



Kinetic Studies of Electrowinning and Electrorefining of Copper in Presence of Mono Carboxylic Acids

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The effect of some acids such as acetic acid, phenyl acetic acid and formic acid on the rate of electrowinning and electrorefining of copper were studied using copper anode and lead anode. It is found that the rate of deposition decreases by adding organic acids and depend on the type of acids. The rate of deposition increases by raising temperature. The ability of different acids to decrease the rate of deposition decreases in order phenyl acetic acid > acetic acid > formic acid.

Key Words: Kinetics, Electrowinning, Electrorefining, Copper.

INTRODUCTION

In electrowinning of metals usually an insoluble anode is used where the evolution of oxygen takes place. Anodic oxygen evolution could adversely affect the performance of the cell by increasing the ohmic drop¹⁻³ and disturbing the uniformity of current distribution⁴⁻⁷. On the other hand, anodic oxygen bubbles were found to enhance the rate of mass⁸⁻¹¹ at the cathode to a modest degree in vertical parallel electrode cells. In electrorefining, a soluble copper anode is used where the anodic reaction is copper dissolution instead of O₂ evolution. Electrorefining and electrowinning of copper are diffusion controlled processes whose rate depend on the physical properties of solution as well as its dynamics.

Surface active substances are being used as additives in electrorefining and electrowinning industries to improve the quality of electro deposit, because they produce a fine grained smooth deposit. These substances have a remarkable effect on the size of gas bubbles and bubble dynamics. Accordingly, the presence of surfactant is expected to affect the performance of electrowinning cells through affecting the behaviour of anodic O₂ bubbles.

Previous studies have shown that SAS reduce the limiting current of uranium¹² and manganese¹³ deposit from phosphoric acid and mercury cathode.

The object of this work is to study: (1) The effect of acetic acid, formic acid and phenyl acetic acid deposition from an electrorefining cell where a soluble copper anode is used at high concentration of electrolyte. (2) The effect of above acids on the limiting current of electrowinning cell containing lead anode where O₂ bubbles evolve.

EXPERIMENTAL

The cell consisted of a rectangular plastic container having the dimensions 5.1 cm × 5 cm × 10 cm with electrodes filling the whole section (Fig. 1). The cathode is rectangular copper sheet of 10 cm height and 5 cm width, the anode is a lead or copper sheet of similar dimensions; electrode separation was

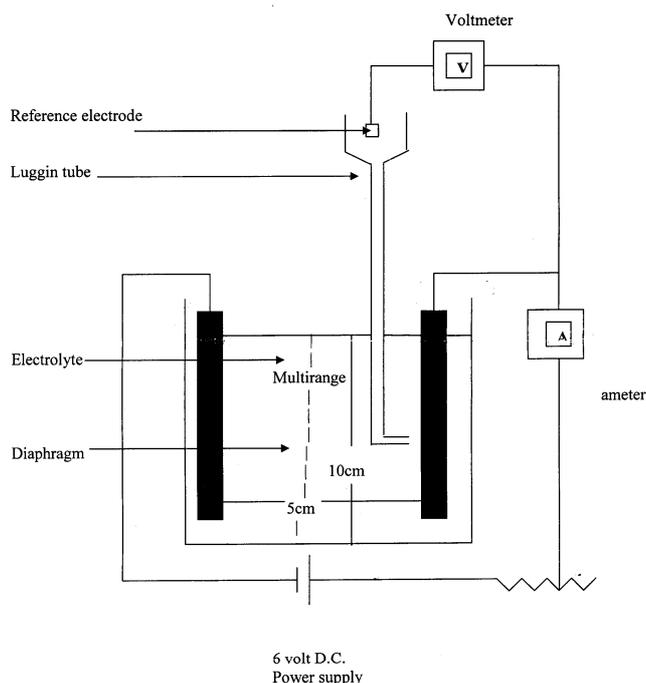


Fig. 1. Electrolytic cell and electrical circuit

5 cm the electrical circuit consisted of 12 V DC power supply connected in series with the cell and multi range ammeter. A voltmeter was connected in parallel with the cell to measure its voltage. The back and sides of the electrodes were covered with epoxy resin. Electrode treatment was similar to that used by Wilke *et al.*¹⁴.

