



Anodic Corrosion Inhibition in Presence of Protic Solvents

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Electropolishing is defined as anodic corrosion. The issue of the effects of corrosion on structural integrity of metal surfaces has been a question of concern for some time. The uses of chemical corrosion inhibitors are common in production and processing operations. Nevertheless, the challenge is to develop a new class of corrosion inhibitors to protect the materials, due to the economic importance of copper. There are several researches deals with acceleration and inhibition of this process. In this paper, the electropolishing process inhibited with different ratio by addition of some organic alcohols (methanol, ethanol, propanol and isopropanol) by addition with concentration (2, 5, 10, 15, 20, 25 and 30 %). The results revealed that these organic alcohols have strongest inhibitive effect ranging from 8.7 to 53.8 %.

Keywords: Electropolishing of copper, Organic alcohols, Limiting current, Inhibition of corrosion. Thermodynamic parameters.

INTRODUCTION

Corrosion is an electrochemical process that involves the rearrangement of electrons between metal surface and an aqueous electrolytic solution. Corrosion of materials is a big problem that receive interest of scientists whose concern in the technological world, scientists are persistent in seeking better and more efficient ways of combating the corrosion of metals. Addition of corrosion inhibitors to the corrosion environment with respect to the other methods of corrosion inhibition has been employed [1,2]. The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media. To be effective, an inhibitor must also transfer water from the metal surface, interact with anodic or cathodic reaction sites to retard the oxidation and reduction corrosion reaction and prevent transportation of water and corrosion-active species on the metal surface. Copper is a material commonly used in heating and cooling systems. Scale and corrosion products have a negative effect on heat transfer and they cause a decrease in the heating efficiency of the equipments which is big problem in industrial processes.

Many corrosion inhibitors can be used eliminate the undesirable destructive effect and prevent metal dissolution. Copper normally does not displace hydrogen from acid solutions and, therefore, is virtually unattached in non-oxidizing conditions. In fact, the uprising hydrogen bubbles induce a radial momentum transfer which enhances the rate of copper corrosion [3].

Corrosion inhibitors can be used to prevent copper dissolution. Amines are known to be very effective inhibitors for metal and alloys in different corrosion media. Benzotriazole, for instances, was studied and found to have excellent inhibition properties in several corrosion environments [4]. The molecule contains nitrogen atoms and it is also useful in preventing copper staining and tarnishing [5]. The electropolishing process reported to be inhibited with different ratio by addition of some organic aldehydes [6] and organic compounds containing polar groups including nitrogen, sulfur, oxygen and heterocyclic compounds with polar functional groups and conjugated double bonds have been reported to inhibit copper corrosion [7-13]. The inhibiting action of these organic compounds is usually attributed to their interactions with the copper surface *via* their adsorption. Polar functional groups are regarded as the reaction center that stabilizes the adsorption process. 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 electrolyte solution [14].

The phenomenon of electropolishing is first discovered by Jacquet [15]. A lot of work has been done on this phenomenon owing to its important as metal finishing process. A great deal of work has been directed to study the mechanism of electro polishing as well as to establish conditions for different metals and alloys involved in the process.

Mechanistic studies have revealed that electro polishing is diffusion controlled process taking place at the limiting

current which is attained most probably when the diffusion layer becomes saturated with Cu^{2+} in, electropolishing of copper.

Therefore, the values of the limiting current which determined the polishing rate depends on the rate of mass transfer of Cu^{2+} from the diffusion layer to the bulk solution. The latter depends on the relative movement of the ions at the anode and in the electrolyte. Earlier works studied the factors affecting the limiting current have overlooked the effect of anode geometry as an important factor in determining the value of the limiting current.

Other work based on electron diffraction showed that the film is an oxide. Hull cell studies by Lurking suggested that, copper oxides are formed during electro polishing of copper in H_3PO_4 [16].

