

## Corrosion of Copper Metal in Presence of Binary Mixtures

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**Abstract:** The rates of copper corrosion were determined in presence and in absence of different compositions of water-ethanol, -ethylene glycol, -glycerol, -dimethyl sulfoxide (DMSO) and -dioxane binary mixtures. The rates of corrosion were found to decrease by increasing the concentration of solvents. The percent inhibition range from 10.9 to 78.2% depends on the nature of solvent and its concentration. The calculated energies of activation prove that the reactions are diffusion controlled. Thermodynamic parameters were calculated. The investigated adsorption isotherms indicate that, protic solvents fit the Langmuir model. The rate of corrosion of copper in presence of diaphragm is less than that in absence of diaphragm due to the prevention of stirring of hydrogen evolved at cathode. The overall mass transfer correlations under the present conditions have been obtained using dimensional analysis method. The results agreed with the previous studies of mass transfer to rotating cylinder in turbulent flow.

**Keywords:** Corrosion, Inhibition, Protic and aprotic solvents.

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### INTRODUCTION

Inhibitors are widely used for protection of materials from corrosion in acid environments by adsorbing onto the surface and retard metal corrosion in aggressive media, so selecting the appropriate inhibitor for metal is very important. Some studies [1–3] have shown that the inhibition of the corrosion process is mainly decided by the formation of donor–acceptor surface complexes between free or  $\pi$ -electrons of an inhibitor, mostly organic compounds, and a vacant d-orbital of a metal. Corrosion inhibition of copper in a wide variety of media has attracted the attention of a number of investigators [4–7]. In general, the adsorption of an inhibitor on a metal surface depends on the nature and the surface charge of the metal, the adsorption mode, its chemical structure, and the type of the electrolyte solution [8]. It has been accepted that the corrosion inhibition process results from the formation of organic inhibitor films on the metal surface. The inhibitor films can be classified as a chemisorbed film, donating a lone pair of electrons attached to a central adsorption atom in a functional group, as an electrostatic adsorption film and as a precipitation and/or a complex film, reacting with dissolved metal ion and organic inhibitor molecule [9]. It is generally accepted that anodic dissolution of copper in organic solvent environments is influenced by its concentration. The anodic dissolution of copper is under mixed control by the electrodisolution of copper

and the diffusion of soluble copper ions from the Helmholtz plane into the bulk solution [10]. The aim of the present work is to study the effect of protic solvents namely ethanol, ethylene glycol and glycerol and aprotic solvents namely DMSO and dioxane on the rate of corrosion of copper. Such investigation included changes in temperature, speed of rotating cylinder (RCE) and concentration of solvents. Physical properties of solvents such as density, viscosity and diffusion coefficient are studied to obtain a dimensionless correlation among all these parameters.

### MATERIALS AND METHODS

All of the reagents and chemicals were of analytical grade and used without further purification. Doubly distilled de-ionized water was used in the preparation of solutions.

#### Apparatus and procedure

**Vertical parallel plates cell:** The cell used in the present work consists of rectangular container having the dimensions of 5x10 cm with electrodes fitting the whole cross section. The electrodes were rectangular copper sheets of 10cm height and 5cm width. Electrode separation was 5cm; a porous PVC diaphragm was used to prevent the stirring effect due to H<sub>2</sub> bubbles. The electrical circuit consisted of a 6v d.c. power supply, a variable resistance and a multirange ammeter connected in a series with cell. A high impedance voltmeter was

connected in parallel with the cell to measure its potential. Five concentrations (6, 8, 10, 12 and 14M) of phosphoric acid were used and protic solvents namely ethanol, ethylene glycol and glycerol and aprotic solvents namely DMSO and dioxane. The steady state anode potential was measured against a reference electrode consisted of copper wire immersed in a cup of luggin tube filled with phosphoric acid-alcohol solution similar to that in the cell, the tip of the luggin tube was placed 0.5-1mm from anode wall. Polarization curves, from which the limiting current was determined, were plotted by increasing the applied current stepwise and measuring the corresponding steady-state potential. Two minutes were allowed for reaching the steady state potential. Before each run, the back of the anode was insulated with polystyrene lacquer and the active surface was polished with fine emery paper, degreased with trichloroethylene, washed with alcohol and finally rinsed in distilled water. The temperature was regulated by placing the cell in a thermostated water bath.

**The rotating cylinder electrode:** The cathode consists of copper metal cylinder 1cm diameter and 7cm length. The disc is insulated by epoxy resin. The anode is made of cylindrical copper metal counter electrode 12cm diameter; it is also acted as reference electrode by virtue of its high surface area compared to that of the cathode.

**Density and viscosity measurements:** The density was measured by using DA-300 Kyoto Electronics density measurement equipment at different temperatures. The viscosity was measured by using Koehler Viscosity Bath (Model K23400 Kinematic Bath) at different temperatures.

## RESULTS AND DISCUSSION

**Leveling process:** Leveling is the principle process in electropolishing [11] and can be explained by mass transfer mechanism [12]. The study of leveling is based on the classical current voltage curves of electrodisolution. Cell with a diaphragm were used to study the effect of hydrogen gas evolved at the cathode on the limiting current. While a cell without diaphragm is used to study the effect of hydrogen gas evolved at the cathode on the rate of mass transfer at the anode i.e. forced convection. Fig. (1) shows the limiting currents,  $I_l$  with and without diaphragm in presence of 20% glycerol and 20% dioxane at 298K as an example.