The organic acids used are acetic acid, formic acid and phenyl acetic acid. Six different concentration of CuSO₄, 0.015, 0.05, 0.075, 0.098, 0.15 and 0.2M were used in 1.5M H₂SO₄, the acid concentration ranged from 5×10^{-5} - 1×10^{-3} M. The volume of solution used for each experiment is 250 mL; copper concentration was estimated in each solution by iodometry.

Polarization curves were constructed by increasing the current stepwise and measuring the steady state cathode potential against a copper reference cathode placed in the cup of luggin tube whose tip was placed about 1 mm from the cathode surface. To make sure that the decrease of Cu²⁺ concentration during polarization was negligible in case of lead anode. The limiting current was measured against potentiostatically using a fresh solution. The galvanostatic and the rapid potentiostatic methods gave almost the same limiting current.

RESULTS AND DISCUSSION

A typical current and cathodic potential curves obtained with and without formic acid when copper anode (Fig. 2a) and lead anode (Fig. 2b) were used. The limiting current I_l obtained from polarization curves was used to calculate the mass transfer coefficient k from the equation:

$$K = \frac{I_l}{ZFC_0} \quad (1)$$

K = Mass transfer coefficient, Z = valency, F = Faraday constant, C_0 = concentration of CuSO₄.

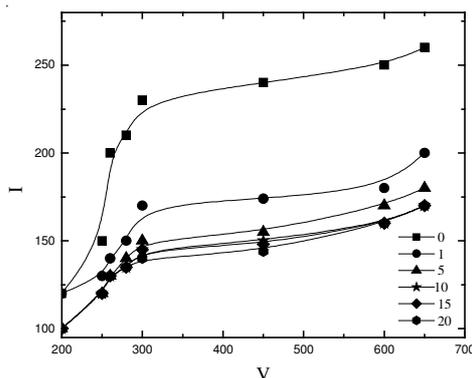


Fig. 2a. Relation between current and cathodic potential in presence of formic acid at 25 °C in case of Cu-Cu anode

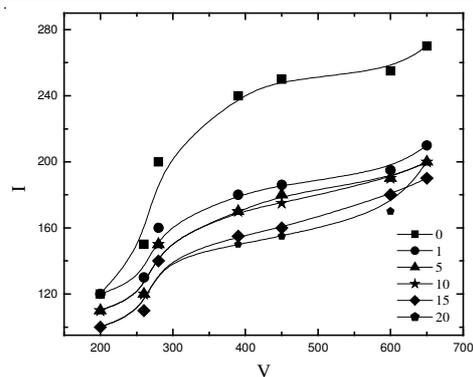


Fig. 2b. Relation between current and cathodic potential in presence of formic acid at 25 °C in case of Cu-Pb anode

Table-1 showed that in absence of organic acids the data fit well with the established natural convection mass transfer equation.

$$Sh = 0.67(Sc \cdot Gr)^{0.25} \quad (2)$$

This equation was derived theoretically from hydrodynamic (boundary layer theory) and confirmed experimentally by Eisenberg *et al.*¹², who studied the natural convection mass transfer at vertical plates and found the same relation as eqn. 2.

Physical properties of the solution (ρ , μ , D) used in the calculation and the dimensionless groups Sh , Sc and Gr were taken from the literature¹⁵.

Also in the absence of organic acids, the blank data, when we used lead anode fits well in to equation which agrees with the earlier findings¹⁶ derived from the hydrodynamic boundary layer theory^{17,18}

$$J = 1.096 (Re \cdot Fr)^{-0.176} \quad (3)$$

The gas discharge velocity V used in calculating J , Re and Fr was calculated from eqn. 4

$$V = \left[\frac{IRT}{4PF} \right] \quad (4)$$

Ahmed *et al.*¹⁷ predicted that $K \propto V$ in presence of organic acids, the following relation was obtained

$$K \propto V^b \quad (5)$$

where b is constant depending on organic substances (Table-2).

