

The electronic spectrum of the Cu(II) complex (recorded in mull) in the solid state does not show any absorption in the range 600-700 nm which excludes the possibility of a square or distorted octahedral geometry for this complex⁴. Keeping in view the steric factors operating in the ligand, the complex is likely to have a tetrahedral geometry^{5,6}. A band observed at 360 nm can be assigned to an electronic transition associated with the ligand. The Cu(II) complex shows a magnetic moment value of 1.74 B.M.

The electronic spectrum of the Ni(II) complex shows a band at 610 nm which is usually observed for square-planar Ni(II) complexes^{7,8}. The spectrum shows another band at 440 nm which may also be assigned to one of the *d-d* transitions expected for square-planar Ni(II). The complex is diamagnetic which conforms to the square-planar geometry of the compound. The pyridine adduct, however, is paramagnetic and its effective magnetic moment (3.17 B.M.) is typical of an octahedral Ni(II) complex⁹. Attempts to prepare similar pyridine adduct with Cu(II) complex were unsuccessful.

The authors thank the authorities of the Indian Institute of Science, Bangalore, and the Propellant Engineering Division of the Space Science Technology Centre, Trivandrum, for the instrumental facilities. One of them (A.N.S.) is thankful to the UGC, New Delhi, for financial assistance.

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Polarographic Behaviour of UO₂(II) & Th(IV) in Ethane-1,2-dithiol

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Received 7 May 1975; accepted 4 October 1975

UO₂²⁺ and Th⁴⁺ ions in ethane-1,2-dithiol give irreversible and diffusion-controlled waves in the presence of 0.1M NaClO₄, 0.002% Triton X-100 and 25% ethanolic media. The values of kinetic parameters, viz. transfer coefficient (α), formal rate constant (K_f^0) for the electrode reactions have been determined by Koutecky's method as extended by Meites and Israel. The values of ΔH , ΔG and ΔS have also been calculated.

IN continuation of our earlier work¹⁻⁵ the polarographic behaviour of organo-sulphur compounds and their complexes with metals¹⁻⁵, in this note is reported the results of investigation on the behaviour of UO₂(II) and Th(IV) ions in the presence of ethane-1,2-dithiol for which there is no reference in the literature.

Ethane-1,2-dithiol (referred herein as EDT) and other chemicals used were of Analar (BDH) grade. A manual polarograph with scalamp galvanometer and SCE as reference electrode was used for recording the polarograms. The capillary had the following characteristics in 25% ethanol, 0.1M NaClO₄ at -0.5 V vs SCE with h_{Hg} value of 40 cm: $m=2.895$ mg/sec, $t=2.39$ sec.

The effects of change in Hg-pressure, temperature and concentration of metal ions on the waves due to UO₂²⁺ and Th⁴⁺ were investigated. The values of kinetic parameters were determined from the polarograms of the solutions containing 1.0 mM UO₂²⁺ or 0.1 mM Th⁴⁺ + 0.1M NaClO₄ + 0.002% Triton X-100 + 25% ethanol + different amounts of EDT. The current was recorded at the end of the drop life instead of average current as the determination of kinetic parameters is based on Koutecky's method which are accurately reproduced by measuring the maximum current⁶.

The conventional log plots of the reduction waves for UO₂²⁺ and Th⁴⁺ in ethane-1,2-dithiol were linear and their slope values indicated the irreversible nature of the waves for both the systems.

The constancy of $I_d/h_{eff}^{1/2}$ in each case and the values of temperature coefficients of 1.138% (for UO₂²⁺-EDT) and 1.838% (for Th⁴⁺-EDT) indicate the diffusion controlled nature of the waves. The plots of i_d vs temperature and $h_{eff}^{1/2}$ are shown in Fig. 1. The limiting current increases linearly with increase in [metal ion]. With increase in EDT the $E_{1/2}$ shifts towards more negative potential showing the complex formation between metal ions and ligand, whereas i_d increases for UO₂²⁺ and decreases for Th⁴⁺ indicating that the aquo-uranyl and aquo-thorium ions differ in size from their complexes of EDT.