It can be noted that a viscous layer is present at the surface of copper anodes during electro polishing as shown by the work of Walton [17].

The objective of this study is to investigate the effect of some organic alcohols (methanol, ethanol, propanol and isopropanol) on the inhibition of copper corrosion in phosphoric acid at different conditions. The rate of copper corrosion is determined by measuring the anodic limiting current.

EXPERIMENTAL

AnalaR grade H_3PO_4 (98 % w/w) and double distilled water used to prepare the electrolyte. The organic alcohols were used in this work are methanol, ethanol, propanol and isopropanol.

The cell and electrical circuit used in the present work showed in previous work [6]. The cell consists of a rectangular plastic container having the dimensions 5.1 cm $\times$ 5 cm $\times$ 10 cm with electrodes filing the whole cross section. The electrodes were rectangular copper sheets of 10 cm height and 5 cm width. Electrodes separation was 5 cm. A porous PVC diaphragm was used to prevent the effect due to H_2 bubbles. The electrical circuit consists of 6V D.C. power supply, while a voltmeter is connected in parallel with the cell to measure the voltage and multi-range ammeter connected in series with cell to measure the current.

Measurements of the limiting current: Polarization curves were obtained by increasing the cell current step-wise and the steady state anode potential against a reference electrode consisted of a wire immersed in a cup of Luggin tube filled with phosphoric acid concentration similar to that in the cell, the tip of the Luggin tube was placed 0.5 cm from the anode. The potential difference between the anode and the reference was measured by high impedance potentiometer. Five phosphoric acid concentrations (6, 8, 10, 12 and 14 M) were prepared from AnalaR grade phosphoric acid distilled water. The anode height varied from 1 to 5 cm. Before each run, the back part of the anode was insulated with polystyrene lacquers and the active surface of the anode was polished with fine emery paper, degreased with trichloroethylene, washed with alcohol and finally rinsed in distilled water. Electrode treatment was similar to that used by Wilke *et al.* [18]. Organic acid concentration were 10^{-5} - 10^{-2} mol L^{-1} . The rate of electro-polishing of copper was determined at 25 °C.

RESULTS AND DISCUSSION

Effect of alcohols concentration on the limiting current density: The observed limiting current density, which represents the rate of copper metal corrosion in phosphoric acid at 25 °C, decrease with increasing the concentration of the organic alcohols under studying.

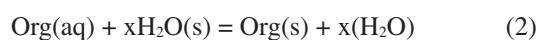
It found that the limiting current decreases with increasing the concentration of alcohols (Table-1). From the practical point of view and on the basis of results obtained the uses of alcohols studied in the concentration range between (2, 5, 10, 15, 20, 25 and 30 %) inhibit the corrosion of copper metal in 8 M H_3PO_4 [19,20]. The limiting current in absence of organic alcohols (I) and in the presence of organic alcohols (I_L), the percentage inhibition can be calculated from the following equation:

$$\text{Inhibition (\%)} = \frac{I - I_L}{I} \times 100 \quad (1)$$

TABLE-1
VALUES OF LIMITING CURRENT AT DIFFERENT MOLE FRACTION OF ALCOHOLS AT DIFFERENT TEMPERATURES

Alcohols	Mole fraction (x)	25 °C	30 °C	35 °C	40 °C
Methanol	0.00000	230	250	300	350
	0.01135	210	220	240	270
	0.02875	200	215	230	250
	0.05882	188	200	215	230
	0.09030	178	190	200	210
	0.12329	170	180	190	200
	0.15789	158	170	180	190
Ethanol	0.19425	145	160	170	180
	0.00792	230	250	270	280
	0.02018	210	230	240	260
	0.04167	190	210	220	230
	0.06459	180	200	210	230
	0.08911	170	180	190	200
	0.11538	160	170	180	190
Propanol	0.14362	145	160	170	180
	0.00302	210	230	250	280
	0.00609	190	210	230	250
	0.01554	180	200	210	230
	0.03226	170	180	190	200
	0.05028	160	170	180	190
Isopropanol	0.06977	150	160	170	180
	0.00302	210	235	250	290
	0.00609	180	205	220	240
	0.01554	160	220	235	250
	0.03226	150	180	200	220
	0.05028	140	160	180	190
	0.06977	135	150	160	170
	0.09090	130	140	150	160

