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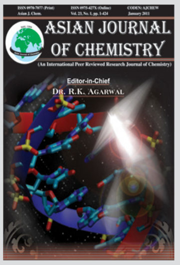

Electrochemical Reduction and Oxidation of Copper, Lead Complex and Metal-Free Phthalocyanine

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In this study, polarographic reduction of crown-ether substituted metal-free (H_2Pc), copper(II) (CuPc) and lead(II) (PbPc) phthalocyanine complexes were examined in aqueous medium on a dropping mercury electrode. All measurements were carried out at 25 ± 1 ºC. A saturated calomel electrode was employed as the reference electrode. Sodium nitrate, potassium nitrate and tetrabutylammonium chloride were used as the supporting electrolytes. Solutions were buffered with $CH_3COONa{\cdot}3H_2O$, K_2HPO_4 and H_3BO_3. Polarograms were recorded at different pH values. In order to find "out whether the electrochemical reactions are diffusion controlled or not, polarograms were also recorded as a function of the mercury column's height. While two reduction waves were observed with H_2Pc, CuPc gave three reduction waves at all pH values within the range of 2-12. PbPc showed one, two or three reduction waves depending on the pH values. From the logarithmic analysis of the current-voltage curves the kinetic parameters (αn and $k^0_{f,h}$) were calculated. The results showed that reduction processes of all complexes on dropping mercury electrode in aqueous medium were diffusion controlled and irreversible. Generally, the reduction half-wave potentials of the complexes were found to shift to more negative values with increasing pH. It was also found that the heterogeneous standard reduction rate constants ($k^0_{f,h}$) of the complexes decrease with increasing pH. These findings were attributed to the involvement of protons in electrochemical reactions. Since it is not possible to determine the oxidation of complexes by polarography, voltamograms by cyclic voltammetry at various solvents at the positive potential side against saturated calomel electrode were recorded, but no oxidation peak could be observed.

Key Words: Phthalocyanine, Lead, Copper, Electrochemical.

INTRODUCTION

In this study, polarographic reduction of crown-ether substituted metal-free (H_2Pc), lead(II) (PbPc) and copper(II) (CuPc) phthalocyanine complexes were examined in different solvent mediums at 25 ± 1 ºC. A dropping mercury electrode was used as the indicator electrode, a saturated calomel electrode was employed as the reference electrode. Polarograms were recorded in aqueous medium and at different pH values. Potassium nitrate was used as the supporting electrode.

The aim of present study is to examine polarographic behviour of lead and copper complexes of phthalocyanine on a dropping mercury electrode. The goal is to calculate the kinetic parameters in each solvent medium and explain mechanisms of electrochemical reactions by using these kinetic parameters after performing logarithmic analysis of the recorded current-voltage curves.

Phthalocyanines: Phthalocyanines have been known for a long time and do solid built substances constitute an important dyestuff group. Their colour range changes from blue to green. They were discovered accidentally as a by-product during the synthesis of *o*-cyanobenzamide with phthalimide and acetic anhydride by Braun and Tcherniac[1]. As a copper complex was synthesized during the synthesis of 1,2-dicyanobenzene from copper(I) cyanide and *o*-dibromo-benzene by Diesbach and Vonderweid[2].

The first phthalocyanine dye, which was patented and released to the market in a large amount in 1935, is a phthalocyanine polysulfonate. After 1935, it was manufactured commercially[3,4].

There are number of articles about the investigation of synthesis and properties of several metal-free and metal phthalocyanines. Nowadays, researchers intensely study phthalocyanines since they have a wide application field[5-10]. A part from being a dyestuff, phthalocyanines have the following important properties: (1) They possess chemical and thermal stability. They don't decompose till 400-500 ºC. They are resistant to strong acids and bases. (2) Extremely pure substances are obtained since phthalocyanines are sublimed without decomposition. (3) 18π-electron system in the macrocylic ring causes intense absorptions in the visible region (molar absorption coefficient $\varepsilon = 2 \times 10^5$).

Synthesis of phthalocyanine complexes: Crown-ether substituted metal-free and metal phthalocyanine complexes (Fig. 1) were synthesized by Bekaroglu and co-workers[11].

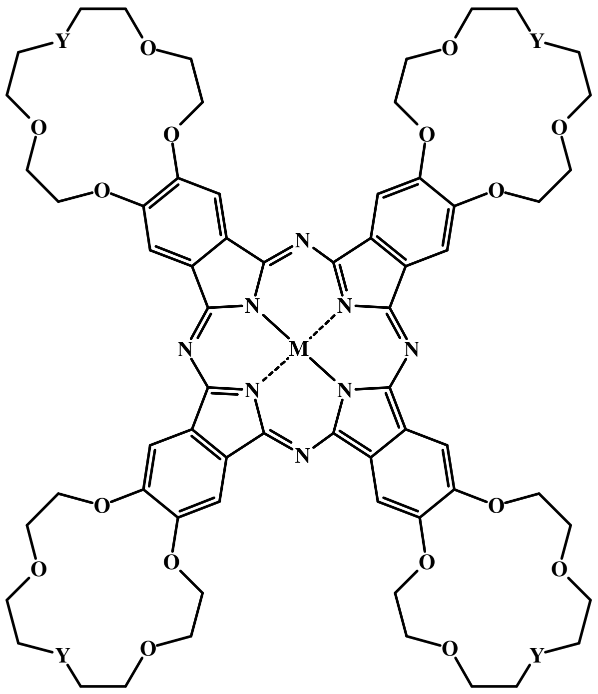

Fig. 1. Synthesis of quaternized, water soluble, crown-ether substituted phthalocyanine metal complexes

EXPERIMENTAL

In this study, current-voltage curves were recorded using linear current polarography (LCP) and alternating current voltammetry methods. The instruments are: Princeton applied research (PAR) Model 273 potentiostat/galvanostat, Metrohm E-261 Model Polarecord: Polarecord consists of two sections; (a) electrode and inert gas system, (b) polarograph and printer system.

Electrodes: The working electrode is a dropping mercury electrode and a saturated calomel electrode was used as the reference electrode. A platinum electrode was used as the working electrode in the experiments performed by applying alternating current voltammetry method.

Electrolysis cell: A coated electrolysis cell was used to study at constant temperature. pH-meter: WTW pH-91 model pH-meter was employed for pH measurements.

Thermostat: Haake brand, ESE type thermostat was connected to the electrolysis cell in order to study at constant temperature.

Sensitive balance: An electronical balance, Sartorius analytical model, was employed for weighing measurements.

