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Electroplating in Steel in Presence of Isopropanol-Water Mixture

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The rate of electroplating of steel in acidified $CuSO_4$ solution in absence and presence of isopropanol alcohol were studied by measuring the limiting current. It found that the rate of electroplating was decreased in presence of alcohol. The rate of inhibition rang from 40% to 66% depending on the concentration of alcohol. Thermodynamic properties E_a, ΔH^*, $\Delta S^*$and ΔG^* were calculated. The value of $E_a < 42$ kJ mol.l^{-1}, which indicate that, reaction, is diffusion controlled.

Keywords: Electroplating of steel, Isopropanol-Water Mixture, Limiting Current. Thermodynamic parameters and Dimensionless group.

1. INTRODUCTION

Copper electroplating is one of the oldest, protective and decorative metallic coating for steel and other basis metals. Therefore, intensive studies were carried out to obtain copper electroplates suitable for different purposes. One of the most important baths used for electroplating copper was cyanide bath [1], but due to the environment consideration, cyanide based baths formulation were replaced by non-cyanide formulations such as sulphate [2-6], chloride [4], pyrophosphate [7] and tartarate bath [1].

Organic additives are added to acidic copper sulphate plating baths to improve the quality of the deposits. The presence of these adsorption compounds in the plating bath results in marked changes in the deposit which can increase brightness, hardness, smoothness, and ductility [8-10]. The effect of thiourea on the electroplating of copper from acidic sulphate bath has been studied [11,12]. This compound acts as brightener and leveler, and in its absence ductile copper deposits are obtained.

Mixed organic solvents are being increasingly used during recent years in many fields. Bright copper has been electrodeposited from aqueous ammonia [13] solutions. Electrodeposition of copper has been studied in presence of ethanol, n-propanol and tert-butanol[14] and methanol, ethylene glycol and glycerol [15]. Electrodeposition of yttrium [16] has been carried out from formaldehyde bath onto different substrates. Electrodeposition of nickel from mixed baths [17] and from nonaqueous baths [18] led to some promising results. In the case of mixed solvent bath, the change in physicochemical properties of the deposit is attributed to the change in solvent composition. Moreover, the effect of aprotic constituent, dielectric constant and state of solvation of ions to be electrodeposited can be easily varied by simply changing the composition of the mixed solvents. During electrodeposition studies of copper and nickel from water–methanol [19] bath, the change in electronic state of metal ion was attributed to the structural changes of solvent.

The goal of the present work is to study the effect of medium composition on the electroplating process of copper from acidified solutions of copper sulfate. Different contents of 40% (v/v) iso-prpanol were mixed with acidified copper sulphate solutions to represent the investigated media at various temperatures under the conditions of natural convection using copper and lead anodes. Physicochemical properties of the medium such as density, viscosity, dielectric constant and state of solvation have been discussed.

2. EXPERIMENTAL PROCEDURE

2.1. Chemicals

BDH iso-propanol, $CuSO_4$ and H_2SO_4 were used. Five concentrations (0.01, 0.05, 0.1, 0.15 and 0.2M) of $CuSO_4$ and 1.5M H_2SO_4 are used and the percent of isopropyl alcohol are 7.5, 23, 38, 54, 70 and 100 v/v.

2.2 Apparatus and procedure

It should mention clearly that, cell was used, one with vertical electrodes figure (1) and one with rotating disk electrode figure (2). Figure (1) show the cell and electrical circuit used in the present work. The cell used in the present work consists of rectangular container having the dimension of (5×5×10 cm) with electrodes fitting the whole cross section. The electrodes were rectangular copper sheet as anode and steel sheet as cathode of 10cm height and 5cm width. Electrode separation was 5cm; the electrical circuit consisted of a 6V D.C. power supply, a variable resistance and a multi range ammeter connected in a series with cell. A high impedance voltammeter was connected in parallel with the cell to measure its potential. Five concentrations (0.01, 0.05, 0.1, 0.15 and 0.2M) of $CuSO_4$ and 1.5M H_2SO_4 are used and isopropyl alcohol used.

The steady state cathode potential was measured against reference electrode consisted of copper wire immersed in a cup of luggin tube filled with acidified $CuSO_4$ – isopropanol solution similar to that in the cell, the tip of the luggin tube was placed 0.5-1mm from cathode wall [15].

