

Electrochemical Studies of Oxovanadium(IV) Complex of 2-Amino-1-cyclopentene-1-dithiocarboxylate

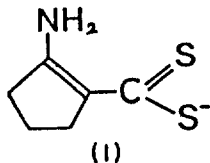
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The redox properties of 2-amino-1-cyclopentene-1-dithiocarboxylate anion (acdc) and its oxovanadium complex, VO(acdc)₂ have been investigated in dimethylformamide (DMF) with polarography and cyclic voltammetry. Bis(2-amino-1-cyclopentene-1-dithiocarboxylate) oxovanadium(IV) exhibits two polarographic oxidation waves and two reduction waves in the potential range from +0.50V to -2.4V vs. the Ag/AgCl (DMF) reference electrode. The second oxidation wave appeared at -0.08V is found to be reversible and is attributed to the formation of VO(acdc)₂⁺. The first reduction process (at -0.60V) is also reversible and this reduction process is caused by the electrode process of formation of VO(acdc)₂⁻ species. The half wave potential for the reduction, V(IV) → V(III) is more positive for oxovanadium complexes containing sulfur donor atoms than other VO(IV) complexes having oxygen or nitrogen donor atoms.

Introduction

2-amino-1-cyclopentene-1-dithiocarboxylate(acdc) anion, (I) is found to be potential chelating agent which forms intensive colored complexes with various metal ions. It was used as spectrophotometric reagent for the determination of Ni(II)¹ and Metalsky *et al.* related antifungal behavior of acdc ligand to its ability to form metal chelate.² Also the preparation of acdc chemically bound to silica and their ion exchange properties with various metal ions have been investigated.³



The physical and chemical properties of these compounds have been extensively reviewed.⁴⁻⁷ There has been some controversy on the mode of chelation of the acdc ligand because both (S,S') and (N,S') bounding to the metal ions are possible. Wasson *et al.* conducted electron spin resonance (ESR), proton nuclear magnetic resonance(NMR), and infrared spectral studies in VO(acdc)₂, and suggested the exclusive use of sulfur atoms of the acdc ligand.⁷

A few electrochemical studies of vanadium(IV) having VOSO₄ chromophore have been made, although electrochemical information on these compounds will be very useful to understand the biological role of vanadium in some living species.^{8,9} The preliminary polarographic investigation of several VO(L)₂ (L; bidentate ligands), VO(acdc)₂ was found to be proper for complete electrochemical study in DMF solvent and seemed to provide a better understanding of redox chemistry of vanadium. It was therefore deemed to execute the present study of electrochemical behavior of VO(acdc)₂.

Experimental

Preparation of Complexes. Ammonium 2-amino-1-cyclopentene-1-dithiocarboxylate, NH₄ acdc was prepared by method described previously¹⁰, and was used without further purification, VOSO₄·3H₂O was also purchased from Aldrich Co. and was recrystallized from water before use.

Oxovanadium(IV) complex of 2-amino-1-cyclopentene-1-dithiocarboxylate (VO(acdc)₂) was prepared by adding aqueous ethanol solution of ammonium 2-amino-1-cyclopentene-1-dicarboxylate dropwise to a stoichiometric amount of vanadyl sulfate in warm water. Reddish-brown precipitate formed immediately was collected by filtration, and washed successively with ethanol and ether. The collected precipitate was dried in vacuum at room temperature. The product is insoluble in water and was not recrystallized. Anal. Calcd. for VO(acdc); C, 37.59%; H, 4.21%; N, 7.31%. Found; C, 37.31%; H, 4.23%; N, 7.66%.