Adsorption isotherm: The adsorption of the inhibitor molecules from aqueous solutions can be regarded as substitution adsorption process between the organic compounds in the aqueous phase and water molecules adsorbed on the electrode surface [$\text{H}_2\text{O}(\text{s})$].



where x (the size ratio) is the number of water molecules displaced by one molecule of inhibitor. The above process

reaches equilibrium when the chemical potential on the left hand equal to that of the right hand side.

Adsorption isotherms are very important in determining the mechanism of electrochemical reactions. the most frequently used isotherms are those of Langmuir, Frumkin, Parsons, Temkin, Flory-Huggins and Bockris-Swinkels [21].

These entire isotherms are of the general form:

$$f(\theta, x)e^{(-a\theta)} = KC \quad (3)$$

where $f(\theta, x)$ is the configuration factor which depends essentially on the physical model and assumption underlying the derivation of the isotherm. The mechanism of inhibition is generally believed to be due to the formation and maintenance of a protective film on the metal surface [22,23].

Application of isotherm: The degree of surface coverage (θ) at constant temperature was determined from the following equation [24,25]:

$$\theta = \frac{I - I_0}{I} \quad (4)$$

Inhibitor adsorption characteristics can be estimated by using the Langmuir isotherm given by the following equation:

$$KC = \frac{\theta}{1 - \theta} \quad (5)$$

The langmuir adsorption isotherm for copper electrode in H_3PO_4 plotted as $\theta/(1-\theta)$ against C at 25 °C which give as straight line that does not pass from the origin *i.e.* Langmuir isotherm does not verified.

Fig. 1 shows the Flory-Huggins adsorption isotherm for copper electrode in H_3PO_4 plotted as $\log \theta/C$ against $\log (1-\theta)$ at 25 °C. A straight line is obtained with a slope X and intercept $\log xK$. The experimental data fits the Flory-Huggins adsorption isotherm which represented by:

$$\log (\theta/C) = \log xK + x \log (1-\theta) \quad (6)$$

where x is the number of water molecules replaced by one molecule of the inhibitor. It is clear that, the surface coverage data are useful for discussing adsorption characteristics. The adsorption of inhibitors at metal-solution interface may be due to the formation of electrostatic or covalent bonding between the adsorbates and the metal surface [26]. The kinetic adsorption isotherm may be written in the form [27]:

$$\log \theta/(1-\theta) = \log k' + y \log C \quad (7)$$

From eqn. 6 a plot of $\log \theta/(1-\theta)$ against $\log C$ should yields a straight line with intercept of $\log k'$ and slop = y , where y is the number of inhibitor molecules occupy one active site. The binding constant of adsorption $K = k'^{1/y}$, where $1/y$ is the number of the active surface sites occupied by one molecule of the inhibitor and K is the binding constant. Fig. 2 indicates linear relationship between $\log \theta/(1-\theta)$ and $\log C$ at 25 °C and the calculated values of $1/y$ and K are given in Table-2. It is obvious that the value of $1/y$ for all compounds are higher than one indicating that, the given inhibitors molecules are attached to more than one active site. The free energy of adsorption (ΔG_{ads}). at different concentration of the alcohols as calculated from the following equation:

$$\Delta G_{ads} = -RT \ln (55.5 K) \quad (8)$$

where value 55.5 is the concentration of water in solution (mol/L).

