Corrosion of copper in phosphoric acid / isopropanol mixtures

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The rate of copper dissolution in presence of phosphoric acid-alcohol mixtures were studied by measuring the limiting current density which shows that, the rate of corrosion is decreased by increasing phosphoric acid concentration, electrode height and mole fraction of alcohol. Thermodynamic parameters are calculated. The rotating disk electrode is used as a tool to study the influence of organic solvent addition on the rate of corrosion of copper. Different reaction conditions such as temperature speed of rotation of copper disk, and the physical properties of solution are studied to obtain dimensionless correlation between all these parameters. The data can be correlated by the following eq.: $Sh = 1.25 \, (Sc)^{0.33} \, (Re)^{0.48}$ It is obvious that the corrosion process follows a laminar flow mechanism.

تم دراسة معدل ذوبان النحاس في مخاليط حمض الفوسفوريك والكحول بقياس شدة التيار المحدد الذي يدل على أن معدل التأكل يقل بزيادة تركيز حمض الفوسفوريك وطول القطب والكسر الجزيئى للكحول. وتم قياس الدوال الثرموديناميكية للتفاعل. وتم استخدام قرص القطب الدوار كطريقة لدراسة تأثير المادة العضوية على معدل التأكل وتم دراسة تأثير الحرارة وكذلك عدد الدورات والخواص الطبيعية للمحاليل للحصول على الدوال الثرموديناميكية وأمكن كتابة العلاقة اللابعدية بين تلك العوامل.

$$Sh = 1.25 \, (Sc)^{0.33} \, (Re)^{0.48}$$

Keywords: Corrosion, Copper, Phosphoric acid, Isopropanol

1. Introduction

The phenomenon of electropolishing was discovered by Jaquet [1, 2] Owing to its importance as a metallic finishing process, a great deal of work has been directed to the study of the mechanism of electropolishing as well as establishing the optimum polishing conditions for different metals and alloys [3]. Mechanisms studies [2, 4, 5] have revealed that electropolishing is a diffusion-controlled reaction which takes place at the limiting current; the limiting current is attained, most probably, when the diffusion layer becomes saturated with Cu^{2+} ions [2, 4], the value of the limiting current which determines the polishing rate depends on the rate of mass transfer of Cu^{2+} from the diffusion layer to the bulk of the solution. The rate of mass transfer depends on the relative movement of the anode and the electrolyte, physical properties of the electrolyte, temperature and geometry of the anode. Organic compounds containing polar group including N, S and O has been reported[6-9] to inhibit copper corrosion. The present work is concerned with the study of the factors affecting the limiting current of the electropolishing of vertical plates in unstirred (H_3PO_4) solution where the mass transfer of Cu^{2+} from the anode surface to the bulk of the solution is carried out mainly by diffusion and natural convection arising from density difference between the interfacial solution (saturated copper phosphate solution in (H_3PO_4) and the bulk solution (H_3PO_4). Previous work on the factors affecting the limiting current [10-12] has overlooked the effect of anode geometry despite its importance in determining the value of the limiting current. On the other hand it has been found that the degree of enhancement depends on the geometry of the cell, electrode separation and physical properties of the solution [13, 14].

The objective of the present work is to investigate the extent to which isopropanol affects the rate of corrosion of copper. Moreover, different reaction conditions such as temperature, speed of rotation of rotating copper disk, and the physical properties of solutions such as density, viscosity and diffusion coefficient are studied to obtain dimensionless correlation between all these parameters.

2. Experimental

2.1. Materials

BDH isopropanol and phosphoric acid were used.

2.2. Apparatus and procedure

It should mentioned clearly that, two cells were used, one with vertical electrodes fig. 1 and one with rotating disk electrode fig. 2. Figs. 1, 2 show the cell and electrical circuit used in the present work. The cell consists of rectangular container having the dimensions 5 x 5 x 10 cm with electrodes fitting the whole cross section. The electrodes were rectangular copper sheets of 10 cm height and 5 cm width. Electrode separation was 5 cm; a porous PVC diaphragm was used to prevent the stirring effect due to H_2 bubbles.

The electrical circuit consisted of a 6 volt d.c. power supply, a variable resistance and a multirange ammeter connected in series with the cell. A high impedance voltameter was connected in parallel with the cell to measure its potential. Four concentrations of H_3PO_4 were used: 6, 8, 10, 12 M; all were prepared from AR grade H_3PO_4.

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 0.5-1 mm 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 thermostat. The physical properties of the solution (ρ, η, D) needed to correlate the data were determined experimentally using standard techniques [15].

The diffusivity of Cu^{2+} in different H_3PO_4-isopropanol mixtures was determined by measures the limiting current of anodic dissolution of copper rotation disc in mixtures at different temperatures and applying the Levich eq. (16)

$$I_l = 0.62 \, Z \, F \, \upsilon^{-1.6} \, D^{2/3} \, \omega^{1/2} C_{Cu^{2+}}$$

where Z valency, F Faraday number 96500 (coulomb l^{-1}), υ = kinematic viscosity (cm^2 s^{-1}), ω, angular velocity (rad S^{-1}), I_l, limiting current (mA).