Polarographic Measurement. Conventional DC polarograms of free ligands and metal complex in dimethylformamide (DMF) were recorded with a Yanaco P-8 type polarograph using 0.1 M tetraethylammonium perchlorate as supporting electrolyte. A three electrode system type was employed for all conventional *dc* measurements. The reference electrode, constructed conventionally in our laboratory, was Ag/AgCl electrode (0.1 M LiCl in DMF). Polarograms of short controlled drop time were recorded with a Yanaco P-8 type polarograph (RT-8). The glass capillary dropping mercury electrode had the following characteristics; mercury column was 67 cm, flow rate of mercury, *m* was 1.645 mg/s, drop time, *t* was 4.60 sec and *m*^{2/3}*t*^{1/6} was 1.797. The dropping mercury electrode (DME) has responded quite accurately in the DMF/0.1 M Et₄NClO₄ medium, and exhibited the useful measurable range started from +0.5 V vs. Ag/AgCl electrode. This voltage range observed is in good agreement with previous results.¹¹

All test solutions were thoroughly degassed with nitrogen gas saturated with DMF and a continuous stream of nitrogen was passed over the solution while measurements were being taken. Test solutions were thermostated at 25°C and an H-type cell was used.

Cyclicvoltammetric and Coulometric Measurements. These measurements were made with a Potentiostat/Galvanostat, Model 273 of EG&G.PAR.. The voltammograms were recorded with X-Y recorder (Model BD 90 from Kipp & Zonen). The working electrodes used for cyclic voltammetry were a platinum electrode and a hanging mercury drop electrode(HMDE). The auxiliary electrode was a small piece of platinum foil. The reference electrode was Ag/AgCl electrode (0.1 M LiCl in DMF). All test solutions were also

degassed using nitrogen gas saturated with DMF. The scanning rate of cyclic voltammetric apparatus was fixed at 200 mV/sec. The working electrode used for controlled potential electrolysis was a cylindrical platinum-mesh electrode and mercury pool electrode. In all electrochemical measurements, high purity DMF solvent was obtained from Fluka Co. (spectroquality, max. H₂O; 0.003%). As no significant electrochemical impurities were found, this solvent was used as received for all measurements.

Results and Discussion

Polarographic and cyclovoltammetric behavior of 2-amino-1-cyclopentene-1-dithiocarboxylate. The polarogram of 2-amino-1-cyclopentene-1-dithiocarboxylate (acdc) ligand exhibits two oxidation waves at +0.34 V (wave 1) and -0.16 V (wave 2) vs. Ag/AgCl electrode (see Figure 1). This electrode reaction occurred at 0.34 V produces radical species. Sodium salt of pyrrolidine dithiocarbamate was reported also to form radicals via one-electron oxidation process in acetone, and dithiocarbamate compound also produces the radical reaction via one electron oxidation process in acetonitrile.¹²

Table 1 summarizes diffusion current (i_d) values measured for the acdc ligand of 10^{-3} M in DMF. Table 2 summarizes the results of dependency of wave height on the concentration of acdc. In the range of 10^{-3} to 10^{-4} M, the wave height is proportional to i_d whereas the height of complicated wave (at +0.34 V) is also proportional to i_d below 10^{-4} M. Plots of the diffusion current (i_d) vs. concentration are linear at lower concentrations. Two oxidation waves are all diffusion controlled.

It has been reported that organic compounds having dithio group is usually adsorbed into the electrode surface of dropping mercury electrode (DME)¹³. Thus, although adsorption significantly affects the behavior of this oxidation step, the limiting current of the overall electrode process is diffusion controlled. For the oxidation wave appeared at -0.16 V vs. Ag/AgCl electrode, a plot of diffusion current (i_d) vs. the square root of the mercury column height, $h^{1/2}$ is also linear. This means that the wave appeared at -0.16 V is diffusion controlled one. The plot of E vs. $\log i/(i_d - i)$ of the wave

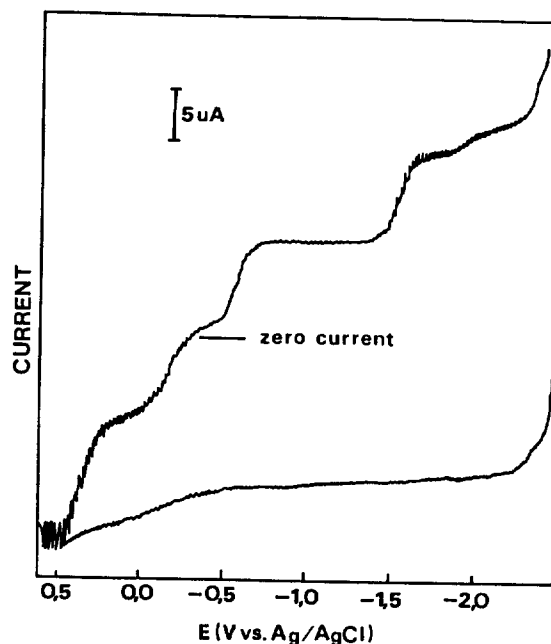


Figure 1. The dc polarogram of acdc in 0.1M tetraethylammonium perchlorate/DMF solution at 25°.