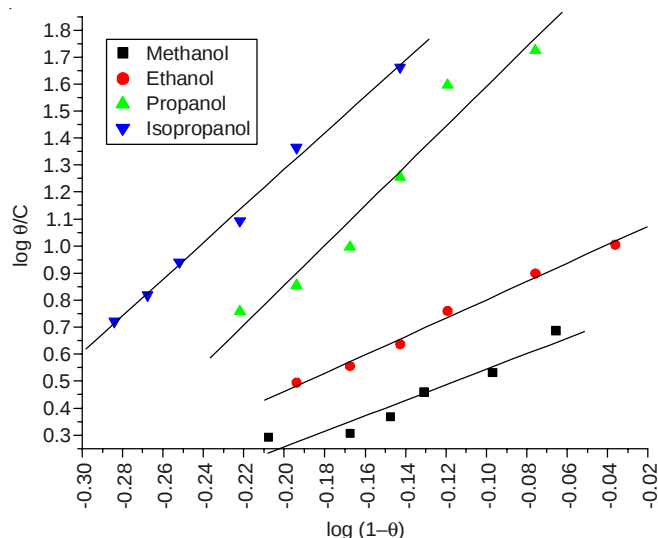


Fig. 1. Flory-Huggins isotherm for methanol, ethanol, propanol and isopropanol

TABLE-2
EFFECT OF ALCOHOLS CONCENTRATION ON
THE PERCENTAGE INHIBITION OF COPPER
ELECTRODE AT DIFFERENT TEMPERATURES

Alcohols	Mole fraction (x)	25 °C	30 °C	35 °C	40 °C
Methanol	0.01135	8.7	12	20.0	22.9
	0.02875	13	14	23.3	28.6
	0.05882	18	20	28.3	34.3
	0.09030	23	24	33.3	40.0
	0.12329	26	28	36.7	42.9
	0.15789	31	32	40.0	45.7
Ethanol	0.19424	37	36	43.3	48.6
	0.00792	8	10.7	12.9	20.0
	0.02018	16	17.9	22.6	25.7
	0.04167	24	25.0	29.0	34.3
	0.06459	28	28.6	32.3	34.3
	0.08911	32	35.7	38.7	42.9
Propanol	0.11538	36	39.3	41.9	45.7
	0.14362	42	42.9	45.2	48.6
	0.00302	16	17.9	19.4	20.0
	0.00609	24	25.0	25.8	28.6
	0.01554	28	28.6	32.3	34.3
	0.03226	32	35.7	38.7	42.9
Isopropanol	0.05028	36	39.3	41.9	45.7
	0.06977	40	42.9	45.2	48.6
	0.00302	4	14.5	16.7	15.4
	0.00609	16	19.4	22.2	20.5
	0.01554	24	32.3	27.8	25.6
	0.03226	32	38.7	33.3	30.8
	0.05028	40	45.2	38.9	35.9
	0.06977	46	51.6	44.4	41.0

The values of ΔG_{ads} are given in Table-3. In all cases, the (ΔG_{ads}) values are negative and lie in the range of 10.2-16.1 KJ/mol. The most efficient inhibitor shows the most negative (ΔG_{ads}) value. This suggests that, they are strongly adsorbed on metal surface. The negative values of (ΔG_{ads}) indicate that the spontaneous ion of the inhibitors. It's found that (ΔG_{ads}) values are more positive than (-40) indicating that the inhibitors are physically adsorbed on the metal surface. Similar results have also been reported by Talati [27].

TABLE-3
VALUES OF K, x, 1/y AND $-\Delta G_{\text{ads}}$ (CALCULATED FREE ENERGY OF ADSORPTION IN KJ mol^{-1}) OF H_3PO_4 OF
SOME ORGANIC ALCOHOLS TO FLORY-HUGGINS AND KINETIC ADSORPTION ISOTHERM CONSTANTS AT 25 °C