The saturation solubility of copper phosphate in different phosphoric acid – isopropanol mixtures concentrations was determined using Perkin Elmer Atomic Absorption Spectrophotometer. The density was determined by using DA-300 Kyoto Electronics at 20, 25, 30 and 35°C. The viscosity is measured using Koehler viscosity Bathing[16] (Model K 23400 Kinematic Baths) at 20, 25, 30, 35°C.

Fig. 2 is a block diagram of apparatus which permits the rotation of disk electrode at accurately controlled angular velocities. The shaft is driven by variable speed motor. The frequency of rotation, recorded as revolution per minute, was counted by an optical tachometer.

The anode consists of copper metal disk of 2cm diameter. The sides and back of the disk, as well as the drive shaft were insulated by epoxy resin. The cathode is made of a cylindrical copper electrode of 12cm diameter; it also acts as a reference electrode because its surface area is very large compared to that of the anode [16-17].

3. Results and discussion

Fig. 3 shows a set of typical current / potential curves obtained at different H_3PO_4 / alcohol concentrations. It is obvious that the limiting current decreases with increasing H_3PO_4 concentration within the range studied (6-12M), this is in agreement with the finding of other authors who worked within the same range of concentration using other anode geometries [10-12]. The effect of H_3PO_4 concentration on the value of the limiting
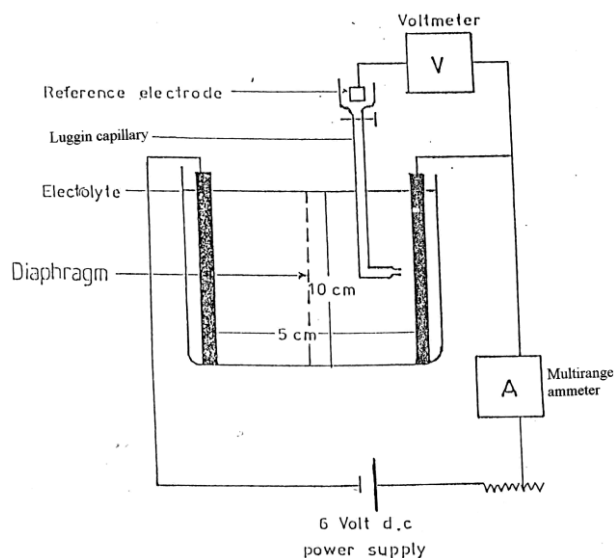
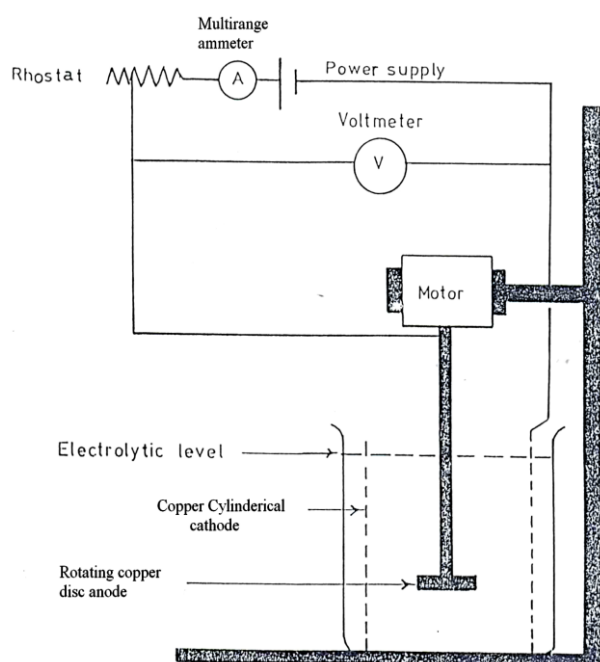Fig. 1. The electrolytic cell and electrical circuit for part (I).

Fig. 2. cell and electrical circuit for part (II).

current can be explained on the basis of the mass transfer eq. (18):

Increasing H_3PO_4 concentration decreases the saturation solubility of copper phosphate [14] (Cu^{2+}) with a consequent decrease in the limiting current according to eq. (1).
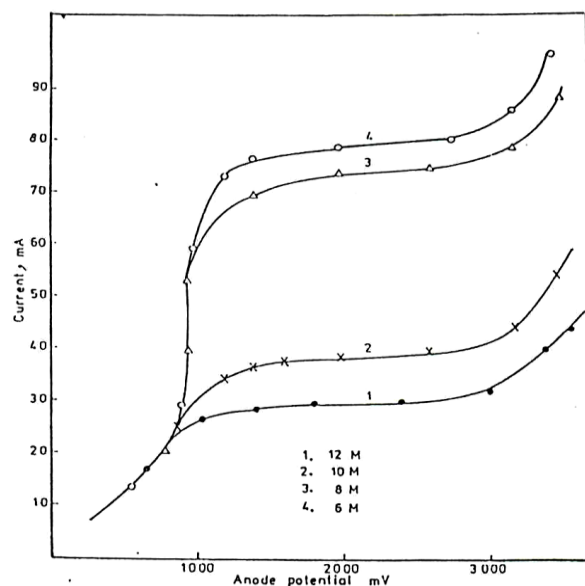

