

**SALH₂. NaNO₃. H₂O'NUN* Cu(II) KOMPLEKSİYLE İLGİLİ
POLAROGRAFİK ÇALIŞMALAR (I) : STANDARD AKTİVASYON
SERBEST ENERJİSİ VE İNTEGRAL ÇÖZÜNME İSİNİN TAYİNİ**

**POLAROGRAPHIC STUDIES ON THE Cu(II) COMPLEX OF
SALH₂. NaNO₃. H₂O* (I) : DETERMINATION OF THE STANDARD
FREE ENERGY OF ACTIVATION AND THE INTEGRAL HEAT OF
SOLUTION**

Ali Rıza ÖZKAYA**

SUMMARY

In this work, polarographic reduction of the Cu (II) complex of schiff base ligand SALH₂. NaNO₃. H₂O was investigated in the solvent media of aqueous 70% Dimethylsulfoxide (DMSO). The reduction of the complex was found to take place in two electrochemical steps indicated by two well - defined polarographic waves. While the first wave involved a two - electron irreversible process, the second wave indicated a one - electron irreversible wave. Also the integral heat of solution ΔH_s , of the complex in aqueous 70% DMSO and th standard free energy of activation, ΔG^\ddagger , for each electrode process have been determined by using the polarographic data.

ÖZET

Bu Çalışmada bir şif bazı ligandı olan SALH₂. NaNO₃. H₂O'nun Cu (II) ile oluşturduğu kompleksin % 70 Dimetilsülfoksit (DMSO) içeren sulu ortamdaki polarografik indirgenmesi incelendi. Sözkonusu kompleksin iki basamakta indirgenerek sırasıyla iki elektron transferinin gerçekleştiği irreversibil palye ile bir elektron transferinin yer aldığı ikinci bir irreversibil palye verdiği görüldü. Ayrıca polarografik verileri kullanarak kompleksin sözkonusu çözücü ortamındaki integral çözünme ısısı (ΔH_s) ve herbir elektrod prosesi için standart aktivasyon serbest enerjisi (ΔG^\ddagger) tayin edildi.

INTRODUCTION

The polarographic reduction of the Ni(II) and Co(II) complexes of SALH₂. NaNO₃. H₂O was studied as a function of pH in our previous reports (1-3). In this report the electrochemical reduction of the Cu(II) complex of the same schiff base ligand was investigated in the solvent media of aqueous 70% DMSO.

* 4', 5' - bis (salicylideneimino) benzo (15 - crown - 5)

** Marmara Üniversitesi Atatürk Eğitimi Fakültesi, Kimya Anabilim Dalı, Kadıköy / İS-TANBUL.

Also the integral heat of solution of the complex and the standard free energy of activation for each electrode process were determined by using the polarographic data.

There has been many reports on the electrochemical reduction of the Cu(II) complexes of various ligands (4-6) and few reports on the electrochemistry of Cu (II) complexes of some schiff base ligands (7,8). However the literature has not contained any report about the polarographic behaviour of the complex used in this work. The structure of the Cu (II) complex of $\text{SALH}_2 \cdot \text{NaNO}_3 \cdot \text{H}_2\text{O}$ is shown in Figure 1.

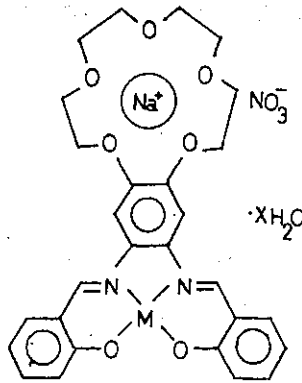


Figure - 1 : The structure of the Cu(II) complex of $\text{SALH}_2 \cdot \text{NaNO}_3 \cdot \text{H}_2\text{O}$. M : Cu(II).

METHOD

The half - wave potentials ($E_{1/2}$) and the values of n or αn for the electrode processes were determined from the plot of E versus $\log I_d - I / I$ according to the following basic equation.

$$E = E_{1/2} + \frac{2.303 RT}{(\alpha) nF} \log \frac{I_d - I}{I} \quad (1)$$

The standard heterogeneous electron transfer rate constant, $k_{f,h}^\circ$, was calculated by making use of the following equation given by Kern and Koutecky methods (9 - 11).

$$k_{f,h}^\circ = \frac{(D/t)^{1/2}}{1.349} \exp\left(\frac{\alpha n F E_{1/2}}{RT}\right) \quad (2)$$

By the theory of absolute rates (12), velocity constant may be written in the form :

$$k_f = \frac{kT}{h} \exp\left(-\frac{\Delta G^\circ_\pi}{RT}\right) \quad (3)$$

and k_f may be identified with $k^\circ_{f,h}$ the velocity constant at the potential of zero charge (p. z. c.), where ΔG°_π becomes the standard chemical free energy of activation with no electrical contribution. Thus from eqns. (2) and (3) :

$$\frac{kT}{h} \exp\left(-\frac{\Delta G^\circ_\pi}{RT}\right) = \frac{(D/t)^{1/2}}{1.349} \exp\left(\frac{anFE_{1/2}}{RT}\right) \quad (4)$$

The values of ΔG°_π was calculated from Equation (4) $E_{1/2}$ including a double layer correction. Diffusion coefficient, D was determined employing the well known Ilkovic equation.