Polarization curves, from which the limiting current was determined, were plotted by increasing the applied current stepwise and measuring the corresponding steady-state potential. One minute were allowed for reaching the steady state potential. Before each run, the back of 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 thermostat. The physical properties of solution (ρ,η,D) needed to correlate the data were determined experimentally using standard techniques [15].

The diffusivity of Cu^{2+} in different $CuSO_4$ iso-propanol mixtures was detrmined by measures the limiting current of cathodic of copper rotation disc in mixtures at different temperatures and applying the Levich equation [16].

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

where Z valency, F faraday number 96500 coulomb/l, υ = kinematic viscosity cm^2/s, ω angular velocity rad/S, I_l limiting current mA.

The density was measured by using DA-300 Kyoto electronics density measurement equipment at different temperatures (20, 25, 30, 35°C). The viscosity was measured by using Koehler viscosity Bath (Model K23400 Kinematic bath) at different temperatures (20, 25, 30, 35°C).

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

The cathode consists of a steel metal disk of 2 cm diameter. The sides and back of the cylinder as well as the drive shaft are insulating by epoxy- resin. The anode is made of a cylinder copper metal electrode of 12 cm diameter; it has also acted as the reference electrode by virtue of its high surface area compared to that of the cathode [20, 21].

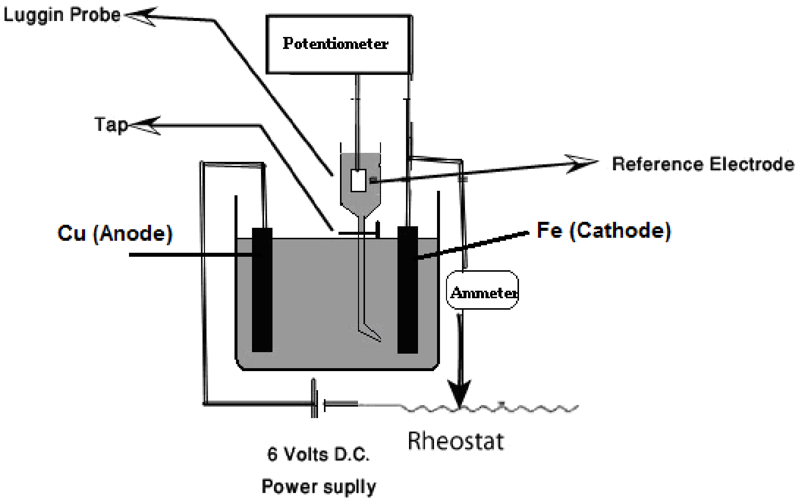

Figure 1. The electrolytic cell and the electrical circuit for part (I)

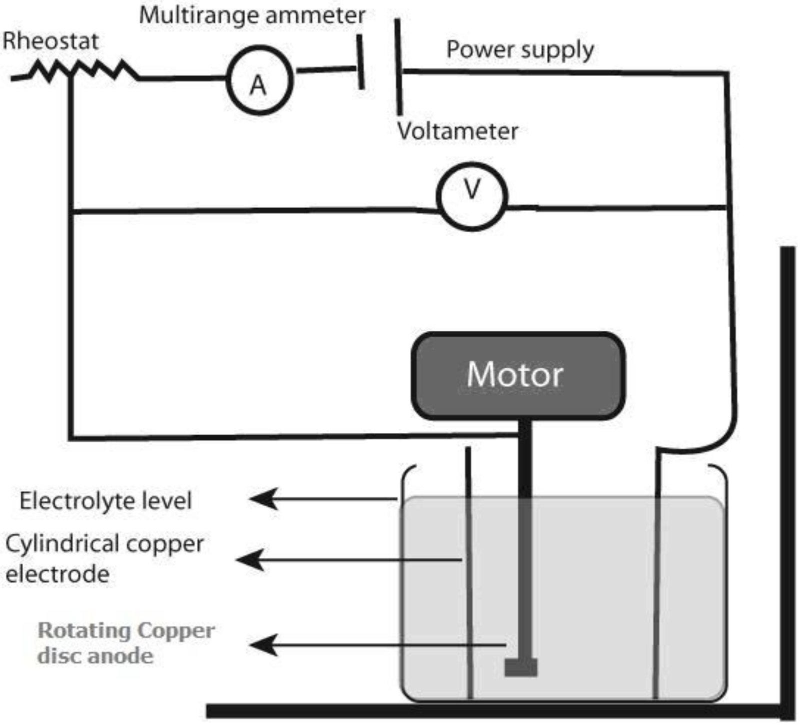

Figure 2. The electrolytic cell and the electrical circuit using rotating cylinder electrode