Since the reduction of UO₂²⁺ and Th⁴⁺ ions in the presence of EDT is irreversible, it is considered expedient to determine the values of transfer coefficient

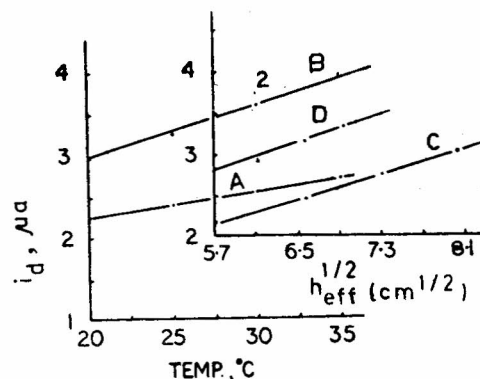


Fig. 1—Plots of i_d versus temperature (curves A and B) and plots of i_d versus $h_{eff}^{1/2}$ (curves C and D) for the systems UO₂²⁺-EDT (curves A and C) and Th⁴⁺-EDT (curves B and D)

TABLE 1 — VALUES OF αn AND $K_{f,h}^0$ AT DIFFERENT CONCENTRATIONS EDT FOR UO_2^{2+} AND Th^{4+} SYSTEMS AT 20°

[EDT] <i>M</i>	<i>i_d</i> (amp.)		- <i>E_½</i> (V)		αn		$K_{f,h}^0$ (cm/sec)	
	UO_2^{2+}	Th^{4+}	UO_2^{2+}	Th^{4+}	UO_2^{2+}	Th^{4+}	UO_2^{2+}	Th^{4+}
0.02	2.275	3.00	0.4900	1.3600	0.4804	0.9416	7.06×10^{-6}	2.50×10^{-21}
0.04	2.875	2.55	0.5382	1.3650	0.4850	0.8022	3.45×10^{-6}	1.23×10^{-18}
0.06	3.050	2.20	0.6240	1.3700	0.4896	0.677	6.86×10^{-7}	2.23×10^{-16}
0.08	3.300	—	0.6452	—	0.5110	—	2.84×10^{-7}	—
0.10	3.360	—	0.7015	—	0.5320	—	8.16×10^{-8}	—

TABLE 2 — VALUES OF αn AND $K_{f,h}^0$ AT VARIOUS TEMPERATURES FOR UO_2^{2+} -EDT AND Th^{4+} -EDT SYSTEMS

Temp. (°C)	<i>i_d</i> (amp.)		- <i>E_½</i> (V)		αn		$K_{f,h}^0$ (cm/sec)	
	UO_2^{2+}	Th^{4+}	UO_2^{2+}	Th^{4+}	UO_2^{2+}	Th^{4+}	UO_2^{2+}	Th^{4+}
20	2.275	3.00	0.4900	1.3600	0.4804	0.9416	0.70×10^{-6}	2.5×10^{-21}
25	2.400	3.25	0.4650	1.3435	0.4856	0.6816	1.15×10^{-5}	5.7×10^{-16}
30	2.550	3.60	0.4540	1.3278	0.4903	0.6624	1.45×10^{-5}	2.1×10^{-15}
35	2.700	3.95	0.4435	1.3025	0.4953	0.6456	1.81×10^{-5}	9.2×10^{-15}

cient (α) and formal rate constant ($K_{f,h}^0$), for the electrode reaction by applying Koutecky's theoretical treatment⁷ as extended by Meites and Israel⁸ and which is based on the plot of E_{de} vs $\log i/i_d - i$.