at near -0.16 V is linear and the slope of the plot is (59 ± 2) mV, showing the electrode reaction is reversible one-electron process. The $(E_{1/4} - E_{3/4})$ value is independent of DME drop-time. This value equals to (65 ± 5) mV (see Table 1), also indicating reversible nature of the electrode reaction.

Also cyclovoltammograms of the acdc ligand were obtained using HMDE (see Figure 2-a). These results are in accordance with polarographic results and wave 1 of polarogram of acdc corresponds to two anodic peaks appeared at +0.41 V and +0.25 V in CV obtained using HMDE. The peak separation between i_{pa} and i_{pc} for the peak 2 of acdc is about 60 mV. The cyclic voltammogram of acdc ligand on the glassy carbon electrode in acetone has been studied previously by us¹⁴; radical formation through the one-electron oxidation reaction (at +0.17 V) leads to the formation of dimer

Table 1. Variation of $(E_{1/4} - E_{3/4})$ Values with Drop Time 10^{-3} M Acdc Ligand

Drop time(sec)	$i_d(\mu A)$				$E_{1/4} - E_{3/4}(mV)$			
	wave 1	wave 2	wave 3	wave 4	wave 1	wave 2	wave 3	wave 4
0.2	1.9	1.2	0.7	1.6	65	65	65	70
0.4	1.6	1.3	0.7	1.8	70	60	70	70
0.8	2.0	1.5	0.7	2.0	75	60	70	70
1.6	2.2	1.6	0.8	2.1	70	60	70	75
3.2	2.3	1.7	0.7	2.3	70	60	70	70

Table 2. Dependency of Wave height(i_d) on the Concentration of Acdc Ligand

Concentration(M)	$i_d(\mu A)$				$E_{1/4} - E_{3/4}(mV)$			
	wave 1	wave 2	wave 3	wave 4	wave 1	wave 2	wave 3	wave 4
1×10^{-3}	2.15	1.25	1.95	2.45	65	60	65	70
5×10^{-4}	1.05	0.95	0.80	1.35	60	50	60	70
1×10^{-5}	0.75	0.55	0.65	0.93	60	60	60	70

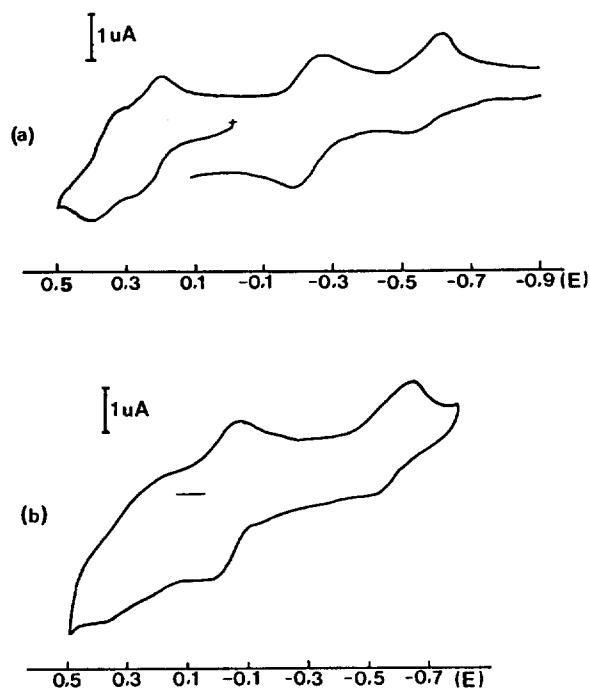
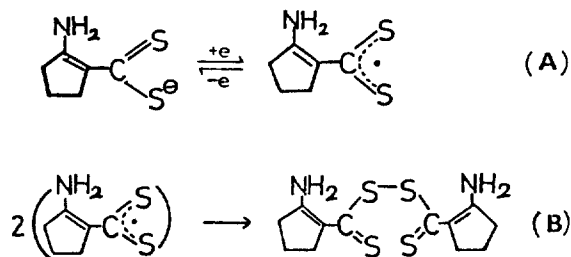