	Flory-Huggins			Kinetic adsorption isotherm			
	x	K	$-\Delta G_{\text{ads}}$	k'	1/y	K	$-\Delta G_{\text{ads}}$
Methanol	3.563	2.13	11.5	1.387	1.620	1.700	11.02
Ethanol	2.950	4.23	13.2	2.663	1.440	4.093	13.15
Propanol	7.363	28.82	17.9	10.277	2.797	1.206	10.19
Isopropanol	1.723	12.37	15.8	9.142	1.173	13.410	16.10

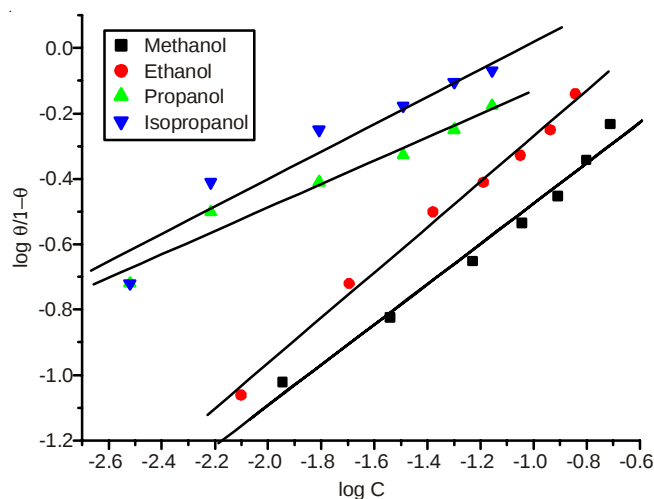


Fig. 2. Kinetic adsorption isotherm for alcohols

Effect of temperature and thermodynamic treatment of the reaction: The effect of temperature on copper electro polishing rate in absence and presence of organic additives was determined in the temperature ranges between (25-40 °C). It was observed that the electro polishing rate increases with temperature for different concentrations of organic additives. Values of E_a that have been derived from the slopes of Arrhenius [28].

It is obviously seen that the E_a values in absence and presence of organic additives are less than $< 40 \text{ kJ mol}^{-1}$, also indicating that the diffusion processes are controlling the electropolishing reaction [29]. In this research, the thermodynamic parameters such as change in free energy (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) were calculated in same way as the related researches did in literature [30-33]. From transition state equation a straight line was obtained, from which ΔH^* and ΔS^* be calculated from the slope and intercept, respectively. The free energy change (ΔG^*) can be represented as follows:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (9)$$

The result indicated that the tested compounds acted as inhibitors through adsorption on copper surface, which resulted in formation of a barrier to mass and charge transfer. The values of ΔH^* reflect the strong adsorption of these compounds on copper surface. The negative values of ΔS^* pointed to a greater order produced during the process of activation.

This can be achieved by the formation of activated complex representing the association or fixation with consequent loss in the degree of freedom of the system during the process. ΔG^* values showed limited increase with rise in the concentration of organic additives revealing that weak dependence of ΔG^* on the composition of the organic additives can be

attributed largely to the general linear composition between ΔH^* and ΔS^* for the given temperature [28,34].

Thermodynamic function of electropolishing of copper in alcohols gives evidence of structural change occurring in the solution as the type of solvents is changed. The effect can arise from the solvent properties and from the salvation properties of ions in different solvents [35]. Table-4 shows the variations of ΔG^* , ΔH^* and ΔS^* with the mole fraction of alcohols. The gradual increases of both ΔH^* and ΔS^* give a good indication of preferential salvation of metal surface in presence of aprotic solvents which is a criterion of specific salvation. The weak dependence of ΔG^* on the composition of the organic solvents can be attributed largely to the general linear compensation between ΔH^* and ΔS^* for the given temperature. Table-4 shows that the free energy change increases positively with increasing dielectric constant of the solvent. This shows that as the dielectric constant decreases more work as required to keep the ions apart and therefore the dissolution of Cu is decreased, as the dielectric constant decrease. There is less spontaneity and less dissolution at lower dielectric constant. Table-4 shows that for any solvent, as the temperature increases the dielectric constant decreases and the force among the ion greater [36]. This is attributed to the fact that as temperature increases, the viscosity of solvent decreases, so salvation decrease and mobility of Cu^{2+} increases, this led to increases in the rate of mass transfer.