The mathematical solution for an electrode reaction at d.m.e. controlled by the kinetics of the electron transfer is given by Eqs. (1 and 2).

$$\frac{i}{i_d} = F(X) \quad \dots(1)$$

$$X = \left(\frac{12}{7}\right)^{\frac{1}{2}} K_{f,h} \left(\frac{t}{D_0}\right)^{\frac{1}{2}} \quad \dots(2)$$

in which t is the drop time, D_0 is the diffusion coefficient of electroactive substance, $K_{f,h}$ is the potential-dependent heterogeneous rate constant described by Eq. (3)

$$K_{f,h} = K_{f,h}^0 \exp \left[-\alpha n F \frac{(E + 0.2412)}{RT} \right] \quad \dots(3)$$

where E refers to the potential of SCE, i and i_d are the currents that actually flow at the end of drop life at potential E and at plateau of the wave respectively.

From the values of X and $F(X)$ given by Koutecky, Meites and Israel⁸ found that $\log X$ varied linearly with $\log \{F(X)/[1-F(X)]\}$. The data can be fitted in Eq. (4).

$$\log X = -0.0130 + 0.9163 \log \frac{F(X)}{1-F(X)} \quad \dots(4)$$

Combining Eq (1)-(4), we get

$$E_{de} + 0.2412 = \frac{0.05915}{\alpha n} \log \frac{1.349 K_{f,h}^0 t^{\frac{1}{2}}}{D_0^{\frac{1}{2}}} - \frac{0.0542}{\alpha n} \log \frac{i}{i_d - i} \quad \dots(5)$$

which may be rewritten as

$$E_{de} = E_{\frac{1}{2}} - \frac{0.0542}{\alpha n} \log \frac{i}{i_d - i} \quad \dots(6)$$

with

$$E_{\frac{1}{2}} = -0.2412 + \frac{0.05915}{\alpha n} \log \frac{1.349 K_{f,h}^0 t^{1/2}}{D_0^{\frac{1}{2}}} \quad \dots(7)$$

The values of kinetic parameters for the present systems were calculated with the help of Eqs. (6) and (7). The value of αn was obtained by equating the slope of E_{de} vs $\log i/i_d - i$ plot to $-0.0542/\alpha n$ and the intercept of the same plot giving $E_{\frac{1}{2}}$ was used to calculate $K_{f,h}^0$. The values of $D_0^{\frac{1}{2}}$ were determined from Ilkovic equation. Since t does not vary appreciably over the range of potential covered by the rising part of the wave, it was considered unnecessary to apply the correction for drop-time⁹.

The values of αn and $K_{f,h}^0$ (Table 1) are affected by the concentration of the ligand because of the change in $E_{\frac{1}{2}}$ and i_d in $K_{f,h}^0$ increases with temperature for both the systems (Table 2). Shift in half-wave potential towards more positive value shows the easier reduction of the complexes at higher temperatures (Table 2) and is in accordance with the irreversible nature of the processes.

The enthalpy of activation (ΔH) for the electrode reaction has been calculated by equating the slope of $\log K_{f,h}^0$ vs $1/T$ plot to $[-\Delta H/2.303R]$ and found to be 7.676 and 10.070 kcal/mole for UO_2^{2+} -EDT and Th^{4+} -EDT systems respectively.

The free energy of activation (ΔG) could be determined from Eq. (8).

$$K_{f,h}^0 = \frac{kT}{h} \phi \exp \left[\frac{-\Delta G}{RT} \right] \quad \dots(8)$$

where k =Boltzman constant, h =Planck's constant, $\phi=2.0 \times 10^{-8}$ cm and other terms have their usual meanings. The values of ΔG for UO_2^{2+} -EDT and Th^{4+} -EDT systems are found to be 13.630 and 27.68 kcal/mole respectively.

The entropy of activation (ΔS) was calculated from the relation

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

and the values are -19.68 and -59.10 cal/deg/mole respectively for UO_2^{2+} and Th^{4+} systems.

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Complexes of Cu(II), Ni(II) & Co(II) with Schiff Bases Derived from Sulphadiazines & Salicylaldehyde

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Received 24 March 1975; accepted 4 October 1975

Conductometric titrations show that Cu(II), Ni(II) and Co(II) form 1:2 complexes with the Schiff base derived from sulphadiazine and salicylaldehyde. Job's method of continuous variation has been applied to determine the stability constants and free energy of formation of the complexes. In addition, Cu(II), Ni(II) and Co(II) complexes with the Schiff base, derived from sulphamerazine and salicylaldehyde, have been studied using Calvin-Bjerrum pH titration technique as modified by Irving and Rossotti. The log K values have been computed by the method of least squares. Free energy changes and probability errors have been also evaluated.