Figure 2. Cyclic voltammogram of (a) acdc ligand and (b) $\text{VO}(\text{acdc})_2$ complex with HMDE.

by coupling. Formation of six-membered ring compound and/or five-membered ring compound with the release of one free sulfur atom has been suggested. The electro-oxidation reaction of acdc at $+0.74 \text{ V}$ (*vs.* Ag/AgCl in acetone) is resulted from the oxidation of dimer formed on the electrode surface.

In this work, in order to analyze the adsorption behavior in DMF, we examined the electrocapillary characteristics of $\text{NH}_4 \text{ acdc}$ solution. The results of this examination suggest that the adsorption electrode process of free acdc ligand and the release of sulfur atom from chemically formed dimer occur simultaneously with the normal electrode process occurred at $+0.34 \text{ V}$ *vs.* Ag/AgCl electrode. Thus, the oxidation wave at $+0.34 \text{ V}$ *vs.* Ag/AgCl electrode is considered to be arisen from the formation of radical anion followed by an oxidation process or/and adsorption of acdc dimer. The electro-oxidation reaction of acdc for wave 1 (at $+0.34 \text{ V}$) can be described by the followings;



The wave 2 (at -0.16 V) which is reversible one-electron process is arisen from the mercury oxidation process. The wave 2 also exhibits the characteristics expected for a reversible charge-transfer process, followed by the chemical reaction. It thus seems that the electrode process associated with wave 2 can be described by the followings;

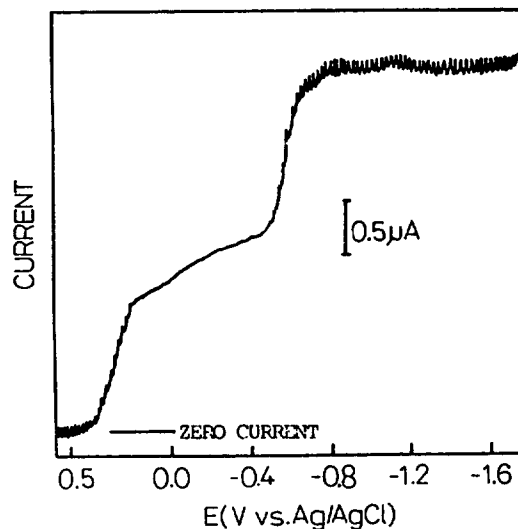


Figure 3. Conventional *dc* polarogram of $\text{Hg}(\text{acdc})_2$ complex in 0.1 M tetraethylammonium perchlorate/DMF solution at 25°C .

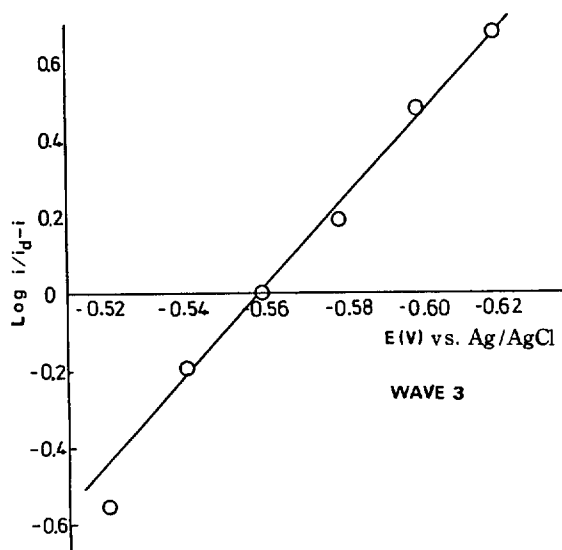
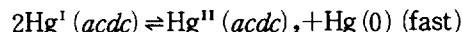
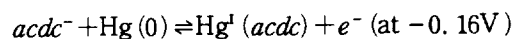


Figure 4. The logarithmic plot of acdc ligand for wave 3.