Isokinetic relationship: Variation in the rate within series may be caused by changes in either, or both, the enthalpy or the entropy of activation the correlation of ΔH^* with ΔS^* is linear relationship may be stated algebraically:

$$\Delta G^* = \beta \Delta S^* + \text{Constant} \quad (10)$$

$$\delta \Delta H^* = \beta \Delta S^* \quad (11)$$

The operator, δ , concerns difference between any two reactions in the series. Substituting from the eqn. 11 into the familiar relationship:

$$\delta \Delta H^* = \delta \Delta G^* + T \delta \Delta S^* \quad (12)$$

We obtain

$$\beta \delta \Delta S^* = \delta \Delta G^* + T \delta \Delta S^* \quad (13)$$

where $\delta \Delta G^* = \text{zero}$, $\beta = T$. In other words, the slope in a linear plot of ΔH^* versus ΔS^* is the temperature at which all reactions that conform to the linear occur at the same rate. β therefore known as the isokienetic temperature. The isokienetic plot of ΔH^* and ΔS^* for different concentration of the organic alcohols, Fig. 3 and Table-4 was found to be linear and the isokienetic temperature (β) was computed from the slope of the plot as 283, 263, 266 and 280 K. These values are much lower than that of the experimental temperature 298 K indicating that the rate of the reaction is entropy controlled.

TABLE-4
VALUES OF E^* AND ALL THERMODYNAMIC PARAMETERS FOR ALL
DIFFERENT CONCENTRATION OF THE ORGANIC ALCOHOLS

Inhibitor	Mole fraction (x)	ΔG^* (KJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)	ΔH^* (KJ mol ⁻¹)	E_a^* (KJ mol ⁻¹)	Dielectric constant
Methanol	0.01135	59.6	133	19.80	22.30	80.37
	0.02875	59.8	165	10.50	13.02	71.02
	0.05882	59.8	170	8.90	11.40	61.24
	0.09030	60.0	174	8.03	10.50	51.53
	0.12329	60.1	181	6.00	8.50	41.46
	0.15789	60.2	182	5.90	8.40	32.20
	0.19424	60.4	179	7.00	9.40	—
Ethanol	0.00792	59.5	173	7.9	10.3	80.37
	0.02018	59.4	173	8.1	10.6	68.66
	0.04167	59.9	177	7.1	9.6	56.49
	0.06459	60.1	169	9.7	12.1	44.67
	0.08911	60.2	182	5.9	8.4	33.89
	0.11538	60.4	181	6.4	8.8	25.00
Propanol	0.14362	59.7	159.5	12.2	14.6	—
	0.00302	60.0	161.9	11.7	14.2	80.37
	0.00609	60.1	169.1	9.7	12.1	66.54
	0.01554	60.2	182.3	5.9	8.4	51.68
	0.03226	60.4	181.1	6.4	8.8	37.51
	0.05028	60.5	179.8	6.9	9.4	26.83
Isopropanol	0.06977	59.7	155.2	13.50	15.90	20.81
	0.00302	60.1	161.2	12.04	14.50	80.37
	0.00609	60.2	136.8	19.40	21.90	65.72
	0.01554	60.5	145.9	17.00	19.50	51.07
	0.03226	60.7	158.0	13.60	16.09	36.28
	0.05028	60.8	172.8	9.20	11.70	24.44