A PERUSAL of literature reveals that condensation products of sulphadiazines with salicylaldehyde and substituted salicylaldehydes are not only good complexing agents¹⁻⁴ but good bacteriostatic agents also⁵⁻⁷. We describe here the results of our studies on Cu(II), Ni(II) and Co(II) complexes with Schiff bases derived from sulphadiazine and salicylaldehyde (SUDSA) and sulphamerazine and salicylaldehyde (SUMRA).

All the chemicals employed were of AR grade. Metal perchlorates were prepared and analysed as reported earlier².

Schiff bases were prepared by condensing sulphadiazine or sulphamerazine and salicylaldehyde in stoichiometric ratio in ethanol. The products obtained were crystallized from acetone.

Conductometric measurements were carried out in 50% acetone using a W.T.W. (German) conductivity bridge and a dip-type conductivity cell (cell constant=0.616 at 20°). 10 ml of 0.005M SUDSA in 50% acetone were diluted to 100 ml and titrated against 0.005M salt solution. The results indicate 1:2 (metal-ligand) stoichiometry for the complexes.

Job's method of continuous variation⁸ was also applied to determine the metal-ligand ratio using $2 \times 10^{-3}M$ solutions. The stability constants were calculated by extrapolation of job curves as suggested by Subbarama Rao and Raghav Rao⁹

TABLE 1—METAL-LIGAND STABILITY CONSTANTS OF SUMRSA COMPLEXES

Ion	Log K_1	Log K_2	Log β	Log K_1K_2	ΔF (kcal/mole)
Cu(II)	4.88	2.72	7.60	2.16	-10.38±0.0023
Ni(II)	4.37	2.13	6.50	2.24	-8.88±0.0043
Co(II)	3.90	1.58	5.48	2.32	-7.49±0.0120

using the expression (1).

$$K_s = \frac{1-\alpha}{4\alpha^3C^2} \quad \dots(1)$$

where α is the degree of dissociation and C is the concentration of metal ion. The stability constant values (log K) of Cu(II), Ni(II) and Co(II) complexes with SUDSA are 8.07, 6.94 and 6.71 respectively while the values for degree of dissociation are 0.0789, 0.1800 and 0.2121 respectively. Values for the change in free energy (ΔF) are -10.84, -9.32 and -9.01 kcal/mole for the Cu(II), Ni(II) and Co(II) complexes respectively.

The Calvin-Bjerrum^{10,11} pH titration technique as modified by Irving and Rossotti¹² was applied to determine the protonation constant of the ligand SUMRSA and formation constants of its complexes.

The experimental procedure involved potentiometric titration of the following mixtures (containing equimolar concentrations of the common constituents) against CO₂-free sodium hydroxide at $\mu=0.2M$ (NaClO₄). (i) Perchloric acid, (ii) perchloric acid +SUMRSA, and (iii) perchloric acid +SUMRSA + metal salt solution.

From the titration curves, it is observed that the metal-ligand curve is well separated from the ligand titration curve indicating that the liberation of protons is due to chelation.

The metal-ligand stability constants were obtained from the analysis of metal-ligand formation curves drawn between \bar{n} and pL values. The proton-ligand stability constant came out to be 5.2.

Least-square method¹³ was used to obtain the metal-ligand stability constants. The values obtained at $\mu=0.2M$ are summarized in Table 1.

The above results reveal that Cu(II), Ni(II) and Co(II) form 1:2 complexes and the sequence of stability is found to be Cu>Ni>Co in accordance with the Irving-Williams¹⁴ series.

The large difference between successive formation constants may be attributed to the greater steric hindrance in the case of SUMRSA.

Authors thank the CSIR, New Delhi, for the award of a junior research fellowship to P.J.

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