Crown-ether substituted metal-free and metal phthalocyanine complexes were synthesized by Bekaroglu *et al.*[11]. $CH_3COONa\cdot3H_2O$ (0.1 M), K_2HPO_4 (0.1 M) and H_3BO_3 (0.1 M) were used for buffering the solutions, HCl and NaOH (solid) were employed to adjust pH, KNO_3 as the supporting electrolyte, distilled water as a solvent and H_2SO_4, KOH and pyrogallol were used to purify nitrogen gas. All the chemicals were analytically pure. Electrochemically pure mercury was obtained by using an electrochemical method in order to purify the mercury used for the working electrode. In addition to KNO_3, $NaNO_3$ and tetrabutyl ammonium chloride were employed as the supporting electrolyte.

Preparations for recording polarograms: After preparing the solution of which polarogram will be recorded inside a clean electrolysis cell, the thermostat was operated at 25 ºC. pH of the solution inside the electrolysis cell was adjusted by adding 1 M HCl solution and solid NaOH. Electrolysis cell was fixed after tapping mercury column and controlling the flow of mercury drops. Nitrogen gas was diffused for 20 min to remove oxygen dissolved in the solution; after the nitrogen gas was passed over a flask containing concentrated H_2SO_4, KOH and pyrogallol, respectively, it was added to the solution.

Determination of the half-wave potentials and $E_{3/4}$, $E_{1/4}$ values of recorded polarograms: From the polarograms, the diffusion current was calculated by subtracting the residual current and the limiting current. E-I values were determined by using these polarograms. The average current values were used for this calculation. $\frac{I_d - I}{I}$ and $\log\frac{I_d - I}{I}$ values were calculated by using I_d and I numerical values (Table-1).

$E_{1/2}$ values were calculated by using

$$E = E_{1/2} + \frac{RT}{nF}\ln\frac{I_d - I}{I}$$

and

$$E_{d.e.} = E_{1/2} + \frac{0.05915}{\alpha n}\log\frac{I_d - I}{I}$$

equations and calculating $\log\frac{I_d - I}{I}$ and E numbers in Casio-3600fx model calculator by using existing regression analysis program. The quarter-wave potential $E_{1/4}$ and the three-quarter-wave potential $E_{3/4}$ were directly calculated by studying on the polarograms recorded on the millimetric paper.

H_2Pc: The reduction of H_2Pc on a dropping mercury electrode in aqueous medium was examined. 0.1 M $CH_3COONa\cdot3H_2O$, K_2HPO_4 and H_3BO_3 were used to buffer the solutions of which polarograms were recorded.

Polarograms recorded at constant pH and different mercury column heights: To determine whether the reduction of 5×10^{-4} M H_2Pc complex on the dropping mercury electrode was diffusion controlled or not, the diffusion currents of polarograms recorded at appropriate pH and different mercury column heights were shown in Table-1. The diagrams of polarograms recorded at h = 24.5 and 43.5 cm and diffusion currents charted on Table-1 *versus* $h^{1/2}$ were exemplified[12].

TABLE-1
DIFFUSION CURRENTS OF POLAROGRAMS RECORDED AT DIFFERENT MERCURY COLUMN HEIGHTS WITH H_2Pc

h (cm)	$h^{1/2}$ ($cm^{1/2}$)	I_d (μA) 1. Peak	I_d (μA) 2. Peak	
24.5	4.95	0.14	0.27	5×10^{-4} M H_2Pc
34.5	5.87	0.17	0.36	0.1 M KNO_3
39.5	6.28	0.18	0.38	Solvent: water
43.5	6.59	0.19	0.46	pH = 8.25

Polarograms recorded at different pH values: The polarograms of buffered 5 × 10^{-4} M H_2Pc solution was drawn at different pH values in the range of pH = 1.87-12.14. H_2Pc displayed two reductions peaks on the plotted polarograms. After calculating the diffusion currents and E-I values of these polarograms, the tables of $E_{1/2}$ and $E_{1/4}$-$E_{3/4}$ values for each polarogram. The polarograms at these pH values were exemplified[12]. The polarograms recorded at pH = 11.09 were shown on Fig. 2. $E_{1/2}$ and $E_{1/4}$-$E_{3/4}$ values of polarograms recorded at different pH values and kinetic parameters were shown in Table-4.

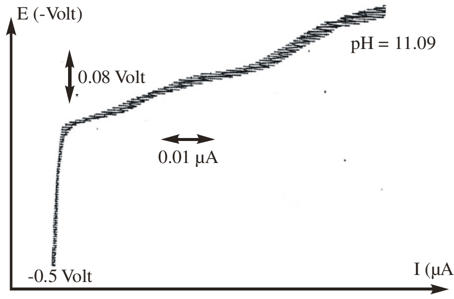

Fig. 2. Polarogram of H_2Pc at pH = 11.09, solvent:water the sensitivity of current and voltage axises was specified on the graphic

PbPc: The reduction of PbPc complex on a dropping mercury electrode in aqueous medium was examined. 0.1 M $CH_3COONa{\cdot}3H_2O$, K_2HPO_4 and H_3BO_3 were used to buffer the solutions of which polarograms were recorded.

Polarograms recorded at constant pH and different mercury column heights: To determine whether the reduction of 5 × 10^{-4} M PbPc complex on the dropping mercury electrode was diffusion controlled or not, the diffusion currents of polarograms recorded at appropriate pH and different mercury column heights were shown in Table-2. The diagrams of polarograms recorded at h = 24.5 and 43.5 cm and diffusion currents charted on Table-2 *versus* $h^{1/2}$ were exemplified[12].

TABLE-2
DIFFUSION CURRENTS OF POLAROGRAMS RECORDED AT DIFFERENT MERCURY COLUMN HEIGHTS WITH PbPc

h (cm)	$h^{1/2}$ ($cm^{1/2}$)	I_d (μA) 1. Peak	I_d (μA) 2. Peak	
24.5	4.95	0.14	0.27	5 × 10^{-4} M H_2Pc
34.5	5.87	0.17	0.36	0.1 M KNO_3
39.5	6.28	0.18	0.38	Solvent: water
43.5	6.59	0.19	0.46	pH = 8.25

Polarograms recorded at different pH values: The polarograms of buffered 5 × 10^{-4} M PbPc solution were taken at different pH's in the range of pH = 2.01-10.75. PbPc gave three reduction peaks on the polarograms, the second and third peak was observed at high pH values. After determining the diffusion currents and E-I values of these polarograms, $E_{1/2}$ and $E_{1/4}$-$E_{3/4}$ values were calculated for each polarogram. The tables of E-I values of the polarograms at pH's 2.01, 3.14, 6.99, 8.92 and 10.75; the polarograms recorded at these pH values were given as an example[12]. The polarograms taken at pH = 10.75 are seen in Fig. 3. $E_{1/2}$ and $E_{1/4}$-$E_{3/4}$ values of the polarograms plotted at different pH's and the kinetic parameters were shown on Table-5.