3. RESULTS AND DISCUSSION

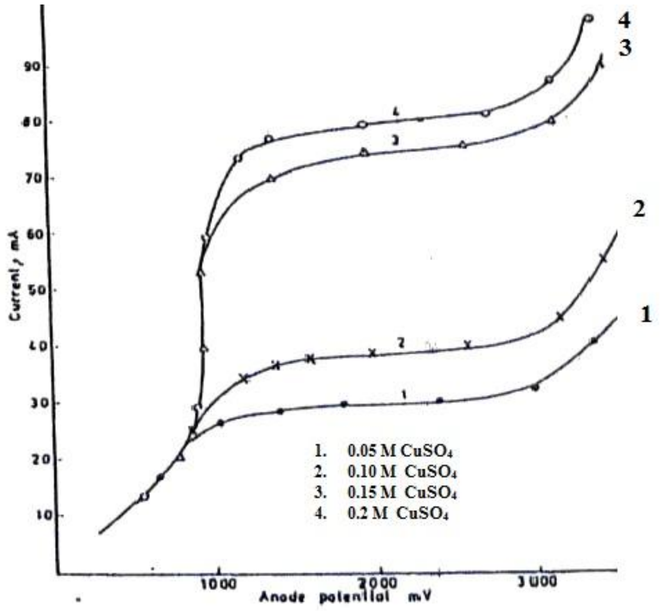

Figure 3. Typical polarization curves obtained in presence of iso-propanol, x = 0.268 at different concentration of $CuSO_4$ at 25°C.

Table (1) gives the values of limiting current at different composition of alcohol and different temperature. Figure (3) shows a set of typical current potential curves obtained at different $CuSO_4$ concentrations. It is obvious that the limiting current decreases with increasing $CuSO_4$ concentration within rang studied; this is in agreement with the finding of other authors who worked within the same range of concentration using other anode geometries [20, 22]. The effect of $CuSO_4$ concentration on the value of the limiting current can be explained based on the mass transfer equation [18]:

Increasing $CuSO_4$ concentration increases in the limiting current according to equation (1).

Table 1. Limiting current-temperature for organic solvent mixtures at different mole fraction

E, kJ.mol^{-1}	**I, mA**					
	x	**20°C**	**25°C**	**30°C**	**35°C**	**40°C**
16.453	1.00	25	28	34	35	42
21.280	0.411	30	34	39	44	53
22.030	0.268	32	38	42	47	55
22.370	0.166	34	40	45	51	58
26.610	0.086	36	44	47	54	61
27.770	0.031	40	48	53	59	67

Figure (4) give the current potential curve of water-isopropanol at different mole fraction of alcohol. It is obvious that limiting current decreases by increasing concentration of alcohol.