Fig. 3. Typical polarization curves obtained in presence of isopropanol $x = 0.268$ at different concentration of phosphoric acid at 25 °C.

$$I_l = \frac{ZFD_{Cu2+}}{\delta} \; ,$$ (1)

where Z valency ,(F) = Faraday in Coulomb, D = diffusion coefficient in $cm^2\ sec^{-1}$ and δ is the diffusion layer thickness in cm.

Also, increasing H_3PO_4 concentration increases the viscosity of the solution, these results in a decrease in the diffusivity of copper ions (D) and an increase in the diffusion layer thickness (δ) with a consequent decrease in the limiting current value according to eq. (1).

3.1. Effect of electrolyte concentration on the polishing current

Fig. 4 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 values of limiting current in acid-(alcohol-water) mixtures is less than in water-acid mixtures. From the practical point of view, we can conclude on the basis of above result that it is preferable to use relatively high organic solvent percentage to inhibit polishing or dissolution of metal at the same phosphoric acid concentration.
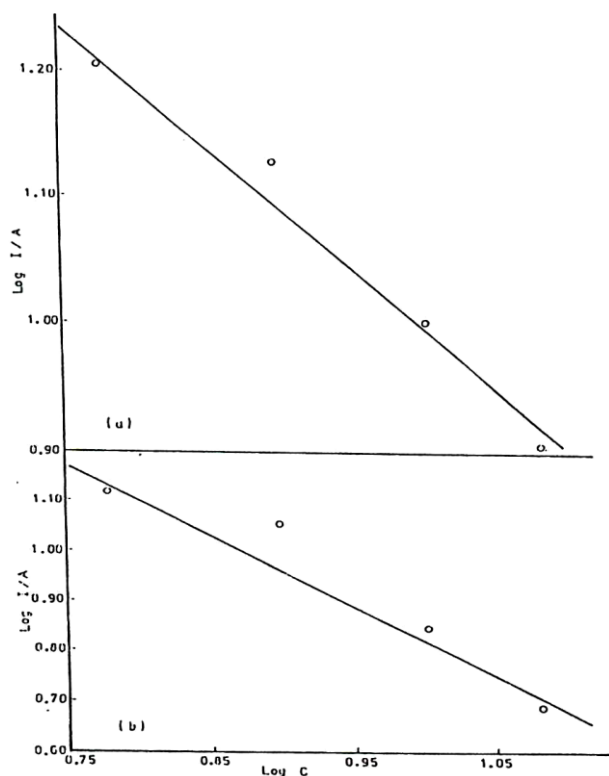
Fig. 4. Effect of phosphoric acid concentration on the limiting current density in presence of isopropanol at 25 °C. (a) X = 0.2682, (b) X = 1.

3.2. Effect of electrode height on polishing current

Fig. 5 shows that the limiting current density decreases with the increase in height. In electropolishing and generally for anodic dissolution of metals, the direction of flow of the hydrodynamic boundary layer and the diffusion layer increase in the downward direction i.e., the resistance o 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 parts of the electrode before the lower part at the limiting current region. This was confirmed by the visual observation (18) during electropolishing. The average limiting current density decreases with the increase in the height according to the equation:
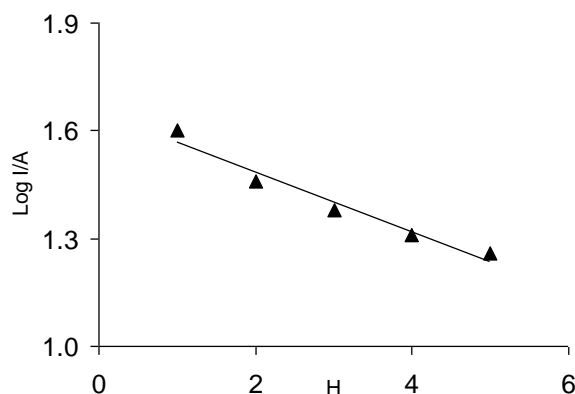
$$I_L = \frac{C}{(H)^\alpha} \; , \qquad (2)$$

Fig. 5. The relation between log I/A and height in presence of 0.2682 (*X*) isopropanol at 25 C.

where C is constant, H is the height, a constant depends on type of solution used, where a = 0.31 in case of phosphoric acid only, 0.9 in case of isopropanol (X = 0.282) and 1.5 in case of isopropanol (X = 1).

The above results were given in the presence of alcohol phosphoric acid mixture as well as in the absence of alcohol [18].

3.3. Structural effects

Corrosion of copper and its inhibition in a wide variety of media, particularly when they contant organic solvents have attracted the attention of a number of investigators [19- 23].