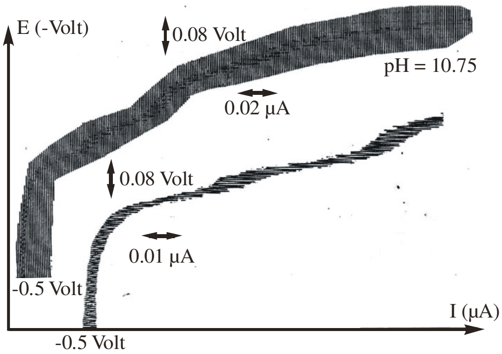

Fig. 3. Polarogram of PbPc at pH = 10.75, solvent:water the sensitivity of current and voltage axises was specified on the graphic

CuPc: The reduction of CuPc complex on a dropping mercury electrode in aqueous medium was examined. 0.1 M $CH_3COONa{\cdot}3H_2O$, K_2HPO_4 and H_3BO_3 were used to buffer the solutions of which polarograms were recorded.

Polarograms recorded at constant pH and different mercury column heights: To determine whether the reduction of 5 × 10^{-4} M CuPc complex on the dropping mercury electrode was diffusion controlled or not, the diffusion currents of polarograms recorded at appropriate pH and different mercury reservoir heights were shown in Table-3. The polarograms recorded at h = 24.5 and 43.5 cm and diffusion currents charted on Table-3 *versus* $h^{1/2}$ were exemplified[12].

TABLE-3
DIFFUSION CURRENTS OF POLAROGRAMS RECORDED AT DIFFERENT MERCURY COLUMN HEIGHTS WITH CuPc

h (cm)	$H^{1/2}$ ($cm^{1/2}$)	Id (μA) 1. Peak	Id (μA) 2. Peak	Id (μA) 3. Peak	
24.5	4.95	0.46	0.35	1.30	5 × 10^{-4} M CuPc
34.5	5.87	0.66	0.35	1.80	0.1 M KNO_3
39.5	6.28	0.74	0.42	1.85	Solvent: water
43.5	6.59	0.80	0.35	2.50	pH = 7.02

Polarograms recorded at different pH values: The polarograms of buffered 5 × 10^{-4} M CuPc solution were taken at different pH's in the range of pH = 2.06-11.95. CuPc gave three reduction peaks on the polarograms. After determining the diffusion currents and E-I values of these polarograms, $E_{1/2}$ and $E_{1/4}$-$E_{3/4}$ values were calculated for each polarogram. The tables of E-I values of the polarograms at pH's 3.00, 4.05, 7.53 and 8.97; the polarograms recorded at these pH values were given as an example[12]. The polarograms taken at pH = 7.53 are presented in Fig. 4. $E_{1/2}$ and $E_{1/4}$-$E_{3/4}$ values of the polarograms plotted at different pH's and the kinetic parameters were shown in Table-4.

Experiments with alternating current voltammetry method: Different voltammograms of the complexes in aqueous medium and by using platinum as the working electrode were recorded in the positive potential region with respect to the saturated calomel electrode, but no oxidation peak was observed. Alternating current voltammetry studies were performed in different solvent mediums, except water in order to expand the positive potential working region at which an oxidation peak can be observed, however, any oxidation peak of the complexes couldn't be observed.

TABLE-4
KINETIC PARAMETERS OF H_2Pc REDUCTION IN AQUEOUS MEDIUM

pH	I_d (μA)	$E_{1/2}$ (-V)	D (cm^2/s)	$E_{1/4}$-$E_{3/4}$ (V)	αn	$K^0_{f,h}$ (cm/s)
			First Peak			
1.87	0.61	0.491	8.42×10^{-7}	0.075	0.69	4.38×10^{-7}
2.03	0.85	0.511	1.64×10^{-5}	0.074	0.70	3.21×10^{-7}
3.02	0.97	0.532	2.13×10^{-6}	0.072	0.72	1.65×10^{-7}
4.18	0.92	0.652	1.92×10^{-6}	0.071	0.73	4.61×10^{-9}
5.04	0.90	0.697	1.83×10^{-6}	0.069	0.74	1.03×10^{-9}
6.28	0.44	0.707	1.09×10^{-7}	0.044	1.18	6.58×10^{-14}
7.09	0.30	0.778	5.09×10^{-8}	0.043	1.20	1.13×10^{-15}
8.25	0.33	0.818	6.16×10^{-8}	0.042	1.22	1.23×10^{-16}
9.23	0.23	0.927	2.99×10^{-8}	0.039	1.30	5.70×10^{-20}
10.09	0.34	0.949	6.54×10^{-8}	0.039	1.32	1.59×10^{-20}
11.09	0.33	0.994	6.16×10^{-8}	0.039	1.31	2.06×10^{-21}
12.14	0.30	1.049	5.09×10^{-8}	0.038	1.34	4.40×10^{-23}
			Second Peak			
1.87	0.39	0.718	2.62×10^{-7}	0.072	0.72	3.14×10^{-10}
2.03	0.38	0.825	3.27×10^{-7}	0.072	0.72	1.75×10^{-11}
3.02	0.82	0.937	1.52×10^{-6}	0.071	0.73	1.26×10^{-12}
4.18	0.90	0.958	1.83×10^{-6}	0.069	0.75	4.32×10^{-13}
5.04	0.86	0.945	1.67×10^{-6}	0.067	0.77	3.48×10^{-13}
6.28	1.46	0.859	4.83×10^{-6}	0.074	0.70	4.19×10^{-11}
7.09	1.11	0.949	2.79×10^{-6}	0.073	0.71	2.07×10^{-12}
8.25	1.04	1.001	2.45×10^{-6}	0.071	0.73	2.57×10^{-13}
9.23	0.68	1.085	1.05×10^{-6}	0.068	0.76	5.76×10^{-15}
10.09	0.65	1.113	9.56×10^{-7}	0.066	0.78	1.22×10^{-15}
11.09	0.54	1.154	6.60×10^{-7}	0.067	0.77	4.16×10^{-16}
12.14	0.58	1.204	7.61×10^{-7}	0.066	0.78	6.87×10^{-17}

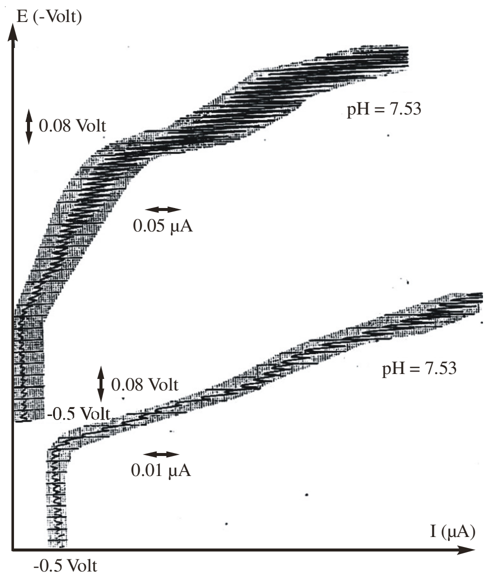

Fig. 4. Polarogram of CuPc at pH = 7.53, solvent:water the sensitivity of current and voltage axises was specified on the graphic

