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SPECTROSCOPY IN CORROSION STUDIES OF COPPER

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دراسة تآكل النحاس بالقياسات الطيفية

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رأفت الخطيب

أستخدمت القياسات الطيفية في دراسة تآكل النحاس في المحاليل المائية المحتوية على أربع من منقصات الاستقطاب هي : ثاني كرومات البوتاسيوم ، وفوق كبريتات البوتاسيوم ، وكبريتات الحديديك والأمنيوم ، وثلاثي كلورو حمض الخليك . وقد أستخدمت خلية من السيليكا لدراسة التآكل وفي نفس الوقت كخلية طيفية ، وقد تبين أن تفاعل النحاس مع هذه المركبات من الرتبة الأولى ذو تحكم انتشاري فيما عدا ثلاثي كلورو حمض الخليك فله تحكم كيناتيكي .

وقد أستخدمت طريقة القياسات الطيفية لدراسة تأثير بعض الأحماض الأمينية وبعض الأمينات على معدلات تآكل النحاس في محاليل منقصات الاستقطاب .

وقد أتضح من هذه الدراسة أن كلا من الأحماض الأمينية والأمينات تسلك كمثبطات وتم حساب معامل التثبيط لها جميعاً ، ووجد أنه يعتمد على عدد مجموعات الأمين في المركب . فكلما ازداد عدد هذه المجموعات كلما كان المركب عاملا مثبطاً أقوى .

وتم إستخدام منحنيات الاستقطاب من النوع حركي الجهد لتوضيح دور منقصات الاستقطاب في كيناتيكا التآكل ، وأتضح أن الدور الرئيسي الذي تلعبه هذه المركبات هو إنقاص إستقطاب الكاثود بتفاعل شامل من الرتبة الأولى .

وفي الخلاصة يمكن القول أن القياسات الطيفية تزودنا بطريقة دقيقة وفعالة وسريعة لدراسة عمليات التآكل وبالذات في الفلزات التي لها كاتيونات ملونة .

Key Words: Activation energy, Amines, Amino acids, Corrosion of copper, Depolarizer, First order, Inhibition, Kinetics of copper dissolution, Potentiodynamic, Spectrophotometric measurements.

ABSTRACT

Spectrophotometric measurements were used to study corrosion of copper in aqueous solutions containing the four following depolarizers: $K_2Cr_2O_7$, $K_2S_2O_8$, $Fe(NH_4)(SO_4)_2$ and CCl_3COOH. A silica cell was used for the corrosion studies as well as spectrophotometric measurements. It was found that the reaction of copper with these compounds is first order and diffusionally-controlled except in the case of CCl_3COOH which proved to be kinetically controlled. The spectrophotometric method was utilized to study the effect of some amino acids and some amines on the corrosion rate of copper in the solutions of depolarizers. It was found that both amino acids and amines act as inhibitors. The inhibition coefficient of amines increased with the number of amino groups in the compound. Potentiodynamic polarization technique was used to clarify the role of depolarizers in the kinetics of the corrosion process. It appears that the main rôle of these compounds is to depolarize the cathodic first order overall reaction. The spectrophotometric method proved to be precise, effective and fast to study corrosion processes, in particular those with coloured metal cations.

INTRODUCTION

The kinetics of copper dissolution in 0.50 M H_2SO_4 containing different inorganic depolarizers: $KMnO_4$, $K_2Cr_2O_7$, $K_2S_2O_8$, $Fe(NH_4)(SO_4)_2$, $Ce(SO_4)_2$ and V_2O_5 at 25°C was studied by El-Cheikh et al [1]. A first order was proved for all depolarizers. Considerable work has been done on the effect of oxidizing agents on corrosion rates of copper in acid solution. The dissolution of cadmium, tin, lead and copper in acid solutions containing organic depolarizers was investigated[2] and it was reported that copper dissolution in excess acid solutions of various types with *p*-benzoquinone as depolarizer is a first order reaction. The rate constant was found to be neither high enough to be entirely diffusionally controlled nor low enough to be entirely chemically controlled. Ammar and Riad[3] reported that the corrosion rate of copper in HCl solution increased with dichromate concentration up to a maximum. Smolyaninov and Khitrov[4] found that the corrosion rate of copper in HCl or H_2SO_4 solution depends on the concentration of $K_2Cr_2O_7$. The change in energy of activation and the temperature coefficient of corrosion indicated that the reaction rate was determined both by diffusion and chemical effects. A linear relation was found between log I, the anodic current, and E, the polarization potential during the anodic dissolution of copper in the presence of H_2O_2, $Cr_2O_7^{2-}$, Fe^{3+}, MnO_4^- and NO_3^-[5]. This behaviour was explained as nondiffusional control of the dissolution process at low currents.