In water-organic solvent mixtures, the variation of physicochemical properties of medium with the composition table 1 has an important role in controlling electropolishing. It has been found that corrosion is inhibited by the organic alcohol and inhibition efficiency has been found to increase with increasing concentration of organic solvents table 2. These results were interpreted on the basis of the fact that these types of corrosion are controlled by diffusion of Cu^{++} from metal surface to bulk solution. The increase in the viscosity of the medium with increase in the percentage of alcohol leads to a marked decrease in diffusion coefficient.

In this study, the aspect of the dependence of the rate of corrosion on the concept of water organic solvent interaction is considered. It is found that addition of alcohol to H_3PO_4 has a marked effect on reducing the acidity of the

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Table 1
Viscosities and densities of phosphoric acid-isopropanol mixtures at different temperatures

Volume percentage of alcohol	d 20°C	ζ 20°C	d 25°C	ζ 25°C	d 30°C	ζ 30°C	d 35°C	ζ 35°C
100	1.7944	21.0450	1.7923	20.0049	1.7962	17.2586	1.7885	12.9579
70	1.7974	17.0488	1.7951	15.0331	1.7930	12.9515	1.7906	10.1855
54	1.7997	14.3444	1.7951	12.7810	1.7951	10.3490	1.7922	8.0084
38	1.8015	12.0964	1.7987	10.2790	1.7962	8.0020	1.7945	5.8177
23	1.8038	9.8198	1.8011	8.0416	1.7990	5.6183	1.7971	4.0051
7.5	1.8053	7.3424	1.8025	5.6332	1.8001	3.2211	1.7985	2.0098

d in g cm^{-3} ζ in Centipoise

Table 2
The relation between the percentage inhibition of corrosion of copper in 10M phosphoric acid in presence of different composition of isopropanol at 25°C

Solvent	Dielectric constant	Composition (v/v)	Limiting current mA.cm^{-2}	% inhibition
	80.37	0	250	0.00
	65.72	10	48	80.95
	58	24	44	82.50
Isopropanol	51	40	40	84.12
	37.5	55	38	84.92
	28.00	70	34	86.50
	18.12	80	28	88.90

medium. This has been attributed to the change in the state of solvation of Cu^{2+} and to increase the proton affinity of water [24, 25]. On addition of alcohol to water, the acidity decreases strongly due to breakdown of the open tetrahedral structure of water [26]. This concept explains the decrease in the rate of electropolishing with the addition of alcohol to the purely aqueous medium, especially in alcohol which is more basic, as indicated in table 3. Furthermore addition of alcohol would not influence the tetrahedral structure of water to the same extent. It has been reported that [27] the dielectric constants of alcohol-water mixtures decrease with increase in alcohol percentage. Table 2 shows that the limiting current decreases with decreasing dielectric constant of mixtures.

According to electrostatic theory, the association of an electrolyte in a solvent containing hydroxyl group appears to increase with increase ionic size.

The effect of solvent is due to: (a) stabilization of the pairs due to the hydrogen bond chains in the alcohol (b) solvation of ions [28] leading to a decrease in coefficient values.

The participation of alcohol in the ion-pair formation equilibrium, therefore, should involve both steric and coulombic effects. On the basis of this approach the structure modification of the alcoholic polymers generated by

added solvents should result in a variable influence of alcohol molecules on ion-pair association of Cu^{++}.

When a higher alcohol is chosen as the solvent system, the pattern of ionic association of hydroxyl solvent may be investigated without such complication as three dimensional structural effects [20].

3.4. Effect of temperature

The activation energy of the process is an important parameter for determining the rate controlling step [25]. The diffusion of the aqueous species is the rate controlling step, ΔE is generally < 43 K Joule/mole while if ΔE values usually >43 K Joule/mole when adsorption of species on the reaction surface and subsequent chemical reaction takes place. Table 4 give the values of ΔE. It is obvious that, the values of ΔE < 40 K Joule/mole. This indicates that electropolishing reaction is controlled by diffusion process.

3.5. Thermodynamic treatment of the results

The values for enthalpy of activation, ΔH^*, entropy of activation ΔS^*, and free energy of activation ΔG^*, can be obtained by using equations:

$$\Delta H^* = \Delta E - RT. \tag{3}$$

$$\frac{\Delta S^*}{R} = \ell n\ A - \ell n\ \frac{aTe}{h}\ . \tag{4}$$

$$\Delta G^* = \Delta H^* - T\Delta S^*, \tag{5}$$

where a is the Boltzman constant, e is constant equals 2.7183 and h is Plank's constant.

Thermodynamic functions of electropolishing of copper in isopropanol gives evidence of structural change occurring in the solution as the type of solvents are changed. The effect can arise from the solvent properties and / or from the solvation properties of the ion in different solvents [30].