The integral heat of solution, ΔH_s , was determined from the plot of $1/T$ versus $\ln s$ (s : solubility) based on the following equation which express the variation of solubility with temperature.

$$\ln s = -\frac{\Delta H_s}{RT} + C ; C : \text{constant} \quad (5)$$

Solubility of the complex at different temperatures in aqueous 70 % DMSO was determined by comparing the diffusion currents of the first wave of the polarograms recorded at these temperatures based on the following expression.

$$\frac{I_d(\text{at } 45^\circ \text{C})}{I_d(\text{at } t^\circ \text{C})} = \frac{s(\text{at } 45^\circ \text{C})}{s(\text{at } t^\circ \text{C})} = \frac{2.14 \text{ mg} / 20 \text{ ml}}{s \text{ mg} / 20 \text{ ml}} \quad (6)$$

EXPERIMENTAL

Cu(II) complex of $\text{SALH}_2 \cdot \text{NaNO}_3 \cdot \text{H}_2\text{O}$ was supplied from the Chemistry Department of Technical University of Istanbul (13). Triply distilled water and ultra pure DMSO were used in the preparation of solution for study. KNO_3 (Merck) was used as the supporting electrolyte in a 0.1 mole dm^{-3} concentration.

The solution for study was prepared by mixing the following :

4 ml of 7.97×10^{-4} Molar SALCu. $\text{NaNO}_3 \cdot \text{H}_2\text{O}$ (M : 672. 11 g / mol) in DMSO.

2 ml of triply distilled water.

4 ml of 0.5 Molar KNO_3 in triply distilled water. 10 ml of DMSO.

The polarograms were performed at different temperatures with an instrument, Metrohm E - 261 Model Polarograph, utilizing a three - electrode configuration . A platinum wire served as counter electrode and a commercial saturated calomel electrode (SCE) was employed as the reference electrode. The working electrode was a dropping mercury electrode (DME) having the following characteristics :

$$m = 2.40 \text{ s}, t = 4.00 \text{ s}, m^{2/3} t^{1/6} = 2.38 \text{ mg}^{2/3} \text{ s}^{-1/2}, h = 45 \text{ cm}$$

The polarographic cell design shown in our previous report (1) was used in this work employing a special cell connected to a thermostat to adjust the temperature.

RESULTS AND DISCUSSION

A typical polarogram of SALCu. $\text{NaNO}_3 \cdot \text{H}_2\text{O}$ recorded at 50°C is shown in Fig. 2. The polarographic data for the electrochemical reduction of the complex at the temperature of 25°C is presented in Table 1. Also the values of ΔG^\ddagger and $k_{f,h}^\circ$ at the potential of zero charge (p. z. c.) for each wave are given in the same table. The p. z. c. was found to be 0.4 V from the electrocapillary curve of the DME in the solution for study.

The complex gives two well defined waves. The value of αn for the first wave (I) calculated from the slope of E versus $\log I_d - I/I$ was found to be 1.85 indicating irreversible nature of the first reduction process. This process is probably ligand based involving SAL(-2) Cu(II) / [SAL (-4) Cu(II)]²⁻ redox couple. The complex exhibits an irreversible second wave (II) with an αn value of 0.71 and this wave may be attributed to the redox couple of [SAL(-4) Cu(II)]²⁻ / [SAL (-4) Cu(I)]³⁻.

Table - 1 : The values of polarographic data, $k_{f,h}^{\circ}$ at the p. z. c. and ΔG° at 25 ° C for each wave of SALCu. NaNO₃. H₂O.

	$E_{1/2}$ (-V vs SCE)	Slope of the log plot (V)	αn	$k_{f,h}^{\circ}$ at the p. z. c. (m/s)	ΔG° kJ / mole
I	0.532	0.032	1.85	2.76×10^{-10}	127.5
II	0.912	0.083	0.71	2.68×10^{-12}	138.9

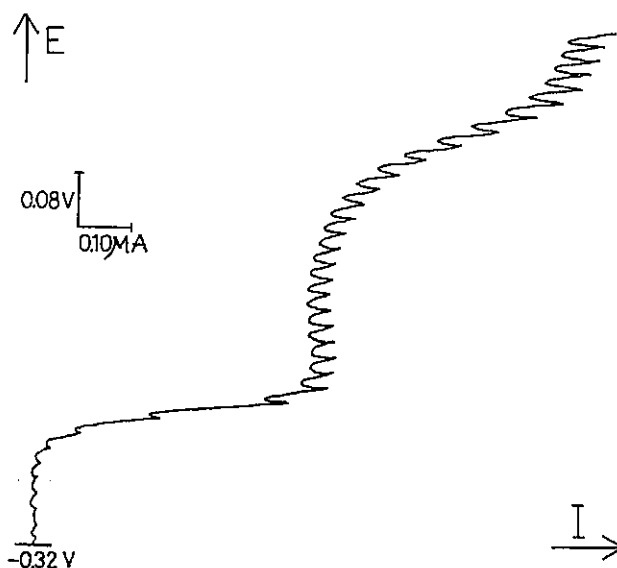


Figure - 2 : A typical polarogram of SALCu. NaNO₃. H₂O in aqueous 70% DMSO at 50 °C.