**Effect of electrode height on limiting current:** Fig. (2) shows that the limiting current density decreases with the increase in height. In electropolishing and generally for anodic corrosion of metals, the direction

of flow of the hydrodynamic boundary layer and the diffusion layer increase in the downward direction i.e, the resistance of mass transfer increases in downward direction. Accordingly, the local limiting current density increases in the upward direction of the anode. This explains why polishing is attained at the upper part of the electrode before the lower part at the limiting current region. This was confirmed the visual observation during electropolishing. The limiting current density decreases with the increase in the height according to Eq. (1):

$$I_l = \frac{C}{H^a} \quad (1)$$

where C is constant, H is the height, a is constant depends on type of solution used, where a =0.64 for 8M  $H_3PO_4$  as example.

**Effect of electrolyte concentration:** Fig. (3) shows the limiting current decreases with increasing  $H_3PO_4$  concentration within the range studied (6-14M). This is in agreement with the finding of other authors who worked within the same range of concentration using other anode geometries [13]. The effect of  $H_3PO_4$  concentration on the value of the limiting current can be explained on the basis of the mass transfer equation, Eq. (2):

$$I_l = \frac{ZFD}{\delta} \quad (2)$$

Where Z is the valence, F is Faraday's constant in Coulomb, D is diffusion coefficient in  $cm^2 sec^{-1}$  and  $\delta$  is the diffusion layer thickness in cm. Increasing  $H_3PO_4$  concentration decreases the saturation solubility of copper phosphate. Also increasing  $H_3PO_4$  concentration increases the viscosity of the solution, these results decrease in the diffusivity of copper ions (D) and an increase in the diffusion layer thickness ( $\delta$ ) with a consequent decrease in the limiting current value according to Eq. (2). Fig. (3) shows the dependence of the polishing current on the bulk concentration of phosphoric acid. The limiting current density decreases with increase in phosphoric acid concentration but the value of limiting current in acid-(solvent-water) mixtures is less than in water-acid mixtures, Fig. (4). From the practical point of view, we can conclude on the basis of above results that it is preferable to use relatively high organic solvent percentage in inhibit polishing or dissolution of metal at the same phosphoric acid concentration.

Table 1: The limiting current and % inhibition for all solvents at different temperatures.

Temp., (K)	v/v	Ethanol		Ethylene glycol		Glycerol		DMSO		Dioxane	
		$I_L$	% Inhibition	$I_L$	% Inhibition	$I_L$	% Inhibition	$I_L$	% Inhibition	$I_L$	% Inhibition
298	0	550	0.0	550	0.0	550	0.0	550	0.0	550	0.0
	5	380	30.9	370	32.7	345	37.3	470	14.5	490	10.9
	10	370	32.7	360	34.5	330	40.0	440	20.0	460	16.4
	15	340	38.2	325	40.9	300	45.5	400	27.3	430	21.8
	20	300	45.5	280	49.1	266	51.6	380	30.9	380	30.9
	30	240	56.4	265	51.8	235	57.3	310	43.6	340	38.2
	40	200	63.6	230	58.2	210	61.8	240	56.4	260	52.7
	50	160	70.9	140	74.5	120	78.2	180	67.3	200	63.6
303	0	580	0.0	580	0.0	580	0.0	580	0.0	580	0.0
	5	410	29.3	390	32.8	362	37.6	490	15.5	510	12.1
	10	390	32.8	380	34.5	345	40.5	460	20.7	490	15.5
	15	365	37.1	350	39.7	325	44.0	430	25.9	450	22.4
	20	320	44.8	290	50.0	280	51.7	400	31.0	400	31.0
	30	265	54.3	280	51.7	250	56.9	340	41.4	340	41.4
	40	240	58.6	260	55.2	230	60.3	280	51.7	300	48.3
	50	190	67.2	165	71.6	150	74.1	220	62.1	230	60.3
308	0	620	0.0	620	0.0	620	0.0	620	0.0	620	0.0
	5	450	27.4	425	31.5	400	35.5	515	16.9	530	14.5
	10	420	32.3	400	35.5	375	39.5	490	21.0	500	19.4
	15	390	37.1	370	40.3	350	43.5	450	27.4	475	23.4
	20	360	41.9	330	46.8	315	49.2	420	32.3	430	30.6
	30	300	51.6	310	50.0	280	54.8	370	40.3	380	38.7
	40	270	56.5	295	52.4	260	58.1	320	48.4	330	46.8
	50	220	64.5	195	68.5	175	71.8	250	59.7	270	56.5
313	0	660	0.0	660	0.0	660	0.0	660	0.0	660	0.0
	5	500	24.2	460	30.3	430	34.8	535	18.9	540	18.2
	10	460	30.3	430	34.8	405	38.6	510	22.7	520	21.2
	15	420	36.4	400	39.4	375	43.2	480	27.3	500	24.2
	20	390	40.9	360	45.5	345	47.7	440	33.3	460	30.3
	30	340	48.5	335	49.2	305	53.8	400	39.4	410	37.9
	40	300	54.5	310	53.0	290	56.1	360	45.5	360	45.5
	50	250	62.1	225	65.9	200	69.7	280	57.6	300	54.5

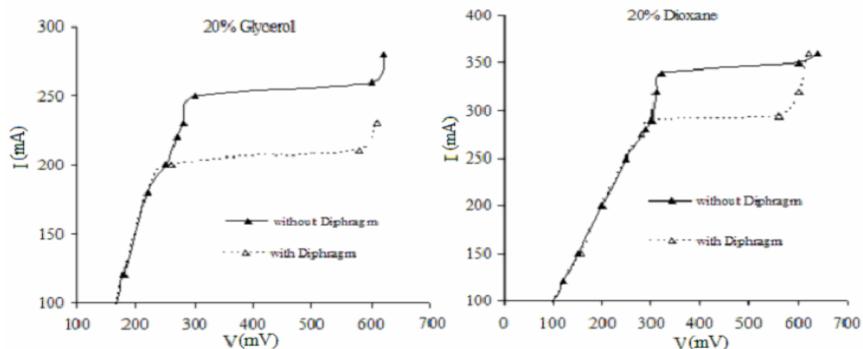


Fig. 1: Limiting currents with and without diaphragm at 298K

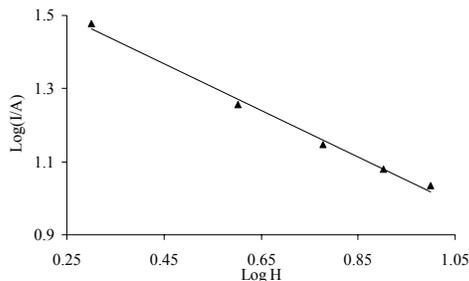


Fig. 2: Variation of limiting current with height in presence of 8M H<sub>3</sub>PO<sub>4</sub> at 298K