As would be expected if the above mechanism is correct, the polarogram of $\text{Hg}(\text{acdc})_2$ in DMF is found to be exactly same as that of the acdc anion (see Figure 3). Thus, the wave 3 (at -0.56 V) can be described by the following;



This electrode process occurred at -0.56 V is diffusion-controlled and one electron transfer process (see Figure 4). Figure 5 shows the polarogram of $\text{NH}_4 \text{ acdc}$ solution when H_2O is added to test solution (5 wt% in H_2O). The wave height of reduction at -0.56 V is decreased as the amount of H_2O added to solution is increased. When H_2O is added to $\text{NH}_4 \text{ acdc}$ solution, $\text{Hg}^{\text{II}}(\text{acdc})_2$ will be decomposed, and the wave height will be decreased. When excess acdc was added to the solution of $\text{Hg}(\text{acdc})_2$, a composite cathodic and anodic

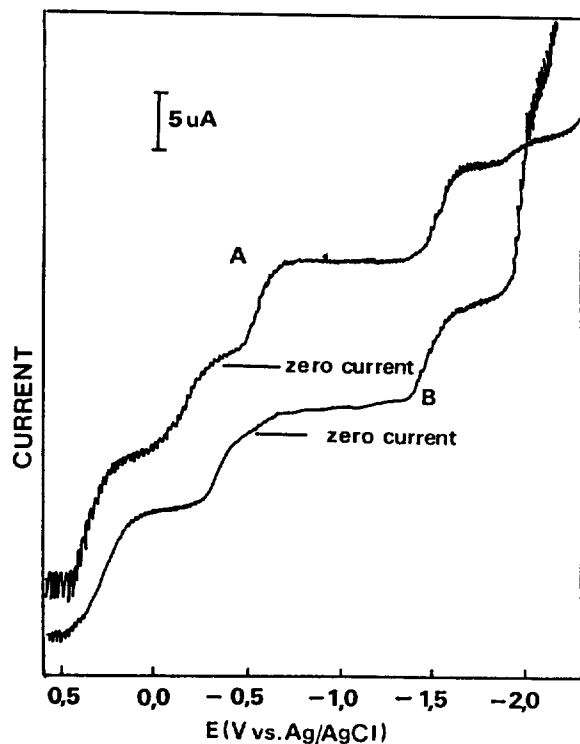


Figure 5. Comparison of the polarogram of (a) acdc ligand in DMF with the polarogram obtained after (b) adding 5% H₂O.

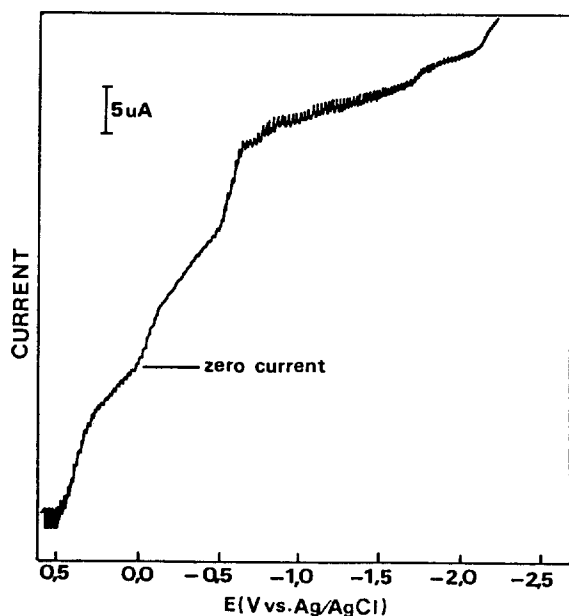


Figure 6. The dc polarogram of VO(acdc)₂ in 0.1M tetraethylammonium perchlorate/DMF solution at 25 °C.

waves could be obtained as the currents generated by mercury redox reaction increases.