Organic acids	b
Formic acid	1.20
Phenyl acetic acid	1.14
Acetic acid	1.05

TABLE-1
GENERAL CORRELATION OF FREE MASS TRANSFER OF BULK SOLUTION

CuSO ₄ conc. (ML ⁻¹)	T (°C)	I _l (mA cm ⁻²)	$K \times 10^3$ (cm S ⁻¹)	η (C poise)	ρ (g cm ⁻³)	$D \times 10^6$ (cm ² S ⁻¹)	ρ_i (g cm ⁻³)	$\rho_i - \rho_{Pb}$ (g cm ⁻³)	Sh	Sc	Gr. 10 ⁻⁶
0.025	26	0.90	0.19	1.17	1.091	6.45	1.870	0.004	289	1664	02.91
0.050	21	0.190	0.20	1.31	1.094	5.64	1.094	0.007	347	2134	04.15
0.075	23	3.20	0.22	1.32	1.93	5.61	1.094	0.011	392	2275	07.08
0.100	24	4.60	0.24	1.26	1.096	5.94	1.087	0.014	401	1939	09.45
0.150	23	8.00	0.28	1.28	1.092	5.90	1.105	0.027	468	1987	17.83

From Table-3, it is noticed that velocity of gas decreases from phenyl acetic acid to formic acids. Plot log K against log V for different acids used. It is found that the values of b were more than one. This shows that effect of those acids on the discharge of velocity of gas is different. The values of b ranged from 1.14 for phenyl acetic acid to 1.05 for acetic acid *i.e.*, the effect on the rate of gas are different.

TABLE-3 RELATION BETWEEN log k AND log V FOR ORGANIC ACID AT 25 °C IN CASE OF LEAD ANODE			
10 ⁻⁵ conc. mol L ⁻¹	I _l	10 ³ (k)	10 ⁴ (V)
Formic acid			
1	174	1.894	11.16
5	155	0.844	9.94
10	155	0.544	9.62
15	148	0.400	9.50
20	145	0.315	9.30
Acetic acid			
1	185	2.890	11.86
5	175	1.369	11.23
10	160	0.834	10.26
15	153	0.598	9.87
20	140	0.430	8.98
Phenyl acetic acid			
1	187	4.64	12.01
5	170	2.84	10.91
10	165	2.06	10.58
15	155	1.56	9.99
20	150	1.25	9.62

Fig. 3a showed the relation between mass transfer coefficient and concentration of organic acids. In this, K decrease with increasing the concentration. Also, Fig. 3b showed that the velocity of gas discharge is decreased with increasing the concentration. If the limiting current in absence of organic compound (II) and in presence of organic compounds (I), the percentage of inhibition can be calculated from the equation.

$$\text{Inhibition (\%)} = \frac{(I_1 - I)}{I} \quad (6)$$

Fig. 4 show that the % inhibition caused by organic acids ranges from 20.7-44 % for cell using lead anode and 21-40 % in case of cell used copper anode. The order of decreasing limiting current is phenyl acetic, acetic and formic acid.

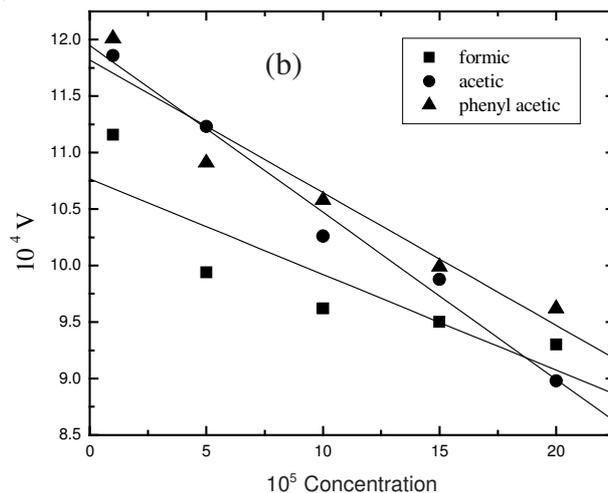
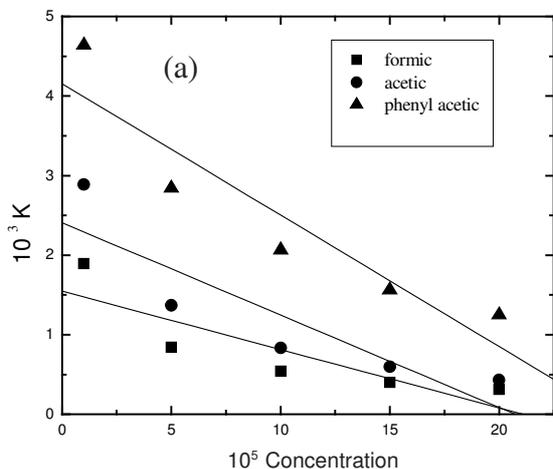