EXPERIMENTAL

The dissolution process of copper metal was followed in a 1.0 cm silica cell in the thermostated cell holder of a CECIL recording spectrophotometer (model 599). Copper metal was in the form of two spirals connected to each other and put vertically in the silica cell (the corrosion and the spectrophotometric cell at the same time) so that the straight part connecting the two spirals do not shield the path way of the incident and transmitted light through the width of the silica cell. The dissolution of copper was monitored at λ_{max} for each component in all cases. The volume of solution in the cell was 3.0 cm^3.

In the present work we applied the first order integrated kinetic equation:

$$kt = \ln\left(\frac{a}{a-x}\right) \quad \text{...(1)}$$

values of a, x and (a-x) were taken from the spectrophotometric measurements of the decay of depolarizer's concentration, Cu^{2+} ions generation and Cu complex formation separately and k was calculated for each of these data.

Four examples were chosen to illustrate the application of spectrophotometric measurements and calculations in studying copper dissolution in solutions of depolarizers.

1. Copper in $K_2Cr_2O_7$ acidified solution:
   $3\ Cu + K_2Cr_2O_7 + 7H_2SO_4$ Æ $3\ CuSO_4 + Cr_2(SO_4)_3 + K_2SO_4 + 7\ H_2O$.........................(2)
   (Absorbance recorded at 440, 600 and 790 nm to follow the concentration of $Cr_2O_7^{2-}$, Cr^{3+} and Cu^{2+} respectively).
2. Copper in $K_2S_2O_8$ without acid:
   $Cu + K_2S_2O_8$ Æ $CuSO_4 + K_2SO_4$..................(3)
   (Absorbance recorded at 790 nm to follow the concentration of Cu^{2+}).
3. Copper in acidified $Fe(NH_4)(SO_4)_2$:
   $Cu + 2Fe(NH_4)(SO_4)_2$: Æ $CuSO_4 + 2FeSO_4 + (NH_4)_2SO_4$ ....(4)
   (Absorbance recorded at 450 and 790 nm to follow the concentrations of Fe^{3+} and Cu^{2+}).
4. Copper in CCl_3 COOH without acid:
   $Cu + 2CCl_3COOH$ Æ $(CCl_3COO)_2Cu + 2HCl$ or $2CHCl_2COOH + CuCl_2$ ....(5)
   (Absorbance recorded at 790 nm to follow the concentrations of Cu^{2+}).

RESULTS AND DISCUSSION

The dependence of absorbance A on wavelength λ at different time intervals of interaction between Cu metal and $K_2Cr_2O_7$ acidified solution is illustrated in Fig. 1. From the values of absorbances at different values of λ_{max}, a and (a-x) are computed.

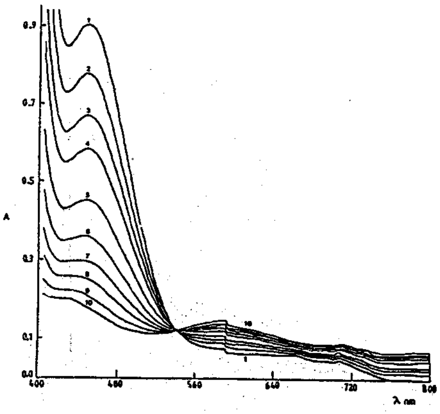

Fig. 1 Absorbance A vs. wavelength λ for the dissolution of copper in $K_2Cr_2O_7$ acidified solution at different time intervals and 25.0° C. Numbers on the curve correspond to time t:

1-0.0 min.	6-21.0 min.
2-3.0 min.	7-27.0 min.
3-6.0 min.	8-33.0 min.
4-9.0 min.	9-42.0 min.
5-15.0 min.	10-51.0 min.