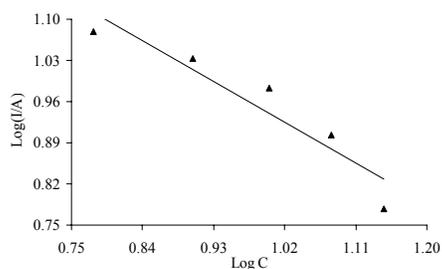


Fig. 3: Effect of H<sub>3</sub>PO<sub>4</sub> concentration on the limiting current at 10 cm height and 298K

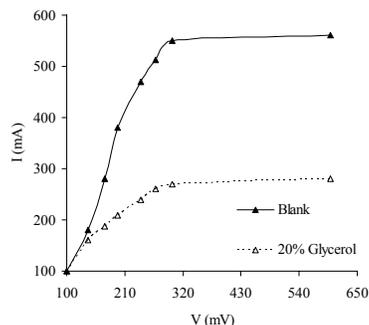


Fig. 4: The relation between current (I) and potential (V) in 8M H<sub>3</sub>PO<sub>4</sub> and in H<sub>3</sub>PO<sub>4</sub>-(glycerol-water) mixture at 298K.

**Effect of the concentration of organic solvents on the limiting current:**

The observed limiting currents, which represent the rates of dissolution of copper metal in phosphoric acid at different temperatures, are found to decrease by increasing the concentration of the organic solvents. It is recommended to use relatively high percentage of organic solvents to inhibit corrosion of metal in 8M phosphoric acids [14]. If the limiting current in absence of organic solvent  $I_b$  and in presence of organic solvent  $I_s$ , the percentage of inhibition can be calculated from Eq. (3).

$$\%Inhibition = \frac{I_b - I_s}{I_b} \times 100 \quad (3)$$

Table (1) shows the % inhibition caused by protic and aprotic solvents. The data shows that, the % inhibition depends on the type of solvent and its concentration. It is obvious that the % inhibition increases with increasing concentration of organic solvents. The decrease in limiting current with increasing the concentration of organic solvents is attributed to (a) the decrease in the solubility of dissolved copper phosphate in phosphoric acid, which is responsible for the limiting current and (b) the decrease in the diffusion layer thickness which represents the resistance to the rate of mass transfer of copper ion from anode surface to bulk solution [15]. An explanation for the decrease of the rate of dissolution may be due to that water molecules bounded by a hydrogen bond to the organic solvent are less nucleophilic than water molecules bounded by a hydrogen bond with each other. Also, the results obtained in case of glycerol are interpreted as the metal surface is preferentially covered by organic solvent molecules [16,17]. Also, the rate of corrosion decreases, since organic solvent concentration increase the local solution viscosity at anode surface with a consequent increase in the diffusivity of copper ion. The rate of corrosion decreases with increasing the concentration of organic solvents, which inhibit the natural convection flow arising from the density difference between bulk solution and solution at the electrode surface as a result of the attraction forces between the anode surface and OH<sup>-</sup> group of the organic solvent [18]. The limiting current is lower in presence of the organic solvents added to H<sub>3</sub>PO<sub>4</sub> solution than in absence of these organic solvents. Organic solvents are weaker acids and thus they have lower rate of corrosion as compared to aqueous solution. The decrease of rate will depend on the organic solvent composition and its structure. It is found that the rate of corrosion decreases in the order: glycerol > ethylene glycol > ethanol, in case of protic solvents and in the order: dimethyl sulfoxide > dioxane, in case of aprotic solvents. Fig. (5) and Table (1) show that inhibition efficiency increases with increasing solvent concentration and that it decreases with an increase in temperature. This is suggestive of a physical adsorption mechanism. It is also clear that from knowledge of the dependence of adsorption on temperature that compounds which obey physical adsorption have plots of isotherms at higher temperatures below those at lower temperature [19].

**Limiting current and water concentration:** The limiting current was found to increase with water concentration, and hence water plays an important role

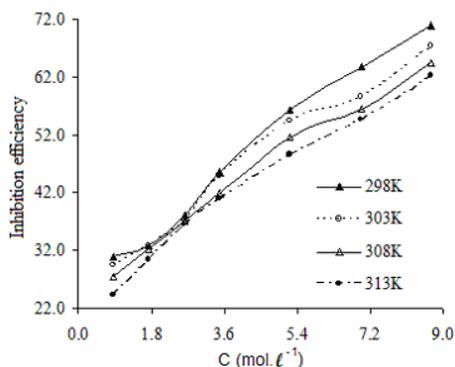


Fig. 5: Plot of inhibition efficiency vs. ethanol concentration at different temperatures

in the kinetics of this reaction. The plot of  $\log I_t$  against  $\log [H_2O]$ , Fig. (6) gave two linear portions separated by a sharp boundary at water concentration of 38.9, 44.4, 44.4, 47.2 and 44.4 mol.l<sup>-1</sup> in ethanol, ethylene glycol, glycerol, dimethyl sulfoxide and dioxane, respectively. This behavior indicates that the internal structure of the medium suffers serious changes [20] on adding organic solvent and reflects the formation of two regions of different medium internal structures, which explains their different behavior towards hydrolysis. The decrease of limiting current on progressive addition of solvent to water is due to (a) the decrease of the number of the free water molecules (b) the decomposition of the tetrahedral structure of water molecules and the interposition of organic solvent molecules in the hydrogen bonding between water molecules and (c) the increase of the hydroxide ion affinity of the medium with the addition of solvent due to the increase in its preferential solvation. Fig. (6) shows that the slope of the line gives the number of water molecules involved in the formation of activated complex. The number of water molecules at lower and higher concentration ranges of solvent are collected in Table 2.