Furthermore, we have found that the reduction potential is approximately equal to that of the reduction wave of Hg(acdc)₂ complex. It is concluded that the anodic wave obtained from the polarogram of solutions containing acdc anions arises from the oxidation of mercury rather than the ligand itself. This oxidation is followed by a rapid disproportion-

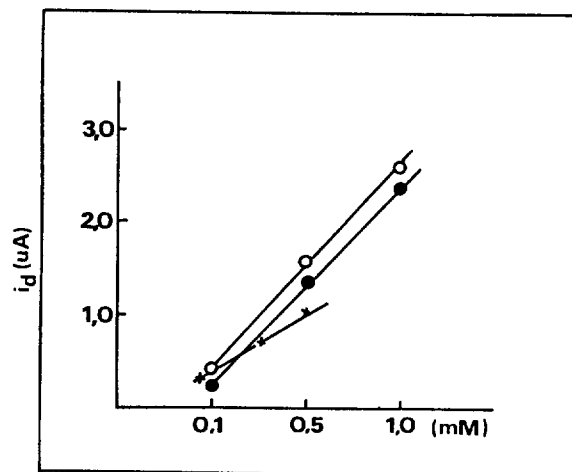


Figure 7. The plot of concentration vs. diffusion current for VO(acdc)₂ complex, ○; wave 1, X; wave 2, ●; wave 3.

Table 3. Variation of Wave Height(*i_d*) with the Change of Mercury Column Height for VO(acdc)₂ Complex

Column height (cm)	<i>i_d</i> (μA)			<i>E</i> _{1/4} - <i>E</i> _{3/4} (mV)		
	wave 1	wave 2	wave 3	wave 1	wave 2	wave 3
60	1.7	1.0	1.4	90	60	70
64	1.7	1.2	1.4	90	60	70
68	1.6	1.4	1.4	90	60	70
72	1.4	1.6	1.4	90	60	65
76	1.8	1.7	1.4	95	65	70

ation step which yields Hg^{II}(acdc)₂. The oxidation wave 1 observed in polarograms of acdc appears in the polarogram of Hg(acdc)₂ and occurs approximately at same potential value. These are certainly due to the oxidations of ligand of Hg^{II}(acdc)₂ or of Hg^I(acdc).

Polarographic and Cyclovoltammetric Behavior of (2-amino-1-cyclopentene-1-dithiocarboxylato) Oxovanadium (IV). The polarogram of oxovanadium complex shows three polarographic waves (Figure 6), *i.e.* two oxidation waves (at +0.31 V and -0.08 V) and one reduction wave (at -0.61 V). The plot of diffusion current, *i_d* vs. concentration, *C* is linear in the range of 1 × 10⁻³-1 × 10⁻⁴ M for these waves, (see Figure 7), while the half-wave potentials were independent of concentration. The plot of diffusion currents vs. the square root of the mercury column height, *h*^{1/2} is linear for wave 2. In case of waves 1 and 2, this plots are nonlinear since these are coupled with other electrode process (see Table 3).

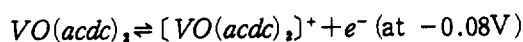
The plots of log *i*/(*i_d*-*i*) vs. potential values for wave 2 and wave 3 are all linear and the slope of these plots are (57 ± 2) mV and (70 ± 5) mV respectively. These results suggest that the electrode reaction of wave 2 is reversible one-electron oxidation, while that of wave 3 is nonreversible reduction. The slope of wave 1 is (72 ± 2) mV, and also indicate that this electrode reaction is irreversible. The number of electrons involved in the redox process was also determined by the coulometric measurements. The reversible nature of the electrode reaction of wave 2 is evidenced further by the fact that (*E*_{1/4}-*E*_{3/4}) value of wave 2 is (60 ± 5) mV and is indepen-

Table 4. Polarographic Data of VO(acdc)₂ in 0.1M Tetraethylammonium Perchlorate/DMF Solution at 25 °C