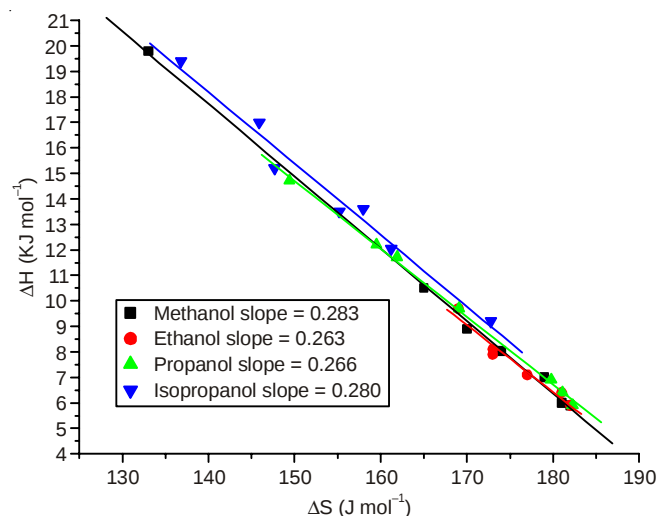
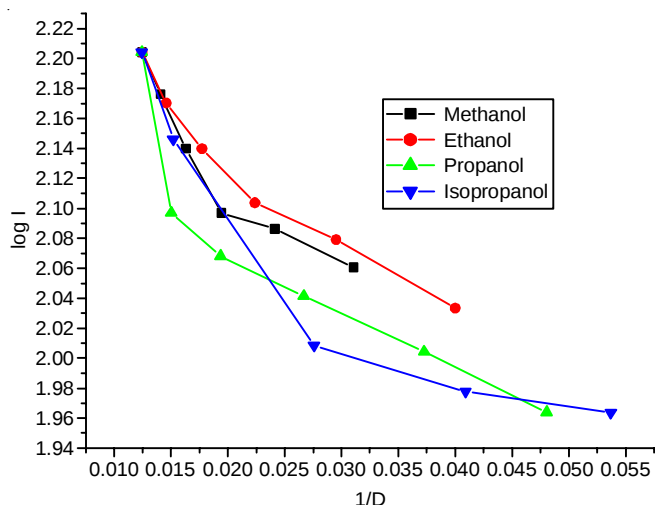


Fig. 3. Isokinetic relationship for methanol, ethanol, propanol and isopropanol

Effect of dielectric constant: The variation of $\log I$ 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. 4). 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 [37], which allows changes in solvent structure with varying solvent composition [38].

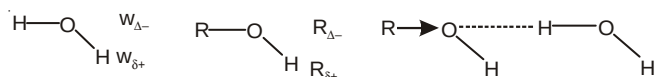
Solvent effect on limiting current

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

Fig. 4. Variation of $\log I$ with the reciprocal of the dielectric constant of the medium, D^{-1} , over the whole range of solvent composition

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 methanol, ethanol, propanol and isopropanol- H_2O 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 $[Cu(H_2O)_4]^{2+}$ in aqueous solution, alcohol molecules may replace some of the ligated water molecules and this would affect the mobility of copper ion [39]. 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_2O or the non-aqueous component toward Cu^{2+} 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_2O and ROH, indicated by Feakins [40] 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 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 methanol, ethanol, propanol or isopropanol- H_2O mixtures more basic and less acidic than in pure water. 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. The inhibition action of alcohols depends on steric effect taking part in the absorption of the inhibitor molecule and their electron charge density, molecular size of such alcohols. The order of inhibition efficiency for the alcohols is

Isopropanol > n-Propanol > Ethanol > Methanol

Conclusion

Electropolishing of copper in phosphoric acid is considered as corrosion rate of copper. It is measured by measuring the limiting current.

- The rate of corrosion decreases by adding of organic alcohols (methanol, ethanol, propanol and isopropanol).
- The rate of inhibition ranged from 8.7-53.8 % depending on the type of the alcohols and its concentration.

The corrosion rate increases by increases the temperature and the activation energy of the reaction is less than 40 k. j. i.e. the reaction is diffusion controlled. All alcohols verify Langmuir, Flory-Huggins and kinetic adsorption isotherm.

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