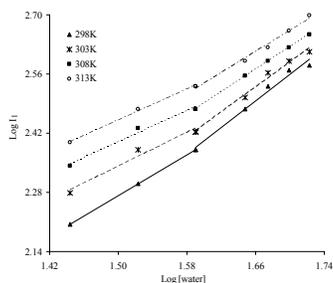


Fig. 6: The effect of water concentration on limiting current for ethanol-water system at different temperatures

Table 2: The number of water molecules for the investigated systems

	Organic solvents				
	Ethanol	Ethylene glycol	Glycerol	DMSO	Dioxane
Intersection Conc.of water	38.89	44.44	44.44	47.22	44.44
Slope at Higher Conc.of water	1.6	1.65	1.54	1.45	1.45
Slope at Lower Conc.of water	1.2	1.46	0.82	1.37	1.33

**Effect of dielectric constant:** The variation of  $\log I_t$  with the reciprocal of the dielectric constant of the medium,  $D^{-1}$ , over the whole range of solvent composition shows non-linear for all the aqueous-solvent system, Fig. (7). The absence of linearity suggests a large differential effect of solvent structure acting on the initial and transition states. This was shown from the extension of the equation of Laidler and Landskroener [21], which allows changes in solvent structure with varying solvent composition [20].

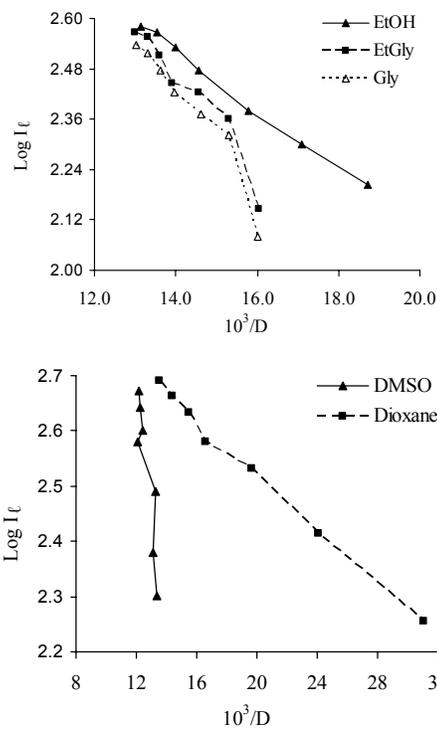
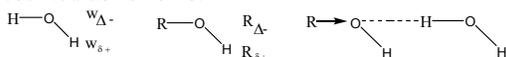


Fig 7: The variation of  $\log I_t$  with  $D^{-1}$  for different organic solvents at 298K.

### Solvent effect on limiting current

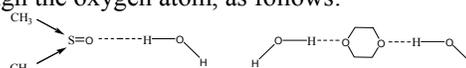
**Protic solvent:** The variation of the physicochemical properties of the medium such as viscosity, density and dielectric constant, as a result of adding organic solvents, was expected to affect the rate of mass transfer process by affecting the diffusivity and activity of the metal ions. The rate of corrosion of copper was studied in ethanol, ethylene glycol or glycerol-H<sub>2</sub>O mixtures of different compositions at 298-313 K. The addition of organic solvent may change the reactive species existing in solution by changing the composition of the solvation shell. Copper ions are solvated with water molecules to form [Cu(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> in aqueous solution, alcohol molecules may replace some of the ligated water molecules and this would affect the mobility of copper ion [22], but in many cases this cannot be separated from the effect of the viscosity of the solvent. Another explanation for the decrease in the rate of corrosion would be that the addition of alcohol has a marked effect on increasing the basicity of the medium. The relative affinities of H<sub>2</sub>O or the non-aqueous component toward Cu<sup>2+</sup> may be expected to arise from the relative solvating capacities of solvent dipoles exerted largely through hydrogen bond formation. The strength of hydrogen bonding should be largely guided by the relative charge densities on the oxygen and hydrogen charge centers of the isolated dipoles. To a first approximation, the isolated dipoles of H<sub>2</sub>O and ROH, indicated by Feakins [23] can be represented as follows:



Owing to the inductive effect of the R-group in alcohols, the negative charge density on the oxygen atom ( $R_{\Delta-}$ ) is presumably somewhat greater than the corresponding quantity in water ( $w_{\Delta-}$ ). As a result, the protonic character of the H atom of -OH group in alcohols ( $R_{\delta+}$ ) is weaker than that in water ( $w_{\delta+}$ ), i.e.,  $R_{\Delta-} > w_{\Delta-}$  and  $R_{\delta+} < w_{\delta+}$ . Furthermore, alcohol molecule is also expected to induce, in a water molecule hydrogen bonded to it, a positive charge on the hydrogen atom. These effects are likely to be relayed over several molecular diameters, rendering all molecules in ethanol, ethylene glycol or glycerol-H<sub>2</sub>O mixtures more basic and less acidic than in pure water. It is easy to predict that glycerol acts as a greater inhibitor while ethanol is the smaller inhibitor. In the case of alcohols with two or more OH groups as in ethylene glycol and glycerol, the viscosity is high because the relatively large number of hydrogen bonds

would require more energy to be ruptured in the formation of the activated state.