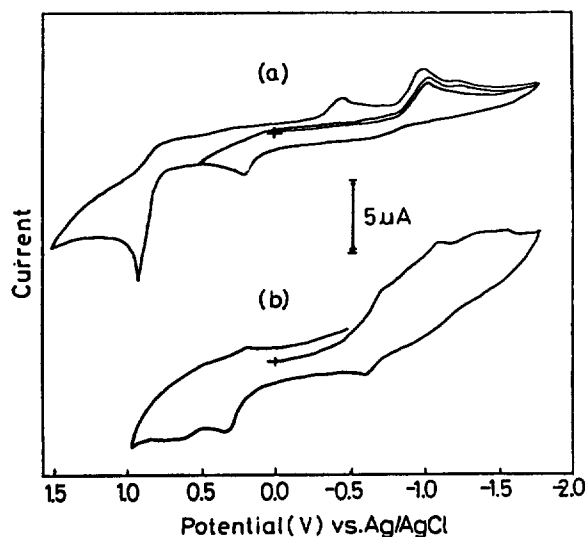
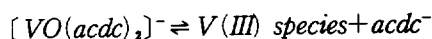
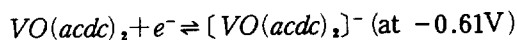
	$E_{1/2}$ (V vs. Ag/AgCl)			i_d (μ A)			$E_{1/4}-E_{3/4}$ (mV)		
	wave 1	wave 2	wave 3	wave 1	wave 2	wave 3	wave 1	wave 2	wave 3
VO(acdc) ₂	0.31	-0.08	-0.60	1.05	1.05	1.04	90	60	70
VO(acdc) ₂ /excess acdc	0.25	—	-0.61	2.30	—	2.85	90	—	70

dent of DME drop-time. The variation of ($E_{1/4}-E_{3/4}$) values against drop time are summarized in Table 3. It indicates that the wave 3 is affected by another one-electron transfer reaction occurring near at the similar reduction potential normal one electron transfer. The oxidation products of ligand are reduced at similar potential to the wave 3.

When a reversible electrode process is observed, it implies that the charge transfer is rapid compared to the time scale of the DC polarographic experiment. The oxidized form in this case generally have the same molecular structure and differ only in their electronic populations. Therefore, we can postulate that following electrode reaction take place in the VO(acdc)₂ complex;



The polarogram of VO(acdc)₂ exhibits an oxidation wave with $E_{1/2}$ value of -0.08 V vs. Ag/AgCl electrode. However, the free ligand does not exhibit any oxidation wave around this potential. This clearly demonstrates that the oxidation wave is attributed to the oxidation of vanadium complex. The other oxidation wave (at +0.31 V) and reduction wave (at -0.60 V) observed for VO(acdc)₂ complex, were also observed at similar potential values in the polarogram of Hg(acdc)₂ (see Figure 3). The reduction wave at -0.61 V is attributed to the reduction of VO(acdc)₂ complex, followed by the chemical reaction as follows;

**Figure 8.** Cyclic voltammogram of (a) acdc ligand and (b) VO(acdc)₂ complex. (scan rate; 200 mV/sec, supporting electrolyte; 0.1M Et₄NClO₄ in DMF, electrode; Pt electrode).

Other reduction waves (around -0.9 V, -1.4 V) of VO(acdc)₂ seem to be associated with the reduction of the free ligand dissociated from the complex and V(III) species are generated from the dissociation of (VO(acdc)₂)⁻ ion. When an excess acdc ligands were added to the VO(acdc)₂ solution, the reduction wave at -0.08 V gradually increased as the free ligand oxidizes Hg(O) to Hg(I) acdc (see Table 4). Also,

Table 5. The Peak Potential(E_p) vs. Ag/AgCl Electrode in Cyclic Voltammogram for Acdc and VO(acdc)₂