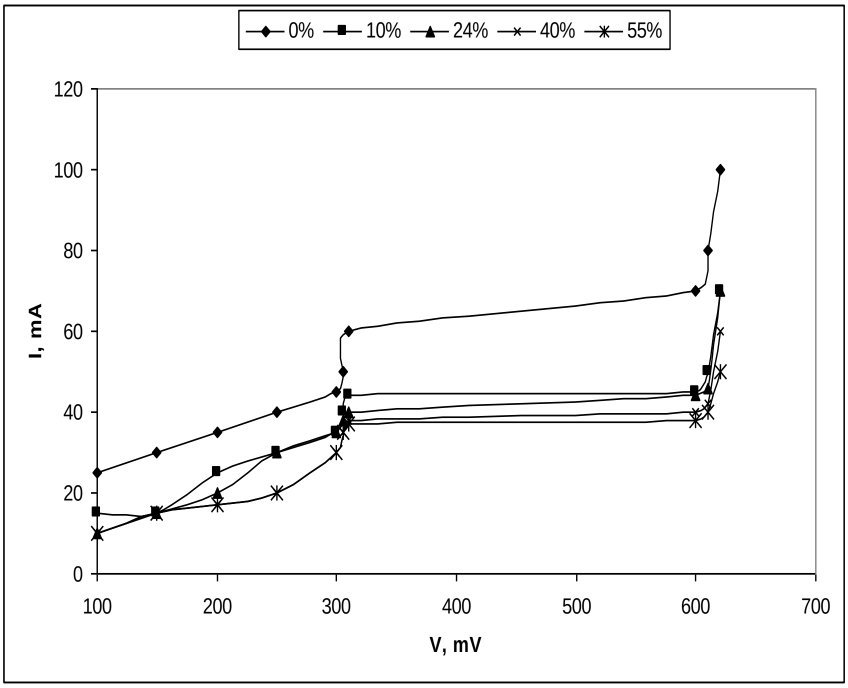

Figure 4. Current potential curves for water-isopropanol alcohol at different mole fraction of isopropanol

Table 2. The relation between the percentage inhibition of electroplating of copper in 0.15M $CuSO_4$ and 1.5 H_2SO_4 in presence of different composition of iso-propanol at 25°C

Dielectric constant	Composition (v/v)	Limiting current ($mA.cm^2$)	% inhibition
80.27	0	280	40
60.72	10	48	45
58.00	20	44	50
51.00	40	40	53
37.50	55	35	57.5
28.00	70	34	66

If I_l, limiting current for blank solution and I for solution in presence of isopropanol.

$$\% \text{ inhibition} = (I_l - I) / I_l \times 100 \qquad (2)$$

Table (2) and figure (5) give the relation between % inhibition and composition of solution at 25°C.

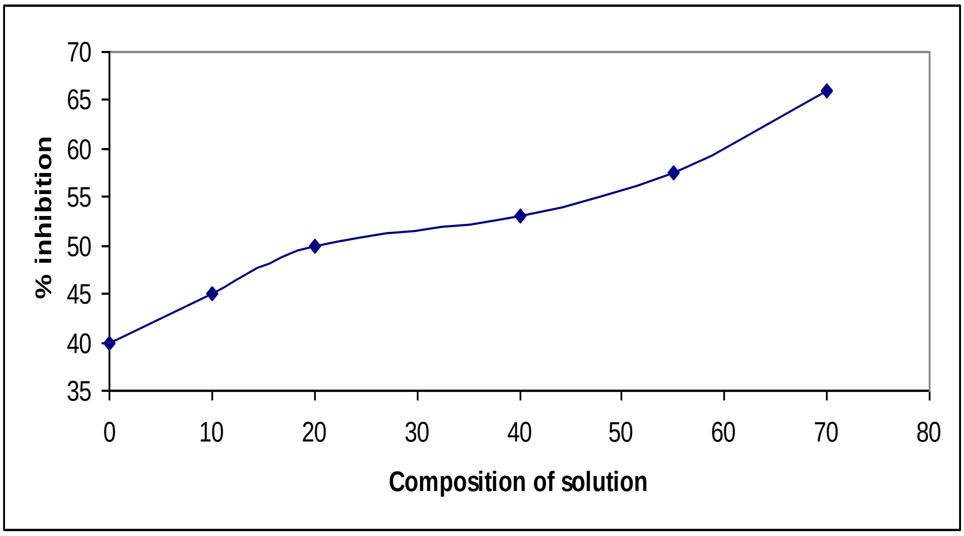

Figure 5. Gives the relation between composition of solution and percentage inhibition at 25°C.

3.1 Structural effects

Electroplating of copper and its inhibition in a wide variety of media, particularly when they contain organic solvents have attracted the attention of a number of investigators [24-27].

In water-organic solvent mixtures, the variation of physicochemical properties of medium with the composition Table (1) has an important role in controlling electroplating.

It has been found that electroplating is inhibited by the organic alcohol and inhibition efficiency has been found to increase with increasing concentration of organic solvents Table (1).

These results take place because these types of reaction are controlled by diffusion of Cu^{++} from bulk solution to metal surface. 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 electroplating on the concept of water organic solvent interaction is considered. It is found that addition of alcohol to $CuSO_4$ marked effect on reducing the acidity of the medium. This has been attributed to the change in the state of solvation of Cu^{2+} and to increase the proton affinity of water [28,29].