The calculated values of ΔG^*, ΔH^* at different temperatures are shown in table 4. Fig. 6 shows the variations of ΔG^*, ΔH^* and

ΔS^* with the mole fraction of the organic solvents. The gradual increases of both ΔG^* and ΔH^* give a good indication of preferential solvation of metal surface in presence of aprotic solvents which is a criterion of specific solvation. Also the weak dependence of ΔG^* on the composition of the organic solvent 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 the dielectric constant of the solvent. This shows that as the dielectric constant decrease more work is required to keep the ions apart and, therefore, the dissolution of Cu is decreased as the dielectric constant decreases. There is less spontaneity and less dissolution at lower dielectric constant. Table 4 shows that for any

Table 3
Limiting current temmprature for organic solvent mixtures at different mole fraction of isopropanol

E (KJ.mol^{-1})	I $t\,^{\circ}C$ X	Limiting current (mA)				
		20	25	30	35	40
16.453	1.00	25	28	34	38	42
21.280	0.411	29.5	34	39	44	53
22.025	0.2682	32	38	42	47	55
23.370	0.1665	34	40	45	51	58
26.613	0.0856	36	44	47	54	61
27.77	0.0310	40	48	53	59	67

Table 4
Thermodynamic parameters for electropolishing process in 10M H$_3$PO$_4$ at different mole fraction of isopropanol

Mole fraction X	$T\,^{\circ}K$	293	298	303	308	313
1.0	ΔH^*	14.016	13.974	13.933	13.891	13.830
	ΔG^*	78.908	50.015	81.124	82.233	83.343
	$-\Delta S^*$	221.475	221.615	221.754	221.890	222.024
0.4117	ΔH^*	18.854	18.812	18.771	18.729	18.688
	ΔG^*	83.297	84.397	85.498	86.599	87.702
	$-\Delta S^*$	219.943	220.084	220.222	220.358	220.492
0.2682	ΔH^*	19.588	19.546	19.505	19.463	19.422
	ΔG^*	83.723	84.817	85.913	87.009	88.106
	$-\Delta S^*$	218.890	219.030	219.169	219.305	219.439
0.1665	ΔH^*	20.931	20.889	20.848	20.806	20.765
	ΔG^*	84.987	86.080	87.175	88.269	89.366
	$-\Delta S^*$	218.622	217.762	218.901	219.037	219.171
0.0865	ΔH^*	24.176	24.134	24.093	24.051	24.010
	ΔG^*	88.114	89.205	90.298	91.390	92.485
	$-\Delta S^*$	218.220	218.360	218.499	218.635	218.769
0.0312	ΔH^*	25.333	25.291	25.250	25.208	25.167
	ΔG^*	88.907	89.991	91.092	92.164	93.252
	$-\Delta S^*$	216.975	217.116	217.300	217.390	217.524

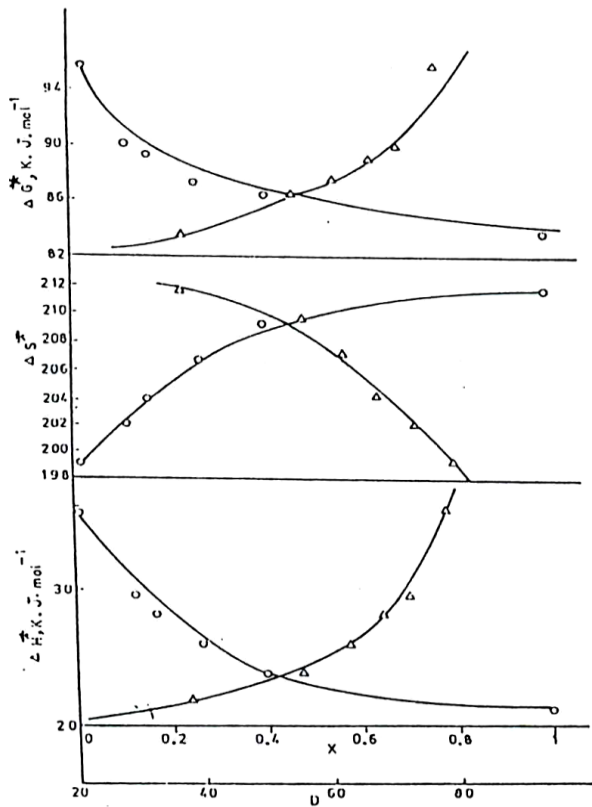ΔH^*, ΔG^* in KJ.mol^{-1} and ΔS^* in $E\,J$.mol$^{-1}K^{-1}$

Fig. 6. Relation between thermodynamic parameters for electro polishing of copper from isopropanol-water mixtures and O fraction X and Δ dielectric constant D.

solvent, as the temperature increases the dielectric constant decreases and the forces among the ions greater, but the rate of mass transfer increases. This is attributed to the fact that as the temperature increases, the viscosity of solvent decreases. So, solvation decreases and mobility of Cu^{2+} increases, this leads to increases in the rate of mass transfer.