Fig. 3. The relation between mass transfer coefficient and concentration of organic acids at 25 °C

The data shows that the efficiency depend on the type of organic acids, its concentration and type of anodes. The above result is discussed as: (i) Organic acid may form thin film on the metal surface¹⁷ which leads to decrease the rate of electro deposition; also adsorption of organic acids on copper surface depends mainly on its structure. (ii) The decrease in the diffusion coefficient (D) of Cu²⁺ in solution containing acids which is due to the increase in the interfacial viscosity (η) in accordance to Stock-Einstein equation^{10,11}:

$$\eta \frac{D}{T} = \text{Constant}$$

where T is absolute temperature.

(iii) Organic acids not only decrease the limiting current through lowering surface tension but also thought other effect such as adsorption on cathode surface¹⁸.

(iv) Adsorption of organic compounds on the Cu cathode may lower the limiting current through current (i) increasing the interfacial viscosity owing to displacement of adsorbed H₂O molecules on the Cu-surface by organic molecules¹⁹ which is supported by adsorption isotherm.

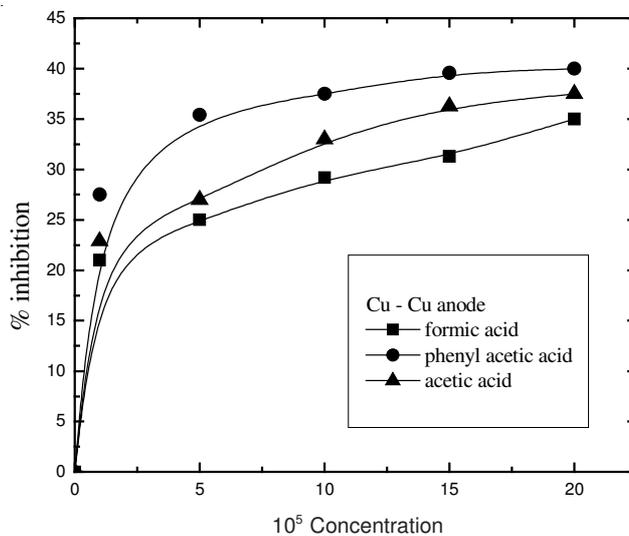


Fig. 4a. Effect of organic acids on the % inhibition of electro deposition at 25 °C in presence of copper anode

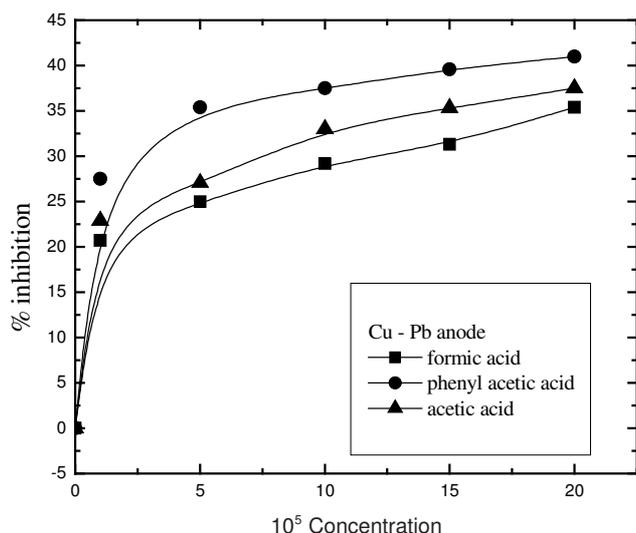


Fig. 4b. Effect of organic acids on the % inhibition of electro deposition at 25 °C in presence of lead anode

Suppose the decrease of the limiting current (Δi_ℓ) with respect to limiting current (i_ℓ) value in the absence of organic substances, the value of (Δi_ℓ) at a given concentration was determined and the degree of surface coverage was evaluated by the relation

$$\theta = \frac{(\Delta i_\ell)}{(\Delta i_\ell)_m} \quad (8)$$

where $(\Delta i_\ell)_m$ is the maximum decreases of limiting current corresponding to full surface coverage. It has been found that the degree of coverage depend on the concentration of organic substances.

