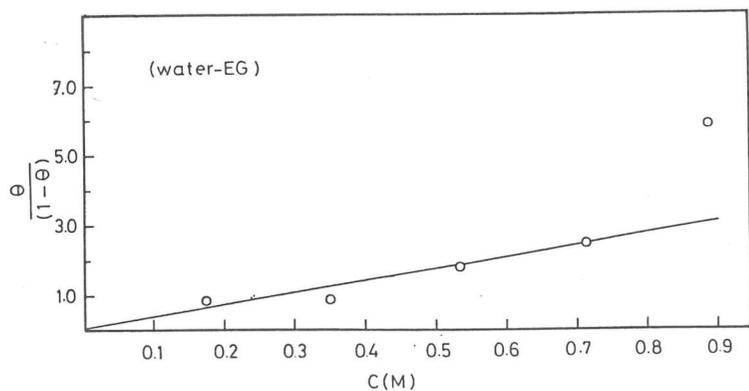


Fig.(9) Fitting Langmuir's adsorption isotherm for water-ethylene glycol solution.

the same value. This may be explained by the interaction between the organic molecules due to the formation of the adsorbed layers on the steel surface which increase the coverage degree so, "a" becomes positive as shown on Table (2).

On the other hand, in water-ethylene glycol mixture the formation of mono-layer at the steel surface (Langmuir's adsorption) causes the low value of adsorption.

Finally, it may be suggested that inhibition of steel pitting by the addition of organic solvents is caused by both the solvent properties and solvent adsorption on the steel surface.

Table(2) Thermodynamic data obtained from Frumkin

adsorption Isotherm.			
Water-organic solvent	a	K(M ⁻¹)	ΔG ^o _{ads} (KJ mol ⁻¹)
Water-ethanol	0.90	1.492	-11.13
Water-dioxan	1.30	1.051	-11.44
Water-glycerol	1.27	1.128	-11.53

CONCLUSION

Pitting corrosion of steel in the chloride medium is inhibited by the presence of glycerol, ethlene glycol, ethanol and dioxane. . In all cases corrosion inhibition is due to surface adsorption of the solvent as supported by the values of ΔG^o_{ads}. Solvent properties are responsible for the inhibition, by increasing the viscosity and decreasing the dielectric constant of the medium.

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