RESULTS AND DISCUSSION

Polarograms: The diffusion currents (I_d), half-wave potentials ($E_{1/2}$) and $E_{1/4}$-$E_{3/4}$ values of the polarograms were discussed as the following; n or αn values were calculated by using $E_{1/4} - E_{3/4} = \frac{0.05915}{n}\log 9 = \frac{0.05644}{n}$ and $E_{1/4} - E_{3/4} = \frac{51.7}{\alpha n}$ Tomes equations which were used as the reversibility-irreversibility criteria by taking $E_{1/4}$-$E_{3/4}$ values into consideration. The diffusion coefficients (D) were calculated by using $I_d = 607nD^{1/2}t^{1/6}m^{2/6}c$ Ilkovich equation; ($k^0_{f,h}$) standard heterogeneous reduction rate constant of electrochemical reactions was calculated in $E_{1/2} = \frac{0.05915}{\alpha n}\log\frac{1.349k^0_{f,h}t^{1/2}}{D_n^{1/2}}$ equation by making use of the diffusion coefficient, an kinetic parameters and half-wave potentials.

$E_{1/2}$, I_d, $E_{1/4}$-$E_{3/4}$, D, αn and $k^0_{f,h}$ values of the reduction of each complex on the mercury dropping electrode in aqueous medium and at different pH's were shown Tables 4-6. The reactions taking place on the dropping mercury electrode were whether reversible or not determined by using $E_{1/4}$-$E_{3/4}$ values. If the electrode reaction is reversible with respect to $E_{1/4} - E_{3/4} = \frac{0.05915}{n}\log 9 = \frac{0.05644}{n}$ equation, $E_{1/4}$-$E_{3/4}$ values will take the numerical values like 0.0564 V (n = 1), 0.0282 V (n = 2) depending on n. The reaction is irreversible if $E_{1/4}$-$E_{3/4}$ values are different from integers like n = 1 and n = 2. An kinetic parameter (αn) for irreversible reactions is calculated by using equation. Since an generally has a numerical value of 0.5, if αn is in the range of 0.30-0.80, this shows that the number of electron in the slow electron reaction is 1 and if it is between 0.8-1.20, the number of electron is 2[13].

To determine whether a proton transfer takes place in the electrochemical reactions together with an electron transfer; if it took place, $E_{1/2}$ values *versus* pH were plotted in order to determine the proton number.

TABLE-5
KINETIC PARAMETERS OF PbPc REDUCTION IN AQUEOUS MEDIUM

pH	I_d (μA)	$E_{1/2}$ (-V)	D (cm^2/s)	$E_{1/4}$-$E_{3/4}$ (V)	αn	$K^0_{f,h}$ (cm/s)
First Peak						
2.01	2.20	0.452	1.09×10^{-5}	0.103	0.50	2.16×10^{-5}
3.14	1.06	0.526	2.54×10^{-6}	0.099	0.52	1.97×10^{-6}
4.07	0.90	0.625	1.83×10^{-6}	0.101	0.51	2.61×10^{-7}
4.84	0.75	0.658	1.27×10^{-6}	0.094	0.55	5.85×10^{-8}
5.97	1.52	0.851	5.23×10^{-6}	0.089	0.58	9.39×10^{-10}
6.99	0.58	0.843	7.61×10^{-7}	0.086	0.6	2.69×10^{-10}
8.06	0.51	0.879	5.88×10^{-7}	0.088	0.59	1.31×10^{-10}
8.92	0.44	0.921	4.38×10^{-7}	0.088	0.59	4.32×10^{-11}
9.98	0.43	0.973	4.18×10^{-7}	0.082	0.63	4.04×10^{-12}
10.75	0.52	1.011	6.12×10^{-7}	0.079	0.65	1.06×10^{-12}
Second Peak						
6.99	1.00	0.970	2.26×10^{-6}	0.77	0.67	3.23×10^{-17}
8.06	0.92	1.024	1.92×10^{-6}	0.75	0.69	4.04×10^{-13}
8.92	0.95	1.102	2.043×10^{-6}	0.072	0.72	1.87×10^{-14}
9.98	0.66	1.140	9.86×10^{-7}	0.069	0.74	2.22×10^{-15}
10.75	0.55	1.184	6.85×10^{-7}	0.069	0.75	3.57×10^{-16}
Third Peak						
8.92	0.72	1.289	1.17×10^{-6}	0.069	0.75	2.17×10^{-17}
9.98	0.74	1.338	1.24×10^{-6}	0.068	0.76	3.55×10^{-18}
10.75	0.66	1.397	9.86×10^{-7}	0.068	0.76	5.38×10^{-19}