The plot of ln a/(a-x) Vs t was correlated using the linear regression technique (least square curve fitting) [6 & 7]. Thus K was calculated from the regression coefficient, and the correlation coefficient (r) was also reported to illustrate extent of the validity of the first order kinetic equation. Data are shown in Table 1 and plots of ln a/(a-x) Vs t in Figure 2.

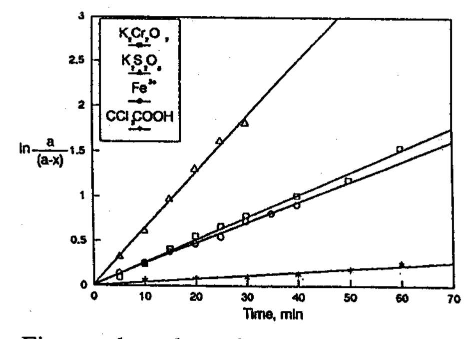

Fig.2. First order plot of ln a/(a-x) vs t for copper dissolution in different depolarizers at 25.0° C.

Table 1

The effect of temperature and type of depolarizer on, K of copper in $K_2Cr_2O_7$ using values of absorbance at 440 nm for $K_2Cr_2O_7$, 790 nm for $K_2S_2O_8$, Fe^{3+} and CCl_3COOH. All experiment data are correlated using linear regression (least square curve fitting)

Dep.	T°C	20.0	25.0	30.0	35.0	40.0	45.0	50.0	Ea KJ mol^{-1}	r
$K_2Cr_2O_7$	K	0.0333	0.0482	0.0518	0.0523	0.0559	0.0624	0.0708	17.6	0.94
$K_2S_2O_8$	K	0.0314	0.0421	0.0459	0.0514	0.0693	0.0708	0.0774	23.5	0.98
Fe^{3+}	K	-----	0.0301	0.0318	0.0379	0.0452	------	------	20.6	0.97
	T°C	45.0	50.0	55.0	60.0	65.0	70.0	75.0		
CCl_3COOH	K x 10^{-3}	1.59	1.74	3.39	4.23	6.93	9.23	14.4	75.4	0.99

r: The correlation coefficient Ea: The activation energy

The fact that r, the correlation coefficient is nearly equal to unity (1.0 in two significant figures) confirms the validity of the first order kinetics with respect to each of the depolarizers. The overall kinetic equation expressing the rate of this process can thus be written as:

$$n_{corr.} = k_1[dep] \qquad (6)$$

where $n_{corr.}$ is the overall rate, k_1 is the specific rate constant and [dep] is the depolarizers concentration.

The surface area of corroding copper metal is included in the value of k_1. Solutions were not deaerated as the concentration of dissolved atmospheric oxygen is insignificant compared to that of the studied depolarizer[1].

The rate of the dissolution of copper in all the studied solutions of the depolarizers was found to increase with increasing temperature and copper surface area.

Careful examination of data in Table 1 reveals that the values of k_1 for copper dissolution in CCl_3COOH solution are lower by almost an order of magnitude than those found for copper in solutions of other depolarizers. This is especially clear at low temperatures. The effect of temperature is more distinct in the case of CCl_3COOH than for the other three depolarizers leading to significantly higher values of Ea, the activation energy (75 compared to 20 KJ mol^{-1}) of copper dissolution in trichloroacetic acid. Generally values of Ea (Table 1) point towards clear diffusion control of the corrosion process in $K_2Cr_2O_7$, $K_2S_2O_8$ and $Fe(NH_4)(SO_4)_2$, while CCl_3COOH dissolves copper metal via a kinetically controlled process.

Data reflecting the effect of amino acids on the rate of copper dissolution through influencing the values of k_1- the first order rate constant are reported in Table 2. From these results it is so clear that k_1 of copper dissolution decreased to a certain extent upon introducing and increasing the concentration of the amino acid. The net effect of the amino acid is thus an inhibitive one.