**Dipolar aprotic solvents:** Dipolar aprotic solvents as DMSO and dioxane have high dipole moment and high dielectric constant. These solvents do not act as donors of hydrogen and the center of positive charge density is usually at a crowded site in the molecules. On the other hand the centre of negative charge density is usually on highly basic atom O, S or N atom, which is highly exposed for intermolecular interaction with positive or acidic centers. DMSO is usually good electron pair donor solvent and hence cation solvators. The strong basicity of DMSO-H<sub>2</sub>O mixture may be explained by considering the detailed charge distribution of the solvent molecule suggested by Feakins [23]. DMSO and dioxane as Lewis bases, normally co-ordinate through the oxygen atom, as follows:



The basic centre for protonation will thus be the oxygen atom. The inductive effect of the two methyl groups, will enhance the polarization of the sulphoxide group resulting the increase of negative charge on the oxygen atom of the DMSO molecule than that on the oxygen atom of the water molecule. The % inhibition in presence of DMSO > Dioxane, this is due to that two oxygen atoms in the dioxane molecule are bonded by hydrogen bonds with water molecules while in case of DMSO, the sulphur atom is free to bind to the copper surface [24]. In dipolar aprotic solvents, the reactivity of the cations is small compared to that in protic solvents, and the rate of corrosion reactions involving cations, as reactants, can increase when the solvent is changed from dipolar aprotic to protic. According to this concept we can predict that solvation of Cu<sup>2+</sup> is higher in aprotic than in protic solvents [25].

**Adsorption isotherm:** The electrochemical processes on the metal surface like the corrosion inhibition was caused by the adsorption of inhibitor [26], and the degree of surface coverage ( $\theta$ ) for different concentrations of organic solvents. The adsorption depends on the chemical structure of the inhibitor [27]. The adsorption of an organic inhibitor adsorbate onto metal-solution interface can be denoted as a substitutional adsorption process between the organic molecules in the aqueous solution, Org<sub>(aq)</sub> and the water molecules on the metallic electrode surface, H<sub>2</sub>O as follows, Eq. (4):



Where X is the number of water molecules replaced by one molecule of organic adsorbate. Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The Langmuir adsorption isotherm is applied to investigate the adsorption mechanism by Eq. (5) [28].

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (5)$$

Where K is the equilibrium constant of adsorption process, C is the inhibitor concentration and  $\theta$  is the surface coverage. The degree of surface coverage  $\theta$  was determined from Eq. (6) [29]:

$$\theta = \frac{I_b - I_s}{I_b} \quad (6)$$

For protic solvents, the relation between C/coverage and C is shown in Fig. (8). It is apparent that linear correlation coefficients are very good, Table (3), and all the slopes are close to 1, suggesting that it is correct to choose the Langmuir adsorption isotherm to explain the adsorption phenomenon of inhibitor molecule.

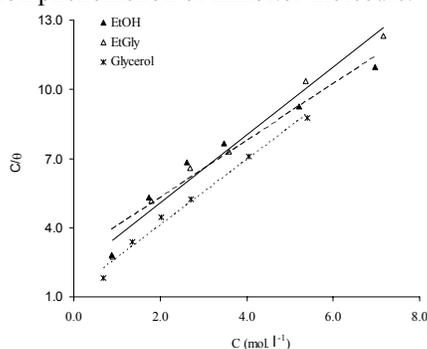


Fig. 8: The relation between C/coverage and C for protic solvents.

Table 3: Some parameters of the linear regression between C/coverage and C at 298K

Solvent	Slope	Linear correlation coefficient, R <sup>2</sup>
Ethanol	1.10	0.945
Ethylene glycol	1.09	0.981
Glycerol	1.15	0.989
Dimethyl sulfoxide	0.84	0.730
Dioxane	0.73	0.640

For aprotic solvents, the linear correlation coefficients are bad, and all the slopes are not close to 1, meaning that the adsorption of inhibitor does not accord with the Langmuir adsorption isotherm. Then, the Temkin adsorption isotherm is employed, and it has the form of Eq. (7) [30-32]:

$$\theta = \left(\frac{\ln K}{-2a}\right) + \left(\frac{\ln c}{-2a}\right) \quad (7)$$

where a is the lateral interaction term describing the molecular interactions in the adsorption layer and the heterogeneity of the metal surface. The regression between coverage and ln C is dealt with; the linear correlation coefficients, molecular interaction parameters and the adsorption coefficients are listed in Table (4). It is clear that the experimental data can be explained using the Temkin adsorption isotherm. Table (4) shows that all the values of a are smaller than zero, indicating that the repulsion exists in the adsorption layer [27].

Table (4): Some parameters of the linear regression between coverage and ln C for aprotic solvents

Temperature	a		Linear correlation coefficient, R <sup>2</sup>	
	DMSO	Dioxane	DMSO	Dioxane
298K	-1.8	-1.7	0.960	0.930
303K	-2.0	-1.8	0.960	0.970
308K	-2.3	-2.1	0.980	0.940
313K	-2.6	-2.3	0.970	0.930

It is well known that the adsorption free energy ( $\Delta G^0_{ads}$ ) is related to the equilibrium constant of adsorption (K) and  $\Delta G^0_{ads}$  can be calculated by Eq. (8) [1,3]:

$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G^0}{RT}\right) \quad (8)$$

The value 55.5 in the above equation is the concentration of water in solution in mol.  $\ell^{-1}$  [33]. The calculated adsorption free energies are listed in Table (5). In all cases, the  $\Delta G^0_{ads}$  values are negative. The negative values of  $\Delta G^0_{ads}$  indicate the spontaneous adsorption of the inhibitor. It is found that the  $\Delta G^0_{ads}$  values are more positive than (-40kJ/mol) indicating that the inhibitors are physically adsorbed on the metal surface [27].