TABLE-6
KINETIC PARAMETERS OF CuPc REDUCTION IN AQUEOUS MEDIUM

pH	I_d (μA)	$E_{1/2}$ (-V)	D (cm^2/s)	$E_{1/4}$-$E_{3/4}$ (V)	αn	$K^0_{f,h}$ (cm/s)
First Peak						
2.06	1.08	0.596	2.64×10^{-6}	0.099	0.52	4.81×10^{-7}
3.00	0.72	0.684	1.17×10^{-6}	0.096	0.54	3.88×10^{-8}
4.05	0.70	0.761	1.11×10^{-6}	0.078	0.66	6.60×10^{-10}
5.08	0.70	0.764	1.11×10^{-6}	0.094	0.55	5.67×10^{-9}
6.02	0.84	0.847	1.59×10^{-6}	0.092	0.56	9.11×10^{-10}
7.02	0.84	1.043	1.59×10^{-6}	0.096	0.54	2.37×10^{-11}
7.53	0.89	0.971	1.79×10^{-6}	0.079	0.65	4.98×10^{-12}
8.97	0.74	1.065	1.24×10^{-6}	0.089	0.58	3.63×10^{-12}
9.95	0.72	1.140	1.17×10^{-6}	0.085	0.61	2.34×10^{-13}
10.95	0.66	1.185	9.86×10^{-7}	0.082	0.63	3.41×10^{-14}
11.95	0.71	1.257	1.14×10^{-6}	0.079	0.65	2.84×10^{-15}
Second Peak						
2.06	0.60	0.901	8.15×10^{-7}	0.083	0.62	4.31×10^{-11}
3.00	0.86	1.018	1.67×10^{-6}	0.081	0.64	1.98×10^{-12}
4.05	0.82	1.026	1.52×10^{-6}	0.076	0.68	4.62×10^{-13}
5.08	1.06	1.006	2.54×10^{-6}	0.069	0.75	1.26×10^{-13}
6.02	0.56	1.116	7.09×10^{-7}	0.068	0.76	6.05×10^{-15}
7.02	0.38	1.249	3.27×10^{-7}	0.069	0.74	5.48×10^{-17}
7.53	0.44	1.225	4.38×10^{-7}	0.069	0.75	8.61×10^{-17}
8.97	0.50	1.307	5.66×10^{-7}	0.069	0.75	9.06×10^{-18}
9.95	0.48	1.375	5.22×10^{-7}	0.069	0.75	1.19×10^{-18}
10.95	0.38	1.408	3.27×10^{-7}	0.067	0.77	1.43×10^{-19}
11.95	0.44	1.478	4.38×10^{-7}	0.068	0.76	3.32×10^{-20}
Third Peak						
2.06	1.80	1.224	7.33×10^{-6}	0.072	0.072	1.16×10^{-15}
3.00	2.40	1.279	1.30×10^{-5}	0.072	0.72	3.30×10^{-16}
4.05	2.00	1.328	9.05×10^{-6}	0.069	0.74	3.01×10^{-17}
5.08	2.10	1.345	9.98×10^{-6}	0.069	0.74	1.93×10^{-17}
6.02	2.70	1.397	1.65×10^{-5}	0.068	0.76	2.26×10^{-18}
7.02	2.25	1.442	1.15×10^{-5}	0.068	0.76	4.96×10^{-19}
7.53	2.65	1.449	1.59×10^{-5}	0.065	0.80	7.25×10^{-20}
8.97	1.86	1.520	7.83×10^{-6}	0.065	0.79	9.00×10^{-21}
9.95	1.84	1.557	7.66×10^{-6}	0.066	0.78	4.84×10^{-21}
10.95	1.98	1.589	8.87×10^{-6}	0.065	0.79	1.07×10^{-21}
11.95	1.88	1.649	8.00×10^{-6}	0.065	0.80	1.00×10^{-22}

For reversible reactions;

$$\text{Slope} = \frac{\partial E_{1/2}}{\partial pH} = -\frac{2.303pRT}{nF} = -\frac{P}{n}0.05915\frac{\text{Volt}}{pH} \quad (25\ °C)$$

For irreversible reactions;

$$\text{Slope} = \frac{\partial E_{1/2}}{\partial pH} = -\frac{2.303pRT}{\alpha n} = -\frac{P}{\alpha n}0.05915\frac{\text{Volt}}{pH} \quad (25\ °C)$$

The proton number (p) was calculated by using above equations. The reduction mechanisms of the complex compounds on the dropping mercury electrode were tried to be etermined by taking into account αn and p values. The polarograms of which half-wave potentials ad slope values were calculated.

The half-wave potentials of the complex molecules' reductions on the dropping mercury electrode in the above mentioned solvent mediums and at different pH's were calculated by the graphical method and from the equation $E = E_{1/2} + \frac{RT}{\alpha nF}\ln\frac{(I_d - I)}{I}$, the diffusion coefficients (D) from the Ilkovich equation and the kinetic parameters (αn and $k^0_{f,h}$) were calculated by using

$$E = E^0 + \frac{RT}{\alpha nF}\ln\frac{I_0}{KD_0^{1/2}} + \frac{RT}{\alpha nF}\ln\frac{I_{d\,red} - I_{red}}{I_{red}}$$

and $E_{1/4} - E_{3/4} = \frac{51.7}{\alpha n_8}$ mV ($E_{1/2}$), (I_d), (D), (slope), (αn) and ($k^0_{f,h}$) values of the polarograms plotted for various solvent mediums and at different pH's can be seen in the related Tables.

During the electrochemical reductions of metal-free phthalocyanine and metal phthalocyanine complexes, an electron transfer usually occurs in each step and 2, 3 or maximum 4 succeeding peaks were observed. Sometimes, the third and especially fourth electron transfer can be observed depending on the solvent and the material of working electrode, it is occasionally not possible[14].

In this experiment, during the reduction of quaternized crown-ether substituted phthalocyanine complexes on a dropping mercury electrode and in aqueous medium, H_2Pc showed 2 peaks and CuPc gave 3 peaks in a wide pH range (pH = 2.00-12.00). In the case of PbPc, a single peak in the range of pH = 2.00-10.75, 2 peaks in the range of pH = 7.00-10.75 and 3 peaks in the range of pH = 8.92-10.75 were observed.

When Tables 4-6 were examined, it can be observed that $E_{1/4}$-$E_{3/4}$ values of both complexes for each peak was different from 0.0564/n V at 25 °C whatever the pH is. This result shows that the reduction of both complexes on a dropping mercury electrode and in aqueous medium was irreversible.

The diffusion current is a linear function of the square root of mercury height in $I_d = f(h^{1/2})$ graphics which were plotted according to diffusion currents of the polarograms recorded for each complex at a suitable pH value and different mercury column heights[12]. This linear variation shows that the reduction of each complex is diffusion controlled. In other words, slow chemical reactions or equilibriums do not exist before or after the electron transfer.

H_2Pc reduction: The results obtained from H_2Pc polarograms recorded in aqueous medium and at different pH's were shown in Table-4. When the half-wave potentials in this table were plotted *versus* pH (Figs. 5 and 6) and the αn values obtained from $E_{1/4}$-$E_{3/4}$ values were substituted in the Slope = $\frac{\partial E_{1/2}}{\partial pH} = -\frac{2.303pRT}{\alpha n} = -\frac{p}{\alpha n}0.05915\frac{\text{Volt}}{pH}$ equation, the p values for one peak were in the range of 0.77-1.32, the p value was approximately 0.5 for 2 peaks.

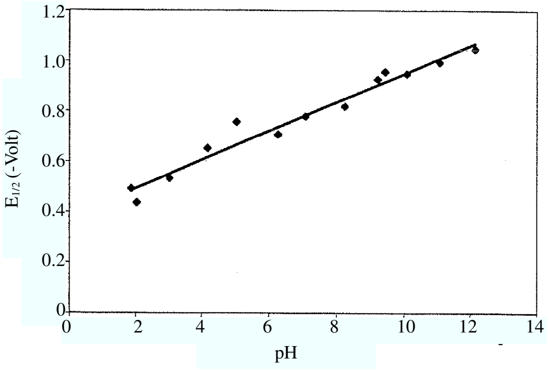

Fig. 5. pH change *versus* $E_{1/2}$ substance: H_2Pc, solvent:water for first peak

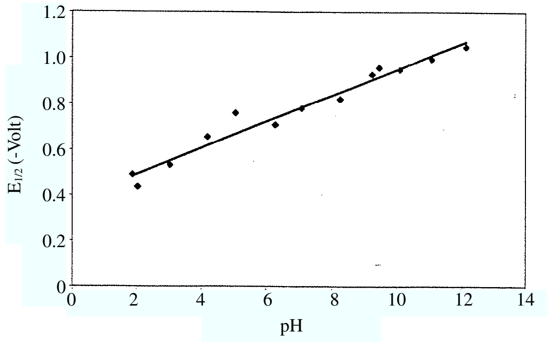

Fig. 6. pH change *versus* $E_{1/2}$ substance: H_2Pc, solvent:water for second peak

The αn has different values between 0.69 and 0.74 for one peak in the pH range of 1.87-5.04. This result shows that the transferred number of electron is 1 (when αn is approximately 0.50). On the other hand, the change in p value between 0.77 and 0.83 in the above-mentioned pH range indicates that one proton transfer occurred together with one electron transfer. The transferred number of electron is 2 if αn has variable values between 1.18 and 1.34 for one peak in the pH's higher than 5.04. In this region, different values were calculated for p in the range of 1.16-1.32, this indicates that 1 proton accompanied to the slow electrochemical reaction and 2 electrons were transferred.