Kinetic isotherm

$$\log\left(\frac{\theta}{1-\theta}\right) = \log k + y \log C \quad (9)$$

Plot of $\log\left(\frac{\theta}{1-\theta}\right)$ against $\log C$ give straight line with

slope y and intercept $\log k$.

Table-4 showed that the number of active sites occupied by a molecule of inhibitor ($1/y$) increases from formic acid to acetic acid *i.e.*, the number of adsorped water molecules on the surface of copper by organic substance increases in the following order formic acid, phenyl acetic acid and acetic acid.

Organic acids	y	$1/y$	k
Formic acid	2.0	0.5	0.012
Phenyl acetic acid	1	1	1.0332
Acetic acid	0.6	1.666	1.0232

The equilibrium constant k value is of particular interest because it considered as a measure of inhibition efficiency of the organic acids. Table-5 showed that formic acid is by far the most superior inhibitor of all the organic substance studied.

10^5 conc. (mol L ⁻¹)	Cu-Cu anode		Cu-Pb anode	
	I_ℓ	Inhibition (%)	I_ℓ	Inhibition (%)
Phenyl acetic acid				
0	240	0	250	0
1	186	21.0	186	20.7
5	180	35.0	180	25.0
10	170	29.17	170	29.16
15	165	31.3	165	31.3
20	155	35.0	155	35.4
Formic acid				
0	240	0	250	0
1	174	27.50	174	27.5
5	155	35.41	155	35.4
10	150	37.5	150	37.5
15	148	39.58	148	39.6
20	144	40.0	144	41
Acetic acid				
0	240	0	250	0
1	185	22.9	185	22.9
5	175	27.0	175	27.08
10	166	33.0	160	33.0
15	153	36.2	153	35.3
20	150	37.5	150	37.5

Application of Langmuir isotherm: For the studied inhibitor²⁰, it was found that the expermental data fits Langmuir, s adsorption isotherm, where is given by:

$$\frac{\theta}{1-\theta} = kc$$

where k is the equilibrium constant of the adsorption process. The data gave straight lines passing through the origin with a slope of k . the constant value k , is related to the standard free energy of adsorption $\Delta G^\circ_{\text{ads}}$. by

$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G^\circ_{\text{ads}}}{RT}\right) \quad (10)$$

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

In Table-6, the thermodynamic data obtained fro the adsorption isotherm are listed. From the calculated standard free energies of adsorption it was found that formic acid is the strongest inhibitors of the compounds. It also appears from Table-6 that the magnitude of K is the determining factor for the inhibition efficiency.

Organic acids	$K (M^{-1}) \times 10^3$	$\Delta G^\circ_{\text{ads}} (KJ mol^{-1})$
Formic acid	0.7142	26.431
Phenyl acetic acid	25.000	35.307
Acetic acid	6.666	32.000

Accordingly, the order of increase in the efficiency of studied compounds is given as formic acid > acetic acid > phenyl acetic acid.

Structural effect: In fact, adsorption at the electrode - solution interface is determined by three types of interaction: electrode - adsorbate, electrode - solvent, adsorbate - solvent

TABLE-7
EFFECT OF TEMPERATURE ON THE LIMITING CURRENT IN PRESENCE OF ACIDS

10 ⁻⁵ conc.	(a) Acetic acid							
	Cu-Cu anode				Pb-Cu anode			
	25 °C	30 °C	35 °C	40 °C	25 °C	30 °C	35 °C	40 °C
0	240	280	320	360	250	290	340	370
1	185	195	224	250	185	190	210	220
5	170	190	220	245	175	180	200	190
10	165	185	210	240	160	170	180	185
15	160	170	185	205	153	160	170	180
20	150	165	180	200	150	155	165	175
	(b) Formic acid							
0	240	280	320	360	250	290	340	370
1	174	185	200	220	174	185	195	205
5	155	180	190	205	155	165	175	185
10	150	160	170	190	150	160	170	180
15	148	155	165	180	148	155	165	175
20	144	150	160	170	144	150	160	170
	(c) Phenyl acetic							
0	240	280	320	360	250	290	340	370
1	186	195	200	210	186	195	205	220
5	180	190	195	200	180	190	200	210
10	170	175	180	190	175	185	195	200
15	165	170	175	185	165	170	185	190
20	155	160	170	180	155	160	175	180