Table5: The adsorption free energies of organic solvents on copper surface at different temperatures.

Solvent	Temperature (K)	G <sup>0</sup> <sub>ads</sub> (kJmol <sup>-1</sup> )
Ethanol	298	-6.95
	303	-6.37
	308	-6.15
	313	-5.89
Ethylene glycol	298	-6.72
	303	-6.50
	308	-6.37
	313	-6.28
Glycerol	298	-7.90
	303	-7.62
	308	-7.53
	313	-7.39

**Effect of temperature:** The corrosion of copper in presence of different solvents was studied by measuring the limiting current over the temperature range (298-313K). Table 1 shows the limiting current obtained in

presence of solvents at different temperatures. The results indicate that the rate of corrosion increases with increasing the temperature. The above behavior is indicative of the occurrence of the inhibition through physical adsorption on the metal surface. The natural logarithm of the limiting current can be represented as a linear function of 1/T, Eq. (9):

$$\ln I_l = \ln A - \frac{E_a}{RT} \quad (9)$$

where A is a pre-exponential factor, R is the gas constant,  $E_a$  is the activation energy and T is the absolute temperature. The pre-exponential factor and apparent activation energy are calculated by regression between  $\ln I_l$  and 1/T. All the dynamic parameters in the presence of organic solvents are listed in Table 6. The activation energy of the process is an important parameter for determining the rate controlling step. If adsorption of the species on the reaction surface and subsequent chemical reaction takes place  $E_a$  values usually  $> 43\text{kcal mol}^{-1}$ . If boundary layer diffusion of the aqueous species is the rate controlling step [34],  $E_a$  is generally  $\leq 28\text{kJ/mol}$ . It is obvious from Table 6 that the values of  $E_a < 28\text{kJ/mol}$ . This indicated that the corrosion reaction is controlled by diffusion processes.

**Thermodynamic treatment of the reaction:** Variation of the thermodynamic parameters of activation with solvent composition, were calculated by applying the least-squares procedures as given in Table 6 and represented in Fig. (9) as a function of the mole fraction, x of the co-solvent. The change of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  with solvent composition is not a linear relationship and this is an indication of specific solvation effects [20]. The weak dependence of  $\Delta G^\ddagger$  on the composition of the organic solvent can be attributed largely to the general linear compensation between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ . Table 6 shows the entropy  $\Delta S^\ddagger$  possesses negative values indicating a highly ordered. The values of isokinetic temperatures were computed from the slope of plots of  $\Delta H^\ddagger$  vs.  $\Delta S^\ddagger$  for different solvent compositions and were found to equal 353.9, 351.1, 354.0, 338.9 and 345.4K for ethanol, ethylene glycol, glycerol, dimethyl sulfoxide and dioxane, respectively indicating that the rate of corrosion is enthalpy controlled [35].

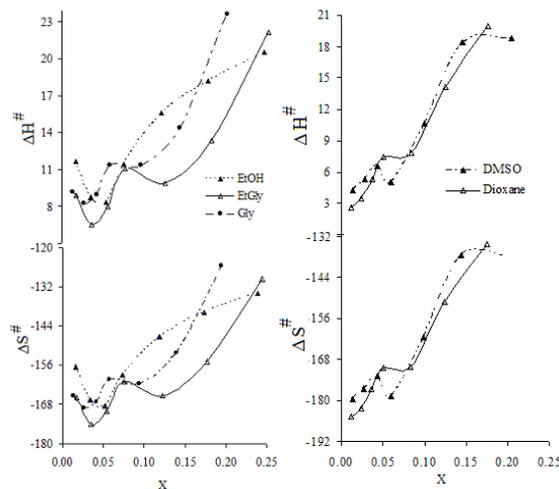


Fig 9: Variation of the entropy and enthalpy of activation with the co-solvent mole fraction.

Table 6: The thermodynamic parameters for the investigated systems.

Solvent	X	$E_a(\text{kJmol}^{-1})$	$\Delta H^\ddagger(\text{kJ mol}^{-1})$	$\Delta S^\ddagger(\text{J mol}^{-1} \text{K}^{-1})$	$\Delta G^\ddagger(\text{kJ mol}^{-1})$
Ethanol	0.016	14.2	11.7	-156.5	59.1
	0.034	11.3	8.7	-166.6	59.2
	0.052	10.9	8.3	-168.6	59.4
	0.073	14.0	11.5	-159.1	59.7
	0.118	18.1	15.6	-147.2	60.2
	0.173	20.7	18.2	-139.7	60.5
0.239	23.1	20.5	-133.8	61.1	
Ethylene glycol	0.017	11.5	8.9	-166.0	59.2
	0.035	9.1	6.5	-174.2	59.3
	0.054	10.5	8.0	-170.1	59.5
	0.075	13.7	11.1	-160.9	59.9
	0.122	12.5	9.9	-165.3	60.0
	0.177	15.9	13.3	-154.8	60.3
0.244	24.7	22.1	-129.6	61.4	
Glycerol	0.013	11.8	9.2	-165.4	59.4
	0.026	10.8	8.3	-169.1	59.5
	0.041	11.5	9.0	-167.3	59.7
	0.057	13.9	11.4	-160.5	60.0
	0.094	13.9	11.3	-161.6	60.3
	0.139	16.9	14.4	-152.3	60.5
0.195	26.2	23.7	-125.5	61.7	
DMSO	0.013	6.8	4.3	-179.5	58.6
	0.027	7.9	5.3	-176.5	58.8
	0.043	9.2	6.7	-172.8	59.0
	0.059	7.6	5.0	-178.6	59.2
	0.098	13.2	10.6	-161.5	59.6
	0.144	21.0	18.4	-137.5	60.1
0.202	21.4	18.8	-137.7	60.5	
Dioxane	0.011	5.1	2.6	-184.7	58.6
	0.023	6.0	3.5	-182.2	58.7
	0.036	7.9	5.3	-176.7	58.9
	0.050	10.0	7.5	-170.6	59.1
	0.083	10.4	7.9	-170.3	59.5
	0.123	16.6	14.1	-151.2	59.9
0.174	22.6	20.0	-134.3	60.7	