3.6. The isokinetic relationship

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

$$\Delta H^* = \beta \Delta S^* + \text{constant}, \tag{6}$$

or

$$\delta \Delta H^* = \beta \Delta S^* \delta. \tag{7}$$

The operator concerns the difference between any two reactions in the series. Substituting from (7) into the familiar relationship

$$\delta \Delta H^* = \delta \Delta G^* + T \delta \Delta S^*. \tag{8}$$

We obtain

$$\beta \Delta S^* \delta = \delta \Delta G^* + T \delta \Delta S^*. \tag{9}$$

It follows that when $\delta \Delta G^*$ equals zero, β equals T. in other words, the slope in a linear plot of ΔH^* versus ΔS^* is the temperature at which all the reactions that conform to the line occur at the same rate. β is, therefore, known as the isokinetic temperature. Fig. 7 shows the plot of ΔH^* versus ΔS^* for different solvents and compositions; the isokinetic temperature β was estimated as 402. This value is much higher than that of the experimental temperature (298 K) indicating that the rate of the reaction is enthalpy controlled [31], i.e., the rate of reaction depends on temperature.

3.7. Data correlation

To obtain an overall mass transfer correlation under the present conditions, where a rotating disk is used, the method of dimensional analysis was used. To identify the variables which affect the rate of mass transfer in the corrosion, the mechanism of forced convection mass transfer should be recalled
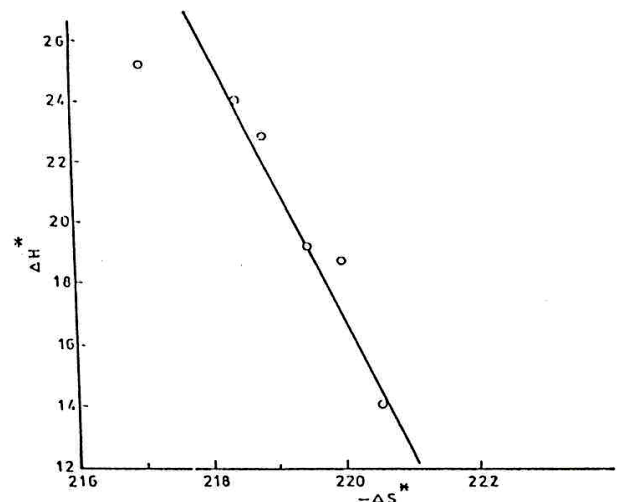

Fig. 7. Variation of ΔH^* with ΔS^* in water-isopropanol mixtures.

first. Forced convection takes place as a result of disk rotation. The thickness of the hydrodynamic boundary layer determines the thickness of the diffusion layer across which diffusion of Cu^{++} from the interface to bulk takes place. The thickness of the hydrodynamic boundary layer at the rotating disk and the diffusion layer are determined by the physical properties of the solution, the geometry of the system (disk diameter) and disk rotation speed. This picture leads to the equation:

$$K = f\,(\rho,\, \eta,\, D,\, V,\, d), \qquad (10)$$

Where:
K is the mass transfer coefficient, sec^{-1},
ρ is the density of bulk, g cm^{-3},
η is the Kinematic viscosity of bulk, cm^2 sec^{-1}, and
D is the diffusion coefficient, cm^2 sec^{-1}.
The dimensionless groups must often used in convective mass transfer where

$K = \dfrac{I}{ZFC_{\circ}}$, mass transfer coefficient

Sherwood number $Sh = Kd/D$
Schmidt number $Sc = y/D$
Reynolds number $Re = Vd/y$
ω is the angular velocity,
V is the disk linear velocity; ($V = \omega$r), and
d is the diameter of disk, cm.

By using the method of dimensional analysis, the above equation can be written as

$$Sh = a\, Sc^b\, Re^c. \qquad (11)$$

Where Sh is Sherwood number, Sc is Schmidt number and Re is Reynolds number, a, b and c are constants; the other equation used was

$$Sh = a\, Sc^{0.33}\, Re^c. \qquad (12)$$

By plotting log $Sh/Sc^{0.33}$ and log Re a straight line was obtained; its slope gives constant c and intercept gives the constant a.

Fig. 8 shows the overall mass transfer correlation for solvent used. Table 5 summarizes the values of dimensionless groups Sh, Sc and Re used in obtaining the correlations shown in fig. 8, the physical properties ρ, η and D used in calculating these dimensionless groups were measured as above and were given in table 5.
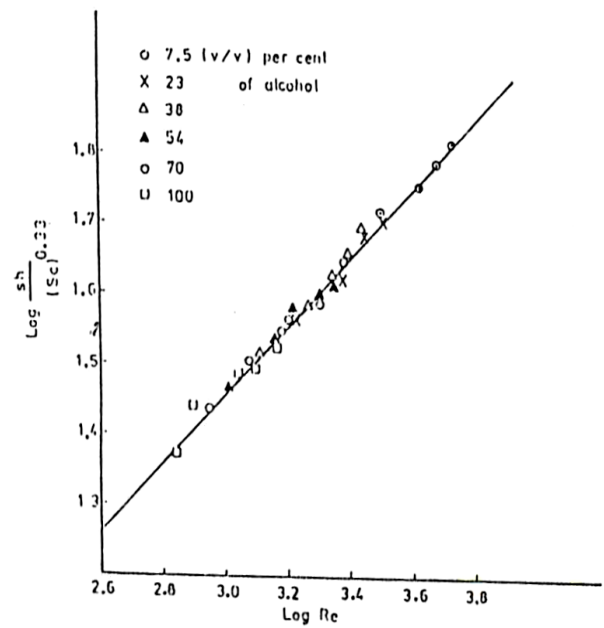

Fig. 8. the overall mass transfer consfer correlation in presence of isopropyl alcohol.