Table 2

The effect of amino acids concentration on the values of K (min^{-1}) and $h_{corr.}$ for the dissolution of Cu spiral (20.0 x 0.05 x 3.14 x 2 x 2 cm^2) in solution of depolarizers using spectrophotometric method

Depolarizer				$S_2O_8^{2-}$	Fe^{3+}	CCl_3COOH
Ligand	Conc. of lig. M	T° C	25.0° C	25.0° C	25.0° C	45.0° C
	0.000	K	0.0482	0.0421	0.0301	0.00159
	0.010	K	0.0411	0.0240	0.0274	0.00136
		$h_{corr.}$	14.7	43.0	8.97	14.5
Glycine	0.050	K	0.0296	0.0214	0.0246	0.00124
		$h_{corr.}$	38.6	49.2	18.3	22.0
	0.100	K	0.0198	0.0209	0.0234	0.00116
		$h_{corr.}$	58.9	50.4	22.3	27.0
	0.000	K	0.0482	0.0421	0.0301	0.00159
	0.010	K	0.0475	0.0149	0.0237	0.00131
		$h_{corr.}$	1.45	64.6	21.3	17.6
Leucine	0.050	K	0.0457	0.0117	0.0230	0.00122
		$h_{corr.}$	5.19	72.2	23.6	23.3
	0.100	K	0.0450	0.0104	0.0194	0.00110
		$h_{corr.}$	6.64	75.3	35.6	30.8
	0.000	K	0.0482	0.0421	0.0301	0.00159
	0.010	K	0.0239	0.0225	0.0107	0.00121
		$h_{corr.}$	50.4	46.6	50.4	23.9
b-Alanine	0.050	K	0.0220	0.0208	0.00766	0.00115
		$h_{corr.}$	54.4	50.6	74.6	27.7
	0.100	K	0.00945	0.0182	0.00428	0.000932
		$h_{corr.}$	80.4	56.8	85.8	41.4

The inhibitive efficiency $h_{corr.}$, is defined as:

$$h_{corr.} = \frac{(k-k')}{k} \times 100 \quad \text{.....................................(7)}$$

where k is the specific rate at zero ligand concentration and k' is the specific rate at particular ligand concentration. Values of Ea confirmed the diffusion control of the corrosion process in solutions of $K_2Cr_2O_7$, $K_2S_2O_8$ and $Fe(NH_4)(SO_4)_2$ only containing amino acids. On the other hand, corrosion of copper in CCl_3COOH solution containing amino acids is definitely nondifussionally controlled.

The effect of some amines, having different numbers of $-NH_2$ groups on the corrosion behaviour of copper in solutions of different depolarizers was studied. The results are represented in Table 3 where k_1 and $h_{corr.}$ are listed. It was found that trien (triethylenetetramine) affects k_1 and h_{corr}. more than dien (diethylenetriamine) and the latter more than en (ethylenediamine). This trend is most probably due to the increase in the number of adsorption and chelating centres per molecule (N-atoms). Data of spectrophotometric study of the corrosion system thus reveal that the amines behave as corrosion inhibitors bringing about a distinct lowering in the rate of corrosion as reflected in the rate by which the absorbance A changes at different λ_{max}.

Table 3

The effect of amines concentration on the values of K (min^{-1}) and $h_{corr.}$ for the dissolution of Cu spiral ($20.0 \times 0.05 \times 3.14 \times 2\ cm^2$) in solution of different depolarizers using spectrophotometric method.