**Effect of Rotation:** The diffusion coefficient of  $\text{Cu}^{2+}$ ,  $D$ , in different temperatures was determined from the values of limiting current density as shown in Table 7 using Eisenberg equation [36]:

$$I_l = knFC_b d^{-0.3} \nu^{-0.344} D^{0.644} U^x \quad (10)$$

where  $k=0.0971$  and  $x=0.7$ ,  $n$  is the number of electrons involved in a redox process,  $F$  is Faraday's constant ( $\text{A s mol}^{-1}$ ),  $U$  is the electrode peripheric velocity =  $\omega r$  in  $\text{cm rad s}^{-1}$  ( $r$  is the radial distance in  $\text{cm}$ ),  $d$  is the characteristic length of the rotating cylinder in  $\text{cm}$ ,  $D$  is the diffusion coefficient for the metal ions in  $\text{cm}^2 \text{s}^{-1}$ , and  $\nu$  is the kinematic viscosity in stoke ( $\nu = \eta/\rho$ ) where  $\eta$  is viscosity in poise and  $\rho$  is density in  $\text{g cm}^{-3}$  [37]. Values of  $D$  and  $\nu$  for all solvents under different conditions are also recorded in Table (7).

The diffusion coefficient,  $D$  of  $\text{Cu}^{++}$  ions in solutions containing organic solvents decreases due to increase in interfacial viscosity,  $\eta$  in accordance [38] with the Stokes-Einstein equation, Eq. (11):

$$\frac{\eta D}{T} = \text{constant} \quad (11)$$

where  $\eta$  is the viscosity of solution ( $\text{g cm}^{-1} \text{s}^{-1}$ ),  $D$  is the diffusion coefficient of copper ions ( $\text{cm}^2 \text{s}^{-1}$ ) and  $T$  is the absolute temperature (K). It is found that the limiting current density increases with increasing rpm. This may be attributed to break down a hydrodynamic boundary layer and diffusion layer are formed. The higher the rpm, the higher solution flow and the thinner the diffusion layer, thus giving a higher rate of transfer of copper ions to the metal surface and, at the same time, through the porous deposit layer formed on the metal which, in turn, enhances the rate of deposit. Table (7) shows the relation between rpm and  $I_l$ , Eq. (12):

$$\omega \propto (I_l)^n \quad (12)$$

The effect of the speed of rotation, rpm on the rate of metal corrosion can also be used to determine whether the corrosion process is diffusion or chemically controlled process. If the rate of corrosion increases by the speed of rotation, then the reaction is diffusion controlled. However, if the rate of corrosion is independent of rotation, so the reaction is likely to be chemically controlled. The angular velocity  $\omega$  is given by Eq. (13):

$$\omega = \frac{2\pi \text{ rpm}}{60} \quad (13)$$

Fig. (10) gives the relation between the limiting current density and the angular velocity,  $\omega^{0.7}$  for organic solvents at 25°C. Straight lines were obtained and the limiting current density increases by increasing the rotation which indicates that corrosion reaction of

copper is a diffusion controlled reaction. The slight decrease of  $D$  values observed in the presence of solvent indicates that the solvent hinders the diffusion of copper(II) ions from anode surface to bulk of solution. A possible explanation is that alcohol is a polar molecule with interfacial activity, which could change the composition and the properties of the double layer on the electrodic surface. Thus, the solvent molecules replace the water molecules on the metallic surface, forming an adsorbed superficial film. This would increase the electrolyte viscosity and lower the dielectric constant at the electrode interface [39]. Consequently, hydrated metal ions or complex ions approach the surface with increased difficulty to enable charge transfer [40].

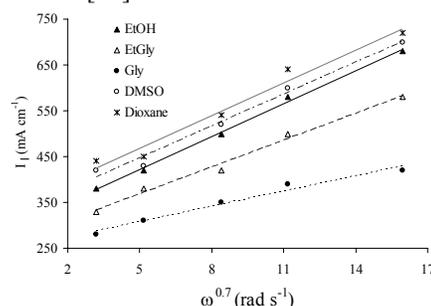


Fig. 10: The relation between the limiting current density and the angular velocity,  $\omega$  to the power 0.7 at different concentrations of organic solvents at 25°C.

**Data correlation:** It was noted that mass transport to an inner RCE in turbulent flow system may be described by empirical dimensionless correlations of the form:

$$\text{Sh} = a \text{Sc}^b \text{Re}^c \quad (14)$$

where  $\text{Sh}$ ,  $\text{Re}$  and  $\text{Sc}$  are the Sherwood ( $\text{Sh} = kd/D$ ), where  $k$  is the mass transfer coefficient  $k = I_l / ZFC_{\text{Cu}^{2+}}$  where  $C_{\text{Cu}^{2+}}$  is saturation solubility of copper phosphate, Reynolds ( $\text{Re} = dU/\nu$ ) and Schmidt ( $\text{Sc} = \nu/D$ ) numbers; respectively and  $a$  and  $b$  are empirical constants,  $c = 0.33$ ; indicating forced convection [34]. By plotting  $\log \text{Sh}/\text{Sc}^{0.33}$  and  $\log \text{Re}$ , a straight line was obtained; its slope gives constant  $c$  and intercept gives the constant  $a$  (Fig. 11).