Alternating αn values between 0.72-0.78 were found for the 2nd peak in the studied pH range (pH = 1.87-12.14) and the p value was approximately 0.50. The alternating an values between 0.72-0.78 indicate that the number of transferred electron is 1 in the slow reaction.

p = 0.50 indicates that there are 2 different reactions taking place with both one proton transfer and without a proton transfer on the dropping mercury electrode.

The following reactions can be proposed for the reduction of H_2Pc on a dropping mercury electrode and in aqueous solution depending on the experimental results.

1. Peak, pH = 1.87-5.04

$$H_2Pc + e^- + H^+ \longrightarrow H_3Pc$$

2. Peak, pH = 1.87-5.04

$$H_3Pc + e^- \longrightarrow [H_3Pc]^-$$

$$H_3Pc + e^- + H^+ \longrightarrow H_4Pc$$

1. Peak, pH = 5.04-12.14

$$H_2Pc + 2e^- + H^+ \longrightarrow [H_3Pc]^-$$

2. Peak, pH = 5.04-12.14

$$[H_3Pc]^- + e^- \longrightarrow [H_3Pc]^{2-}$$

$$[H_3Pc]^- + e^- + H^+ \longrightarrow H_4Pc$$

PbPc reduction: The results obtained from PbPc polarograms recorded in aqueous solution and at different pH's were shown in Table-5. When the half-wave potentials in this table were plotted *versus* pH (Figs. 7-9) and the αn values obtained from $E_{1/4}$-$E_{3/4}$ values were substituted in the

$$\frac{\partial E_{1/2}}{\partial pH} = -\frac{2.303pRT}{\alpha n} = -\frac{p}{\alpha n}0.05915\frac{Volt}{pH}$$ equation, the

p values for the 1st and 2nd peak were in the range of 0.42-0.54, while the p value for the 3rd peak was approximately 0.69.

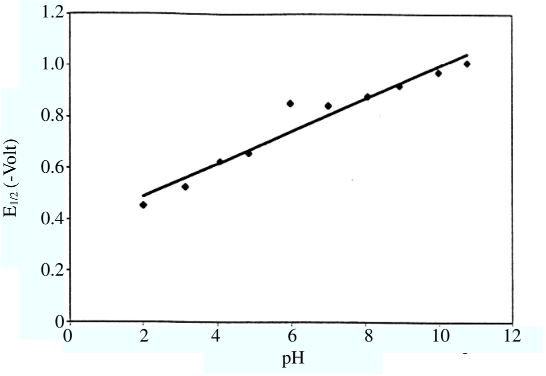

Fig. 7. pH change *versus* $E_{1/2}$ substance: PbPc solvent:water for first peak

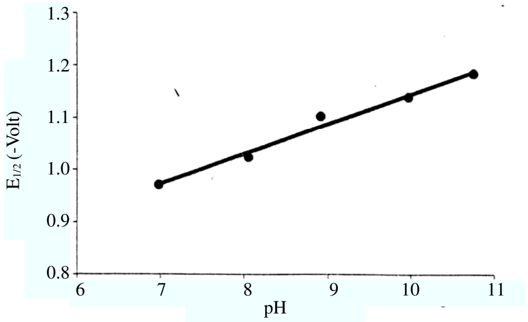

Fig. 8. pH change *versus* $E_{1/2}$ substance: PbPc, solvent:water for second peak

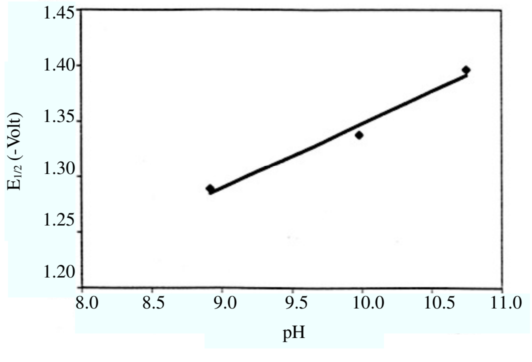

Fig. 9. pH change *versus* $E_{1/2}$ substance: PbPc, solvent:water for third peak

The αn has variable values between 0.50 and 0.65 for the 1st peak in the pH range of 2.01-10.75. This result shows that the transferred number of electron is equal to 1 (when αn is approximately 0.50). On the other hand, the change in p value between 0.42 and 0.54 in the above-mentioned pH range indicates that the two same reactions took place together with one proton transfer and without a proton transfer.

The number of transferred electron is 1 if αn has different values between 0.67 and 0.75 for the 2nd peak in the pH range of 6.69-10.75 (when αn is approximately 0.50).

The number of transferred electron is equal to 1 if αn is approximately equal to 0.75 for the 3rd peak in the pH range of 8.92-10.75. In this pH range , the p value was calculated approximately 0.69, this result indicates that one electron transfer occurred together with a proton transfer.

The following reactions can be proposed for the reduction of PbPc on a dropping mercury electrode and in aqueous solution depending on the experimental results:

1. Peak pH = 2.01-10.75

$$PbPc + e^- \longrightarrow [PbPc]^-$$

$$PbPc + e^- + H^+ \longrightarrow PbPcH$$

2. Peak pH = 6.69-10.75

$$[PbPc]^- + e^- \longrightarrow [PbPc]^{2-}$$

$$[PbPc]^- + e^- + H^+ \longrightarrow [PbPcH]^-$$

$$PbPcH + e^- \longrightarrow [PbPcH]^-$$

$$PbPcH + e^- + H^+ \longrightarrow PbPcH_2$$

3. Peak pH = 8.92-10.75

$$[PbPc]^{2-} + e^- + H^+ \longrightarrow [PbPcH]^{2-}$$

$$[PbPcH] + e^- + H^+ \longrightarrow [PbPcH_2]^-$$

$$PbPcH_2 + e^- + H^+ \longrightarrow PbPcH_3$$

CuPc reduction: The results obtained from CuPc polarograms recorded in aqueous solution and at different pH's were shown in Table-6. When the half-wave potentials given in this table were plotted *versus* pH (Figs. 10-12) and the αn values obtained from $E_{1/4}$-$E_{3/4}$ values were substituted in the

$$\frac{\partial E_{1/2}}{\partial pH} = -\frac{2.303pRT}{\alpha n} = -\frac{p}{\alpha n}0.05915\frac{Volt}{pH}$$ equation, the

changing p values for the 1st peak in the range of 0.59-0.74, for the 2nd peak 0.59-0.70 and for the 3rd peak in 0.50-0.56 range were calculated.