interaction. The first two types depend strongly on the charge of the electrode surface. At the same time, adsorption on the electrode surface depends not only on the adsorption power of the compound and the character of the metal but also on the electrode potential and on the heterogeneity of the surface²².

Also, the inhibition efficiency of a given compound depends on the number of centers of adsorption and on the charge density of the inhibitor. All the studied compounds have the same center of adsorption which is carboxylic group.

Dissimilarity in the shape of adsorption curves of different inhibitors may be due to a variation in the mode of adsorption. The later depends on the chemical structure of each inhibitor and the charge density of carboxylic groups. Aliphatic acids as well as aromatic acids are adsorbed on copper surfaces through their carboxylic groups, leaving their chain to cover a part of surface. The inhibition action of those compounds depend on the number of function group taking part in the adsorption and their electron charge, molecular size, mode of interaction and complexing ability of additives²³. The order of inhibition efficiency for acids is: formic acid > acetic acid > phenyl acetic acid.

Effect of temperature: The rate of electro deposition was examined at different temperature (25, 30, 35 and 40 °C) for blank solution as well as in presence of acids Table-7 showed that the limiting current increases by increasing temperature. The reaction rate can be regarded as on Arrhenius process, the rate of which is given

$$I_l = A \exp\left(-\frac{E_a}{RT}\right) \quad (12)$$

where k = mass transfer coefficient, A = preexponential factor, E_a = activation energy, R = gas constant, T = absolute temperature.

The integrated form of Arrhenius equation is given as

$$2.303 \log I_l = -\frac{E_a}{RT} + \ln A \quad (13)$$

Thermodynamic treatment of the reaction: From the integrated form of Arrhenius equation

$$\ln (K) = \frac{-E}{RT} + \ln (A) \quad (14)$$

where R is the gas constant, E is the activation energy and A is the frequency factor. The values of E are given in Table-8.

The values for enthalpy of activation $\Delta H^\#$, entropy of activation $\Delta S^\#$ and free energy of activation $\Delta G^\#$, can be obtained by using the following equations:

$$\Delta H^\# = E - RT \quad (15)$$

$$\frac{\Delta S^\#}{R} = \ln A - \ln \frac{\alpha T e}{h} \quad (16)$$

$$\Delta G^\# = \Delta H^\# - T\Delta S^\# \quad (17)$$

It is noticed that all values of $\Delta S^\#$ are highly negative values, indicating a more ordered system and non-random distribution of the acids on the electrode. These values are found to be independent on the type of acids and the number of the substituted present in each acid.

In general, it is found that the values of E and $\Delta H^\#$ increase as the acid concentration increases as in Table-8, which may be attributed to that; the acids increase the local solution viscosity at the Cu surface with a consequent decrease in the diffusivity of Cu²⁺ ion and also, the acids molecules accelerate the natural convection flow arising from the density difference between the bulk solution and solution at electrode surface due to repulsion force between the Cu and the COOH group of the acid, leading to decrease in the rate of deposition.