On addition of alcohol to water, the acidity decreases strongly due to breakdown of the open tetrahedral structure of water [30]. This concept explains the decrease in the rate of electroplating with the addition of alcohol to the purely aqueous medium, especially in alcohol, which is more basic, as indicated in Table (1). Furthermore, addition of alcohol would not influence the tetrahedral structure of water to the same extent. It has been reported that [31] the dielectric constants of alcohol-water mixtures decrease with increase in alcohol percentage. Table (1) 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[32,33] 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. Based on 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 [24].

3.2 Effect of temperature

The activation energy of the process is an important parameter for determining the rate-controlling step [29]. The diffusion of the aqueous species is the rate controlling step, ΔE_a is generally < 43 K Joule/mole while if ΔE_a values usually >43 K Joule/mole when adsorption of species on the reaction surface and subsequent chemical reaction takes place. Table (3) gives the values of ΔE_a. It is obvious that, the values of $\Delta E_a < 40$ K Joule/mole. This indicates that electroplating reaction is controlled by diffusion process.

3.3 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:

$\Delta H^{*} = \Delta E - RT$ (3)
$\Delta S^{*}/R = \ln A - \ln \alpha Te/h$ (4)
$\Delta G^{*} = \Delta H^{*} - T\,\Delta S^{*}$ (5)

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

Thermodynamic functions of electroplating of copper in isopropanol give 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 [34].

The calculated values of ΔG^{*}, ΔH^{*} at different temperatures are shown in Table (3).

Table (3) 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 (3) 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 decreased as the dielectric constant decreases. There is less spontaneity and less dissolution at lower dielectric constant. Table (3) shows that for any solvent, as, the temperature increase the dielectric constant decreases and the forces among the ions greater, but the rate of mass transfer increases.

Table 3. Thermodynamic parameters for electroplating of steel at different mole fraction of isopropanol

D	mole fraction	T, K	293	298	303	308	313
65.7	1.0000	ΔH^{*}	14.011	13.974	13.933	13.891	13.830
		ΔG^{*}	78.905	80.015	81.124	82.233	83.343
		$-\Delta S^{*}$	221.475	221.615	221.754	221.890	292.024
58	0.4117	ΔH^{*}	18.854	18.812	18.771	18.729	18.685
		ΔG^{*}	83.357	84.397	85.498	86.588	87.702
		$-\Delta S^{*}$	219.943	220.085	220.222	220.538	220.492
51	0.2692	ΔH^{*}	19.588	19.541	19.505	19.463	14.422
		ΔG^{*}	83.723	84.817	85.913	87.009	88.101
		$-\Delta S^{*}$	219.90	219.03	219.169	219.305	219.439
37.5	0.1665	ΔH^{*}	20.931	20.889	20.845	20.806	20.765
		ΔG^{*}	84.987	87.08	87.175	88.269	89.361

		$-\Delta S^*$	218.62	217.78	218.901	219.037	219.171
28	0.0865	ΔH^*	24.174	24.134	24.093	24.051	24.011
		ΔG^*	88.114	89.205	90.295	91.39	99.846
		$-\Delta S^*$	218.220	218.361	214.919	218.635	218.77
18.12	0.0312	ΔH^*	25.333	25.291	25.25	25.203	25.167
		ΔG^*	88.907	89.991	91.092	92.164	93.252
		$-\Delta S^*$	216.974	217.116	217.3	217.39	217.54

This is attributed to the fact that as the temperature increases, the viscosity of solvent decreases. Therefore, salvation decreases and mobility of Cu^{2+} increases, this leads to increases in the rate of mass transfer.

3.4 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 $\Delta H^*$with ΔS^* is a linear relationship which may be stated algebraically:

$$\Delta H^* = \beta\ \Delta S^* + \text{constant} \qquad (6)$$

Or

$$\delta\ \Delta H^* = \beta\ \Delta S^* \delta \qquad (7)$$

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

$$\delta\ \Delta H^* = \delta\ \Delta S^* + T\ \delta\ \Delta S^* \qquad (8)$$

we obtain

$$\beta\ \Delta S^* \delta = \delta\ \Delta G^* + T\ \delta\ \Delta S^* \qquad (9)$$

It follows that when $\delta\ \Delta G^*$ equals zero, β equals T in other words, the slope in a linear plot of ΔH^* versus $\Delta S^*$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. 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 [35], i.e., the rate of reaction depends on temperature.