The αn has variable values between 0.52 and 0.65 for the 1st peak in the pH range of 2.06-11.95. This result shows that the number of transferred electron is equal to 1. On the other hand, the change in p value between 0.59 and 0.74 in the above-mentioned pH range indicates that one electron transfer took place together with one proton transfer.

The number of transferred electron is equal to 1 if αn has different values between 0.62 and 0.76 for the 2nd peak in the pH range of 2.06-11.95 (when α = 0.50). The change in p value between 0.59 and 0.73 in the above-mentioned pH range can be explained as one electron transfer took place together with one proton transfer.

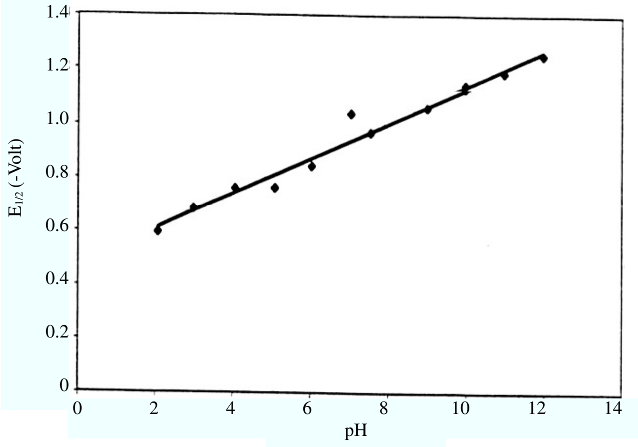

Fig. 10. Change of $E_{1/2}$ *versus* pH substance, CuPc solvent:water for first peak

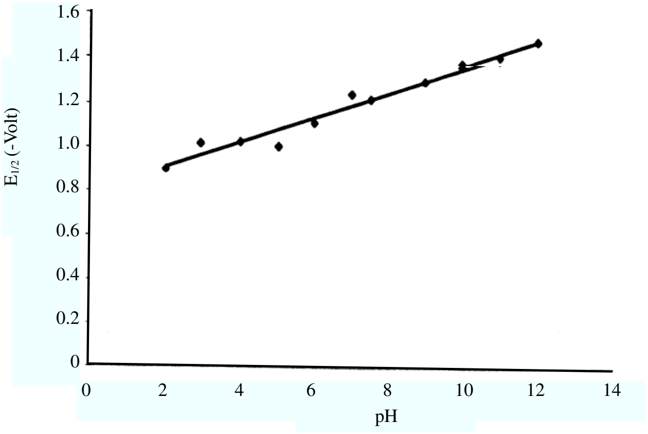

Fig. 11. Change of $E_{1/2}$ *versus* pH substance: CuPc, solvent:water for second peak

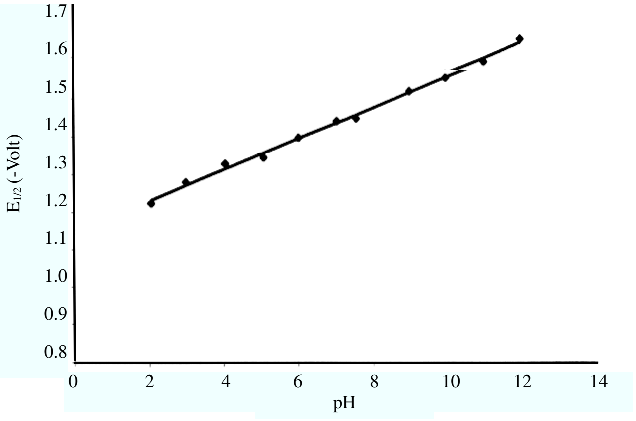

Fig. 12. Change of $E_{1/2}$ *versus* pH substnace: CuPc, solvent:water for third peak

The number of transferred electron is equal to 1 if αn has changing values between 0.72 and 0.80 for the 3rd peak in the pH range of 2.06-11.95. In this pH range, the p has different values between 0.50 and 0.56, this result indicates that one electron transfer occurred together with a proton transfer.

The following reactions can be proposed for the reduction of CuPc on a dropping mercury electrode and in aqueous solution depending on the experimental results:

1. Peak pH = 2.06-11.95

$$CuPc + e^- + H^+ \longrightarrow CuPcH$$

2. Peak pH = 2.06-11.95

$$CuPcH + e^- + H^+ \longrightarrow CuPcH_2$$

3. Peak pH = 2.06-11.95

$$CuPcH_2 + e^- \longrightarrow [CuPcH_2]^-$$

$$CuPcH_2 + e^- + H^+ \longrightarrow CuPcH_3$$

Metal-free phthalocyanine and metal phthalocyanine complexes have an 18π-electron aromatic ring system. The phthalocyanine ring is -2 charged in this structure and usually shown as Pc (-2). When the previous studies concerning the redox reactions of these complexes were examined, maximum 4 reduction peaks and one electron transfer in each step were usually observed. The reduction of metal or phthalocyanine ring is primarily possible depending on the type of metal within the phthalocyanine ring system. The possibility of alternative reductions depending on the type of metal is related to the role of metal in the energy levels of complex's orbital acting a part in the redox reactions and consequently in its electronic structure. Therefore, the reduction first takes place in metal and subsequently ring reduction occurs during the reduction of metal phthalocyanines containing cobalt, iron, chromium, manganese and some other metals. The reduction of phthalocyanines containing zinc, copper, aluminum, nickel and some other metals completely occurs on the ring and Pc(-3), Pc (-4), Pc(-5) and Pc(-6) species form. When the first reduction potential of phthalocyanine ring is compared with the reduction potential of redox-active metal inside the ring, the reduction potential of metal has more positive values than the ring[14]. When the results obtained from the previous studies in literature were taken into consideration, it appears that in this study, the reduction processes corresponding to the polarographic peaks obtained with H_2Pc and CuPc complexes took place in the phthalocyanine ring of the complexes. When the half-cell potentials corresponding to the first reduction peaks of H_2Pc and CuPc complexes are compared (Tables 4 and 6), it can be seen that these values are close to each other. These values show that the reduction processes of CuPc complex took place in the phthalocyanine ring. The number of studies investigating the electrochemical behaviours of PbPc in literature is comparatively less[15,16]. However, when the half-cell potentials obtained for this complex are compared with those belonging to the other complexes (Tables 4-6), it is clear that the reduction processes of PbPc complex took place on the ring.