TABLE-8a
THERMODYNAMIC PARAMETER IN PRESENCE OF ACIDS FOR Cu-Cu ANODE

10 ⁻⁵ conc.	E _a (KJ mol ⁻¹)	ΔH [#] (KJ mol ⁻¹)	ΔS [#] (J mol ⁻¹ K ⁻¹)	ΔG [#] (KJ mol ⁻¹)
Acetic acid				
0	20.98 ± 0.678	18.50 ± 0.677	-137 ± 2.2	59.14 ± 1.3
1	16.15 ± 2.01	13.67 ± 2.01	-155 ± 6.6	60.13 ± 3.98
5	19.30 ± 0.826	16.82 ± 0.826	-145 ± 2.7	60.30 ± 1.63
10	19.41 ± 0.674	16.93 ± 0.674	-145 ± 2.2	60.38 ± 1.33
15	12.83 ± 1.16	10.35 ± 1.16	-168 ± 3.8	60.49 ± 2.30
20	14.74 ± 0.494	12.26 ± 0.494	-162 ± 1.6	60.60 ± 0.976
Formic acid				
0	20.98 ± 0.677	18.50 ± 0.677	-137 ± 2.2	59.14 ± 1.3
1	12.12 ± 0.96	9.64 ± 0.96	-169.7 ± 3.1	60.25 ± 1.89
5	13.90 ± 2.01	11.42 ± 2.10	-164.0 ± 6.8	60.46 ± 4.15
10	11.93 ± 1.40	9.41 ± 1.40	-171 ± 4.6	60.62 ± 2.77
15	10.07 ± 1.11	7.59 ± 1.11	-178 ± 3.6	60.66 ± 2.19
20	8.72 ± 0.651	6.25 ± 0.651	-182 ± 2.1	60.72 ± 1.29
Phenyl acetic				
0	20.98 ± 0.677	18.50 ± 0.677	-137 ± 2.2	59.14 ± 1.3
1	6.05 ± 0.507	3.56 ± 0.507	-189 ± 1.6	60.06 ± 1.00
5	5.32 ± 0.716	2.85 ± 0.716	-192 ± 2.3	60.12 ± 1.41
10	5.61 ± 0.734	3.13 ± 0.734	-191 ± 2.40	60.30 ± 1.45
15	5.77 ± 0.753	3.29 ± 0.753	-191 ± 2.46	60.37 ± 1.49
20	7.89 ± 0.790	5.41 ± 0.790	-184 ± 2.5	60.54 ± 1.56

TABLE-8b
THERMODYNAMIC PARAMETER IN PRESENCE OF ACIDS FOR Cu-Pb ANODE

10 ⁻⁵ conc.	E _a (KJ mol ⁻¹)	ΔH [#] (KJ mol ⁻¹)	ΔS [#] (J mol ⁻¹ K ⁻¹)	ΔG [#] (KJ mol ⁻¹)
Acetic acid				
0	20.98 ± 0.678	18.50 ± 0.677	-137 ± 2.2	59.14 ± 1.3
1	9.62 ± 1.52	7.14 ± 1.51	-177 ± 4.9	60.11 ± 2.99
5	7.05 ± 0.714	4.56 ± 0.714	-186 ± 2.3	60.23 ± 1.41
10	7.67 ± 0.791	5.19 ± 0.791	-185.2 ± 2.5	60.42 ± 1.56
15	7.89 ± 0.790	5.41 ± 0.790	-184 ± 2.5	60.54 ± 1.56
20	8.13 ± 0.811	5.65 ± 0.811	-184.3 ± 2.6	60.62 ± 1.60
Formic acid				
0	20.98 ± 0.677	18.50 ± 0.677	-137 ± 2.2	59.14 ± 1.3
1	8.46 ± 0.02	5.98 ± 0.02	-181 ± 0.655	60.22 ± 0.369
5	9.16 ± 0.076	6.68 ± 0.076	-180 ± 0.025	60.51 ± 0.150
10	9.44 ± 0.083	6.96 ± 0.083	-179 ± 0.270	60.59 ± 0.165
15	8.77 ± 0.457	6.29 ± 0.457	-182 ± 1.50	60.64 ± 0.903
20	8.72 ± 0.651	6.24 ± 0.651	-182 ± 2.10	60.72 ± 1.29
Phenyl acetic				
0	20.98 ± 0.677	18.50 ± 0.677	-137 ± 2.2	59.14 ± 1.3
1	8.58 ± 0.690	6.11 ± 0.690	-181 ± 2.2	60.08 ± 1.36
5	7.97 ± 0.047	5.50 ± 0.047	-183 ± 0.154	60.14 ± 0.093
10	7.05 ± 0.721	4.57 ± 0.721	-186 ± 2.36	60.20 ± 1.42
15	7.88 ± 1.23	5.40 ± 1.23	-184 ± 4.0	60.37 ± 2.44
20	8.35 ± 1.31	5.88 ± 1.31	-183 ± 4.3	60.53 ± 2.59

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