	Depolariser		$Cr_2O_7^{2-}$	$S_2O_8^{2-}$	.
Ligand	Conc. of Lig. M	T° C	25.0°C	25.0°C	45.0°C
	0.000	K	0.0482	0.0421	0.00159
	0.010	K	0.0450	0.0403	0.00134
		$h_{corr.}$	6.639	4.28	15.7
en	0.050	K	0.0440	0.0395	0.00125
		$h_{corr.}$	8.71	6.18	21.4
	0.100	K	0.0423	0.0379	0.00116
		$h_{corr.}$	12.2	9.98	27.0
	0.000	K	0.0482	0.0421	0.00159
	0.010	K	0.0460	0.0302	0.00115
		$h_{corr.}$	4.56	11.9	27.7
Dien	0.050	K	0.0400	0.0205	0.00104
		$h_{corr.}$	17.0	51.3	34.6
	0.100	K	0.0143	0.0101	0.000960
		$h_{corr.}$	70.3	76.0	39.6
	0.000	K	0.0482	0.0421	0.00159
	0.010	K	0.0434	0.0160	0.00109
		$h_{corr.}$	9.96	62.0	31.4
Trien	0.050	K	0.0321	0.00936	0.000866
		$h_{corr.}$	33.4	77.8	45.5
	0.100	K	0.00201	0.00298	0.000364
		$h_{corr.}$	95.8	92.9	77.1

It is interesting to mention that $h_{corr.}$ caused by amines is somewhat greater than $h_{corr.}$ caused by amino acids in the same solution. This may be attributed to the nature of amino acids and their lower adsorbability.

Values of Ea computed from the effect of temperature on k_1 show pure diffusion control of the corrosion process of copper in presence of $K_2Cr_2O_7$ and $K_2S_2O_8$ solutions containing the amines (Ea < 30 KJ mol^{-1}). On the other hand, Ea of copper interaction with solution of CCl_3COOH containing the amines was found to be much higher than 40 KJ mol^{-1} which points clearly to a pure kinetically controlled corrosion process.

It is interesting to note that we studied the dissolution process of copper metal in the solution of studied depolarizers using the potentiodynamic polarization technique. The diffusion control of the process was proved. The order of the overall cathodic process calculated from ln C- ln I relation was found to be around unity (Table 4). This confirms the principal role of depolarizers in the dissolution of copper.

In conclusion, we found it convenient and accurate to use spectrophotometric measurements in studying corrosion processes.

Table 4

The order n of the overall cathodic reduction of the depolarizer at a copper cathode and the effect of the depolarizer's concentration (C) on the cathodic diffusion current (Id) at different potentials and 20.0°C.

$K_2Cr_2O_7/H_2SO_4$, $K_2S_2O_8/H_2SO_4$, $K_2S_2O_8$,
$Fe(NH_4)(SO)_4)2/H_2SO_4$, CCl_3COOH/HCl, CCl_3COOH

(All data are correlated and the correlation coefficient [r] is reported).

E(mv) vs SCE	conc.. of dep / log c =	$1.0x10^{-3}$ / -3.00	$5.0x10^{-3}$ / -2.30	$1.0x10^{-2}$ / -2.00	$5.0x10^{-2}$ / -1.30	n	r
200	log I	0.699	1.78	1.95	2.70	1.12	0.96
150	($K_2Cr_2O_7$ +	0.778	1.78	2.00	2.60	1.02	0.95
100	H_2SO_4)	0.845	2.00	2.04	2.60	1.01	0.96
145	log I	0.040	1.08	1.78	---	1.30	0.93
115	($K_2S_2O_8$ +	0.230	1.20	2.04	---	1.70	0.98
80	H_2SO_4)	0.340	1.30	2.23	---	1.80	0.98
150	Log I	0.699	1.30	1.84	---	1.09	0.98
100	($K_2S_2O_8$)	1.18	1.39	2.00	---	0.73	0.88
50		1.20	1.54	2.17	---	0.88	0.92
150	log I	0.301	1.48	1.74	2.76	1.22	0.99
100	(Fe^{3+} +	1.04	1.52	1.88	2.81	1.05	0.98
50	H_2SO_4)	1.18	1.58	1.98	3.18	1.18	0.96
65	log I	1.26	3.08	3.40	4.20	1.43	0.97
45	(CCl_3COOH +	2.45	3.30	3.70	4.50	1.03	1.0
0	HCl)	2.70	3.50	3.80	4.60	1.12	1.0
180	log I	1.80	1.82	2.30	2.80	0.93	0.98
150	(CCl_3COOH)	2.10	2.40	2.80	3.60	0.90	0.97
100		2.30	2.78	3.00	3.85	0.91	0.99

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