$$\text{Sh} = 0.091 \text{Re}^{0.716} \text{Sc}^{0.33} \quad \text{for ethanol} \quad (15)$$

$$\text{Sh} = 0.099 \text{Re}^{0.718} \text{Sc}^{0.33} \quad \text{for ethyleneglycol} \quad (16)$$

$$\text{Sh} = 0.099 \text{Re}^{0.717} \text{Sc}^{0.33} \quad \text{for glycerol} \quad (17)$$

$$\text{Sh} = 0.093 \text{Re}^{0.719} \text{Sc}^{0.33} \quad \text{for DMSO} \quad (18)$$

$$\text{Sh} = 0.093 \text{Re}^{0.719} \text{Sc}^{0.33} \quad \text{for dioxane} \quad (19)$$

Fig. (12) shows the overall mass transfer correlation for all solvents used, from which, the data can be correlated by the following equation, Eq. (20):

$$\text{Sh} = 0.113 \text{Re}^{0.7} \text{Sc}^{0.33} \quad (20)$$

Table 7: Physical properties  $\eta$ ,  $\rho$  and D used in calculated dimensionless groups.

Solvent	rpm	298K				303K				308K				313K			
		$l_r$	D	$\eta$	$\rho$												
Ethanol	50	380	1.43E-04	1.437	1.370	420	1.57E-04	1.380	1.368	440	1.66E-04	1.370	1.300	470	1.60E-04	1.200	1.365
	100	420	7.87E-05			500	9.69E-05			530	1.04E-04			560	9.89E-05		
	200	500	4.85E-05			530	5.00E-05			560	5.34E-05			600	5.18E-05		
	300	580	3.93E-05			610	4.00E-05			640	4.23E-05			670	3.96E-05		
	500	680	2.89E-05			720	2.97E-05			750	3.11E-05			780	2.88E-05		
Ethylene glycol	50	330	4.16E-04	9.880	1.391	350	4.01E-04	8.500	1.385	370	4.13E-04	8.300	1.370	395	4.32E-04	8.100	1.360
	100	380	2.44E-04			410	2.41E-04			440	2.55E-04			470	2.66E-04		
	200	420	1.34E-04			450	1.31E-04			475	1.35E-04			500	1.38E-04		
	300	500	1.13E-04			550	1.15E-04			600	1.25E-04			650	1.34E-04		
	500	580	8.18E-05			630	8.18E-05			680	8.70E-05			720	8.98E-05		
Glycerol	50	280	3.30E-04	12.100	1.799	300	3.21E-04	10.270	1.787	320	2.95E-04	8.000	1.790	340	2.66E-04	5.820	1.790
	100	310	1.82E-04			330	1.75E-04			350	1.59E-04			370	1.43E-04		
	200	350	1.04E-04			375	1.00E-04			400	9.23E-05			430	8.50E-05		
	300	390	7.88E-05			420	7.71E-05			450	7.13E-05			480	6.49E-05		
	500	420	5.07E-05			440	4.76E-05			460	4.24E-05			490	3.85E-05		
DMSO	50	420	1.45E-04	1.260	1.200	450	1.60E-04	1.260	1.130	475	1.69E-04	1.240	1.100	500	1.78E-04	1.200	1.080
	100	430	7.08E-05			460	7.81E-05			500	8.61E-05			550	9.72E-05		
	200	520	4.48E-05			550	4.85E-05			590	5.24E-05			630	5.65E-05		
	300	600	3.60E-05			640	3.95E-05			680	4.20E-05			720	4.47E-05		
	500	700	2.63E-05			740	2.84E-05			780	2.98E-05			840	3.26E-05		
Dioxane	50	440	1.47E-04	1.220	1.120	470	1.59E-04	1.200	1.080	500	1.72E-04	1.180	1.060	520	1.63E-04	1.040	1.040
	100	450	7.17E-05			480	7.72E-05			520	8.59E-05			580	9.11E-05		
	200	540	4.48E-05			570	4.75E-05			600	5.05E-05			650	5.12E-05		
	300	640	3.76E-05			670	3.93E-05			700	4.13E-05			740	4.03E-05		
	500	720	2.59E-05			750	2.68E-05			800	2.92E-05			860	2.92E-05		

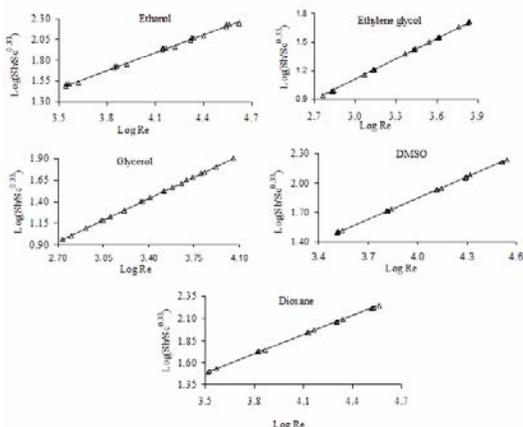


Fig. 11: The overall mass transfer correlation for all solvents at different temperatures

The exponents in the above equations denotes a highly turbulent flow, which agree with the previous mass transfer study in aqueous media. In our present study, a forced convection mechanism [41] is obtained which agree very well with similar relationships reported before [25,34,36,42,43].

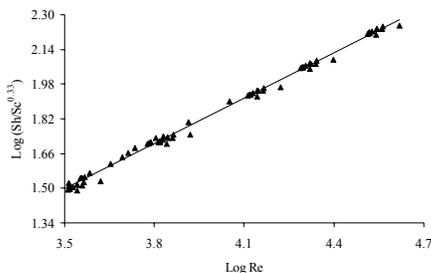


Fig. 12: The overall correlation for all solvents.

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