One electron transfer usually takes place in each step in the succeeding reduction processes of the phthalocyanine ring. In addition, the first two reduction peaks were observed in almost all the studies without depending on the solvent medium and the material used as a working electrode, on the other hand, the third and fourth reduction peaks were observed in a very few study[14]. The reduction peaks obtained in this study with H_2Pc, CuPc and PbPc complexes are in accordance with the studies in the literature. When the results of H_2Pc complexes were examined (Table-4), it appears that two electrons transfer took place in the reduction process corresponding to the first reduction peak in the pH range of 6.28-12.14. In this pH range, it can be concluded that the two different reduction processes corresponding to Pc(-2)/Pc(-3) and Pc(-3)/Pc(-4) redox pairs were observed as a single peak. Although a single electron transfer usually occurs in each step during the reduction of phthalocyanine ring, the studies in which the first two reduction peaks were observed as a single peak, the peaks corresponding to two electrons transfer were observed are present in the literature[17,18].

After examining Tables 4-6, it can be seen that the standard rate constants ($k^0_{f,h}$) of H_2Pc, PbPc and CuPc reductions on the dropping mercury electrode and at different pH values are too small. This situation shows that the reduction processes took place irreversibly, in other words, slowly. Additionally, the standard rate constant values decreases as pH increases, that is to say, the rate of electrochemical reaction decreases. The decrease in the electrochemical reaction rate as pH increases stems from a proton transfer together with an electron transfer to the phthalocyanine ring; because H^+ ion concentration in the medium decreases as pH increases, the rate decreases since the reaction takes place with a proton transfer. If the half-cell potentials decreases as pH increases or shifts to more negative potentials, this points out that a proton transfer occurs together with an electron transfer. Although there are number of papers investigating the electrochemical behaviours of different metal-free and metal phthalocyanine complexes, almost all of these studies occurred in non-aqueous medium. Since most of the synthesized phthalocyanine complexes do not dissolve in water, the studies investigating the electrochemical behaviours of these complexes in water and especially their pH effect are limited. This study became complementary to those in the literature in terms of examining the pH effect because the analyzed phthalocyanine complexes are soluble in water in a wide pH range (pH = 1-13).

The diffusion coefficients of H_2Pc, CuPc and PbPc complexes and their reduced species have quite small values (Tables 4-6). Since these complexes are made of large macromolecules, the smallness of diffusion coefficients are in accordance with the molecular structure. In some studies, it is stated that crown-ether substituted phthalocyanine complexes are dimerized as a result of the formation of sandwich type complexes after some cations like Na^+ and K^+ enter into the cavity of crown ethers[19]. Since the polarograms were recorded by using KNO_3 as the supporting electrolyte in the study, this may cause that the diffusion coefficients have quite small values in the formation of sandwich type complexes. It is easily understood whether the crown-ether substituted phthalocyanine complexes show sandwich type complex formations, aggregation and dimerization reactions. In other words, these types of events cause some important characteristic changes in the electronic spectrum of these complexes. There are some studies determining that these types of events cause the decrease of diffusion coefficients[20]. However, it is not possible to observe the effects of these types of events in the electrochemical studies clearly as in the case of electronic spectrums[20,21]. In this study, the polarograms of complexes were recorded by using KNO_3, $NaNO_3$ and tetrabutylammonium chloride as the supporting electrodes in order to observe this effect of alkali metal ions (Na^+, K^+). However, a change in the diffusion currents and coefficients of polarograms recorded with different supporting electrolytes could not be observed.

REFERENCES

1. F.H. Moser, The Phthalocyanines Properties, CRC, Boca Raton, Florida, pp. 1-20 (1983).
2. H. De Diesbach and E. von der Weid, *Helvetica Chim. Acta*, **10**, 886 (1927).
3. R.P. Linstead, Phthalocyanine, British Association for the Advancement of Science Report, pp. 465-466 (1933).
4. A.B. Lever, *Adv. Inorg. Chem. Radiochem.*, **7**, 27 (1965).
5. K.R.V. Reddy, J. Keshavayva, B.E.K. Swamy, M.N.K. Harish, H.R. Mallikarjuna and B.S. Sherigora, *Dyes Pigm.*, **80**, 1 (2009).
6. M. Naksi and A. Cihan, *Transition Met. Chem.*, **32**, 89 (2007).
7. S. Arslan and I. Yilmaz, *Transition Met. Chem.*, **32**, 292 (2007).
8. S. Arslan and I. Yilmaz, *Polyhedron*, **26**, 2387 (2007).
9. A. Koca, A.R. Ozkaya, M. Selcukoglu and E. Hamuryudan, *Electrochim. Acta*, **52**, 2683 (2007).
10. A. Kalkan and Z. Altuntasbayir, *I.T.U. Journal/C Science*, **6**, 86 (2008).
11. E. Musluoglu, V. Ahsen, A. Gul, O. Bekaroglu and O. Bekaroglu, *Chem. Ber.*, **124**, 2531 (1991).
12. I. Cince, Ph.D. Thesis, The Investigation of Electrochemical Reduction and Oxidations of Lead and Metal-Free Phthalocyanine Complexes, Marmara University, Turkey (2000).
13. J.E. Strassner and P. Delahay, *J. Am. Chem. Soc.*, **74**, 6232 (1952).
14. C.C. Leznoff, A.B.P. Lever, Phthalocyanines: Properties and Applications, VCH, Weinheim, Vol. 3 (1993).
15. M. El-Meray, A. Louati, J. Simon, A. Giraudeau, M. Gross, T. Malinski and K.M. Kadish, *Inorg. Chem.*, **23**, 2606 (1984).
16. E. Ough, T. Nyokong, K.A.M. Creber and M.J. Stillman, *Inorg. Chem.*, **27**, 2724 (1988).
17. N. Tan, O. Bekaroglu and F. Kadirgan, *J. Electroanal. Chem.*, **364**, 251 (1994).
18. J.T.S. Irvine, B.R. Eggins and J. Grimshaw, *J. Electroanal. Chem.*, **271**, 161 (1989).
19. A.I. Okur, A. Gui, A. Cihan, N. Tan and O. Bekaroglu, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **20**, 1399 (1990).
20. A.R. Ozkaya, A.I. Okur, A. Gul and O. Bekaroglu, *J. Coord. Chem.*, **33**, 311 (1994).
21. A. Sastre, A. Gouloumis, P. Vazguez, T. Torres, V. Doan, B.J. Schwartz, F. Wudl, L. Echegoyen and J. Rivera, *Org. Lett.*, **1**, 1807 (1999).