The solubilities of the complex at different temperatures were calculated by comparing diffusion currents of the first wave at these temperatures and presented in Table 2. The integral heat of solution, ΔH_s , for the complex in aqueous 70% DMSO was determined from the slope of $1/T$ versus $\ln s$ and found to be 54.7 kJ / mole. As a result of the high value of ΔH_s , the solubility of the complex increases considerably with temperature.

Table - 2 : The solubility of SALCu. $\text{NaNO}_3 \cdot \text{H}_2\text{O}$ as a function of temperature in aqueous 70 % DMSO.

t (° C)	I_d (μ A)	(mg / 20 ml)
20	0.100	0.40
25	0.136	0.55
30	0.200	0.81
35	0.325	1.31
40	0.445	1.80
45	0.530	2.14
50	0.530	-

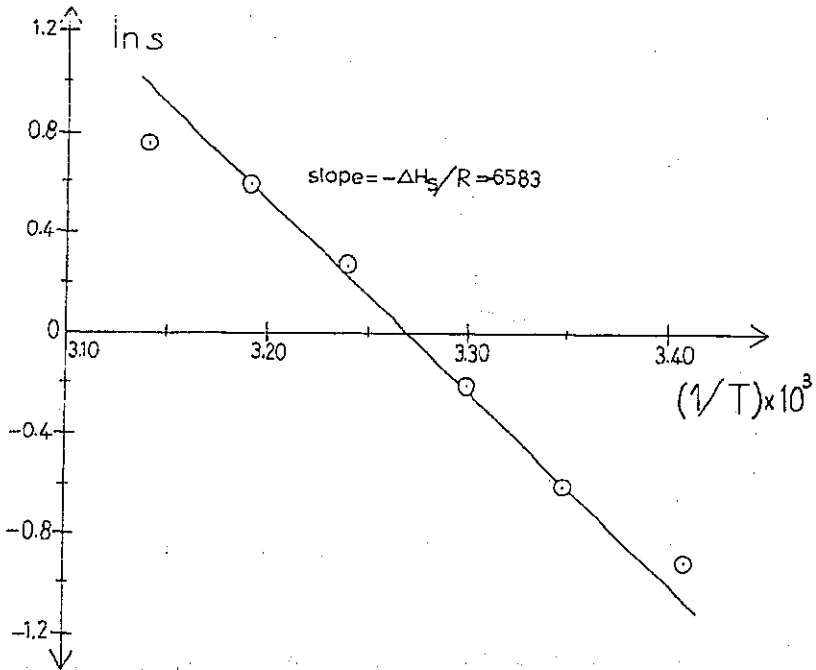


Figure - 3 : The variation of solubility of SALCu. $\text{NaNO}_3 \cdot \text{H}_2\text{O}$ as a function of temperature.

REFERENCES

1. Özkaya, A. R., Şahin, M. : *Tr. J. of Chem.*, **16** (3), 204 (1992).
2. Özkaya, A. R., Şahin, M. : *Tr. J. of Chem.*, **17** (1), 24 (1993).
3. Özkaya, A. R., Şahin, M. : *M. Ü. Fen Bilimleri Enstitüsü Dergisi*, **8** (1991), in press.
4. Chitalata, P. K., Mandloi, S. N., Verma, M. S., Nigam H. L. : *Indian J. Chem., Sect. A*, **22A** (1), 87 (1983).
5. Upadhay, M., Gangopadhyay, S., Banerjea, P. : *J. Indian Chem. Soc.*, **62** (12), 1029 (1985).
6. Malyszko, J., Scendo, M.: *J. Electroanal. Chem. Interfacial Electrochem.*, **250** (1), 61 (1988).
7. Chjo, K. H., Choi, Y. K., Seo, S. S., Lee, S. J. : *J. Corean Chem. Soc.* , **35** (1), 24, (1991).
8. Chjo, K. H., Kim, J. S. : *Taeahan Hwahakhoz Chi*, **31** (6), 509 (1987).
9. Koutecky, J. : *J. Czechoslav. Chem. Communs. Eng. Edn.*, **21**, 836 (1956).
10. Koutecky, J. : *Collection Czechoslav. Chem. Communs.*, **18**, 597 (1953).
11. Kern, D. M. H. : *J. Am. Chem. Soc.*, **76**. 4234 (1954).
12. Eyring, H., Glasstone, S., Laidler, K. J. : *J. Chem. Phys.*, **7**, 1053 , (1939).
13. Gül, A., Okur, A. İ. , Cihan, A., Tan, N., Bekaroğlu Ö. : *Synt. React. Inorg. Met. Org. Chem.* , **16** (6), 871 (1980).