Fig. 8 shows that the data can be correlated for isopropanol by the following equation:

$$Sh = 1.835\, (Sc)^{0.33}\, (Re)^{0.48}. \qquad (13)$$

The exponent in the above equation denotes a laminar flow which agrees with the previous mass transfer studies in aqueous media [33]. It should be emphasized that the correlations obtained in our present study forced convection mechanism, which agrees very well with the relationship.

$$Sh = 0.62\, (Sc)^{0.33}\, (Re)^{0.5}, \qquad (14)$$

given by Riddford for mass transfer to a rotating disk in laminar flow systems [32- 35].
Fig. 8 can be represented for $9.544 \times 10^7 >$ $Sc.\ Re < 1.02413 \times 10^8$ by eq. (14). The laminar flow in phosphoric acid – isopropanol mixtures may be explained [31] as follow; organic solvent affect the rate of mass transfer through affecting viscosity, density, dielectric constant and solvation which affect also the diffusivity and activity of copper ions.

Table 5
General correlation of free convection mass transfer in presence of isopropanol at 25 ˚C

Volume % of alcohol	rpm	I_l (mA.cm^{-2})	K x 10^4 (cm.s^{-1})	γ cm^2.s^{-1}	D x 10^7 (cm^2.s^{-1})	Sh	Sc	Re
7.5	360	95	5.790		7.8942	1467.127	39586	2411.52
	502	105	6.4005		7.1484	1790.675	43714	3362.56
	607	115	7.0101	$\nu = 0.03125$	7.1058	1973.064	43978	4069.92
	680	130	7.9244		7.8430	2020.757	39844	4555.09
	790	150	9.1435		8.6870	2105.100	35973	5291.95
23	360	85	5.3644		7.6925	1394.709	57978.551	1689.686
	502	100	6.3110		7.6497	1649.999	58302.94	2356054
	607	112	7.0683	$\nu = 0.0446$	7.8635	1797.749	56717.74	2848.879
	680	126	7.9518		8.6168	1845.65	51759.354	3191.628
	790	140	8.8354		9.0186	1959.37	49453.352	3707.924
38	360	80	5.1749		7.7527	1334.99	73703.35	1318.86
	502	96	6.2098		7.9420	1563.79	71946.61	1838.99
	607	110	7.1154	$\nu = 0.05714$	8.4480	1684.52	67367.3	2223.66
	680	125	8.0857		9.3979	1720.75	60800.82	2491.19
	790	134	8.6679		9.3215	1859.77	61299.15	2894.18
54	360	78	5.6053		9.2305	1214.52	77027.25	1059.91
	502	96	6.8989		9.8218	1404.81	72389.99	1477.92
	607	110	7.9050	$\nu = 0.0711$	10.4476	1513.27	68053.91	1787.06
	680	112	8.0487		9.8572	1633.06	72130.02	2002.09
	790	130	9.3422		11.0155	1696.19	64545.41	2325.93
70	360	74	5.8988		10.3828	1136.26	80614.04	900.358
	502	80	6.3770		9.0950	1402.31	92028.59	1255.44
	607	90	7.1742	$\nu = 0.0837$	9.4120	1524.48	88929.03	1518.04
	680	105	8.3699		10.8917	1536.93	76847.51	1700.68
	790	120	9.5656		11.8918	1608.77	70384.64	1975.79
100	360	70	7.1116		14.7684	963.08	75566.75	675.27
	502	78	7.9244		13.5372	1170.76	82439.50	941.577
	607	85	8.6356	$\nu = 0.1116$	13.3555	1293.19	83561.08	1138.53
	680	102	10.3626		16.1225	1285.48	69220.03	1275.51
	790	110	11.1754		16.1355	1385.19	69164.27	1481.84

References

[1] P. A. Jacquet. C. R. Acad. Sci. p. 202, p. 402 (1963).

[2] P.A. Jacquet, Met. Rev. Vol. 1, p.157 (1956).

[3] W.J.M. Tegart, Electrolytic Polishing of Metals and Alloys, 2nd Ed. London (1959).

[4] W.G. Elmore, J. Applied Physics. Vol. 10, p. 724 (1939).

[5] J. Edwards, J. Electrochem. Soc. Vol. 100, p. 139c (1953).

[6] A.G. Chrusty, A. Low, V. Otieno-Alego M. Stol and R.D. Webstar, "Voltammetric and Raman Micropectroscopic Studies an Artificial Copper Pits Grown in Simulated Potable Water", J. App. Electrochem. Vol. 34, p. 225 (2004).