3.5 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.

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 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 $K = I/ZFC_o$, mass transfer coefficient

Sherwood number $Sh = Kd/D$

Schmidt number $Sc = \upsilon/D$

υ = Kinamatic viscosity = η/ρ

Reynolds number $Re = Vd/\upsilon$

ω is the angular velocity,

Vis 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.

Table 4. General correlation of free convection mass transfer in presence of isopropanole at 25°C

Volume % of alcohol	rpm	I_l mA.cm^{-2}	K x 10^4 cm.s^{-1}	υ cm^2.s^{-1}	D x 10^7 cm^2.s^{-1}	Sh	Sc	Re
7.5	360	95	5.790	0.03125	7.8942	1467.127	39586	2411.52
	502	105	6.4005		7.1484	1790.675	43714	3362.56
	607	115	7.0101		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	0.0446	7.6925	1394.709	57978.551	1689.686
	502	100	6.3110		7.6497	1649.999	58302.94	2356.54
	607	112	7.0683		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	0.05714	7.7527	1334.99	73703.35	1318.86
	502	96	6.2098		7.9420	1563.79	71946.61	1838.99
	607	110	7.1154		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	0.0711	9.2305	1214.52	77027.25	1059.91
	502	96	6.8989		9.8218	1404.81	72389.99	1477.92
	607	110	7.9050		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	0.0837	10.3828	1136.26	80614.04	900.358
	502	80	6.3770		9.0950	1402.31	92028.59	1255.44
	607	90	7.1742		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	0.1116	14.7684	963.08	75566.75	675.27
	502	78	7.9244		13.5372	1170.76	82439.50	941.577
	607	85	8.6356		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

Figure (6) shows the overall mass transfer correlation for solvent used. Table (4) summarizes the values of dimensionless groups Sh, Sc and Re used in obtaining the correlations shown in figure (6), the physical properties ρ, η and D used in calculating these dimensionless groups were measured as above and were given in Table (4).

Figure (6) shows that the data can be correlated for isopropanol by the following equation:

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

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.

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

given by Riddford for mass transfer to a rotating disk in laminar flow systems [38-40].

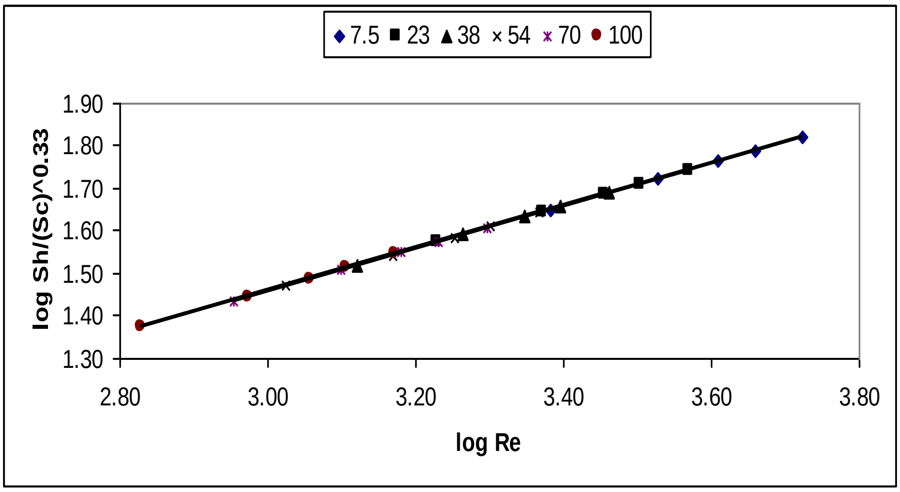

Figure 6. Overall mass transfer correlation

Figure (6) can be represented for 9.544 x 107 > Sc. Re < 1.02413 x 109 by last equation. The laminar flow in $CuSO_4$ - isopropanol mixtures may be explained [34] as follow; organic solvent affect the rat of mass transfer through affecting viscosity, density, dielectric constant and solvation which affect also the diffusivity and activity of copper ions.

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