[7] D.Q. Zhan. L.X. Gao and G.D. Zhou. J. Appl Surf. Sci. Vol. 225, p. 287 (2004).

[8] H. Htamacic, J. Telegdi, K. Papp and E. Stupnisek-Lisac, "Protective Properties of an Inhibitor Layer an Copper in Neutral Chloride Solution", J. Appl. Electrochem. Vol. 34, p. 545 (2004).

[9] H.M.A, S. Chem, L. Niu, S. Zhao, S.Li and D. Li, "Inhibition of Copper Corrosion by Several Schiff Baes in Aerated Halide Solution", J. Appl Electrochem. Vol. 32, p. 65 (2004).

[10] D.R. Gabe, Corrosion Science, Vol. 12, p. 113 (1972).

[11] R.W.K. Monocycombe, R.R. ad Hughan, J. Counc. Sci. Ind. Res. Aust. Vol. 20, p. 297, (1947).

[12] A. Hickling and J.K. Miggins, Trans. Inst. Met. Fin. Vol. 29, p. 274 (1953).

[13] T.P. Moar and G.P. Rothwell, Electrochim. Acta. Vol. 9, p. 135, (1964).

[14] M.G. Fouad, F.N. Zein and M.I. Ismail, Electrochem. Acta, Vol. 16, p. 1477, (1971).

[15] V.A. Ettel, B. Tilak and A.S. Gendron, J. Electrochem. Soc. p. 867, (1974).

[16] Amira Hossam El-Din, "Kinetics of Electroplating of Some Metals in Presence of Some Organic Compounds", M.Sc. Thesis Chemistry Department, Faculty of Science, Alex. Univ. (2005).

[17] V.G. Levich, Physicochemical Hydrodynamics, Prentice-Hall, Inc.., Engle Wood Cliffs, N. Y. (1962).

[18] N. Ibl, Advances in Electrochemistry and Electrochemical Engineering, Ed. P. Delahay and C.W. Tobias, Vol. 2 Interscience, New York (1962).

[19] M. El Achouri, M.R. Infante, F. Izquierdo, S. Kertit, H.M. Gouttoyn and B.N. Ciri Corros. Sci. Vol. 43, p.19 (2001).

[20] D. Chebabe, Z. Ait Chikb, A. Stihiti and Z. Zucchi, corros Sci. Vol. 45, p. 309 (2003).

[21] J.M. Bastidos, J.L. Polo and E. Como, "Substitutional inhibition Mechansim of Mild Steel Hydrochloric Acid Corrosion by Hexylamine and Dodeylamine", J. Appl. Electrochem Vol. 30, p. 1173 (2000).

[22] L. Nunez. E Reguera, F. Corvo, E. Conzalz and C. Vazquez, Corros Sci. Vol. 47, p. 461 (2005).

[23] El Warraky, H. A. El Shayeb and E. M. Sherif, Anti Corros, Methods, Methods Mater. Vol. 51, p. 52 (2004).

[24] F. Franks and D.J.G. Ives, Quart Rev., p. 20, (1966).

[25] F. Franks in Physicochemical processes in Mixed Aqueous Solvents, (Ed), F. Franks American Elsevier, New York, p. 50 (1967).

[26] E.A. Brande and E.S. Stern, J. Chem. Soc., p.1976 (1948).

[27] P. Rohdewald and L. Modener, "Dielectric Contants of Amide-Water Systems", J. Phys. Chem, Vol. 77, p. 373 (1973).

[28] G. Pisoia and G. Pecki, "I on-Pair Association of Cesium aand Tetraethyl Ammonium Perchlorates in Ethanol-Acetone Mixtures at 25 Dat", J. Phys. Chem., Vol. 74, p.1450 (1970).

[29] D.F. Evans and P. Garadam, Ibid, Vol. 72, p. 3281 (1968).

[30] J.M. Mcintyre and E.S. Amis, "Electromotive Fpore of the Silver-Silver Iodide Hydrogen Iodide Cell and the Methanol Media, J. Chem. Eng. Data, Vol. 13, p. 371 (1968).

[31] A.M. Mousaa, M.M. El-Banna and I.A.S. Mansour, "Cinnamic Acid Derivatives as Inhibitors for the Corrosion of Steel in Sulphuric Acid", Bull. of Electrochemistry, India, Vol. 7, p. 164 (1991).

[32] F. Walsh, a First Course in Electrochemical Engineering, the Electrochemical Consultants Remsey U.K. (1995).

[33] A. Taha, S.A. Sallam and A.M. Ahmed, "Corrosion of Cooper in Phospheric Acid Ethanol Mixture", Anti-Corrosion Methods and Matterials Vol. 41, p. 10 (1994).

[34] M. Eisenberg, C.W. Tobias and C.R. Wilke, J. Electrochem. Soc. Vol. 102, p. 415 (1955).

[35] A.C. Riddford, Advan., Electrochem. Eng. Vol. 4, p. 47 (1966).