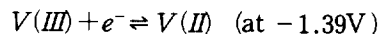
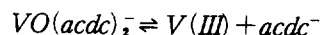
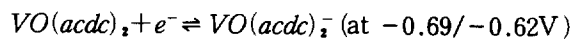
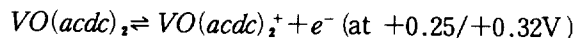
	Reaction	Pt electrode	HMDE	Remark
		(E_{pc}/E_{pa})	(E_{pc}/E_{pa})	
acdc ⁽¹⁴⁾	$NH_2C_5H_6CS_2 \xrightleftharpoons[+e]{-e} NH_2C_5H_6CS_2^+$	/ +0.19V		Chemical Rxn.
	$2NH_2C_5H_6CS_2 \longrightarrow (NH_2C_5H_6CS_2)_2$			
	$(NH_2C_5H_6CS_2) \xrightleftharpoons[-2e]{+e} (NH_2C_5H_6)_2C_2S_3 + S$	/ +0.93V		
	reduction of $NH_2C_5H_6CS_2^-$	-0.98V / -1.25V		
	$acdc^- + Hg(0) \xrightleftharpoons[+e]{-e} Hg(acdc)$		-0.26V / -0.18V	Chemical Rxn.
VO(acdc) ₂	$2Hg(acdc) \rightleftharpoons Hg(acdc)_2 + Hg(0)$			
	$Hg(acdc)_2 \xrightleftharpoons[+e]{-e} Hg(acdc) + acdc^-$		-0.60V / -0.53V	
	$VO(acdc)_2 \xrightleftharpoons[+e]{-e} VO(acdc)_2^+$	+0.25V / +0.32V	-0.05V / +0.01V	Chemical Rxn.
	$VO(acdc)_2 \xrightleftharpoons[+e]{-e} VO(acdc)_2^-$	-0.69V / -0.62V	-0.61V / -0.54V	
	$VO(acdc)_2^- \longrightarrow V(III) + acdc^-$			
	$V(III) \xrightarrow{+e} V(II)$	-1.39V /		

Table 6. Polarographic Data for Oxidation and Reduction of Some Oxovanadium Complexes

Compounds	$E_{1/2}$ (V vs. Ag/AgCl)				Remark
	wave 1	wave 2	wave 3	wave 4	
VO(acdc) ₂	0.31(ox. I)	-0.08(R)	-0.60(Q.R)	-1.53	DMF
acdc	0.34	-0.16	-0.56		DMF
VO(acdc) ₂	0.32(ox)	-0.40			DMF/H ₂ O
VO(mpno) ₂	0.57(ox.R)	-1.09	-1.76(I)		acetone ^a
mpno	-0.21	-0.50			
V(dtc) ₃	0.35(ox.I)	-1.08(R)			DMF
VO(dtc) ₂		-1.35(I)			DMF ^b
VQ ₃	0.45(ox.I)	-1.48(R)			DMF
VO(Q) ²	0.76(ox.I)				DMF ^c
VO(salene) ₂	0.30(ox.R)	-1.55(R)			acetone ^d
VO(acdc) ₂	0.81(ox.R)	-1.90(R)			DMSO ^e

R = reversible, I = irreversible, Q.R = quasi-reversible, OX = oxidation, Q = 8-quinolinol, dtc = dithiocarbamate. mpno = mercaptopyridine-N-oxide. ^areference 15. ^breference 16. ^creference 12. ^dreference 17. ^ereference 18.

cyclovoltammogram of the acdc ligand and VO(acdc)₂ complex were obtained using hanging mercury drop electrode (HMDE) (see Figure 2) and Pt electrode (see Figure 8). In VO(acdc)₂ complex, voltammogram obtained by the use of HMDE are in accordance with the polarographic results exactly. The reversible electrode process was confirmed by the observation of the peak separation of anodic and cathodic process, and is found to be reversible, one-electron transfer process, which is further confirmed by the coulometric measurements. However, when the platinum electrode is used, the peak potential for the reaction, VO(acdc)₂ - VO(acdc)₂⁺ + e is shifted to more positive potential region (see Table 5). We also assigned the CV peaks obtained using platinum electrode for the electrochemical process of VO(acdc)₂, based on CV data of free ligand, acdc (see Figure 8). In cyclic voltammogram (CV) of the VO(acdc)₂ complex, the new peaks appear at +0.25/+0.32, -0.69/-0.62, -1.39 V vs. Ag/AgCl electrode. We assigned these peaks as follow;



The half-wave potential of the first reduction wave (at

-0.61 V) of oxovanadium (IV) complexes containing sulfur as donor atoms is more positive than those of other complexes having oxygen or nitrogen donor atoms when comparisons are made among oxovanadium (IV) complexes (see Table 6). Sulfur containing ligands seem to stabilize the lower oxidation state of vanadium while oxygen or nitrogen containing ligands provide better coordination environment for the higher oxidation state of vanadium as suggested by Sawyer et al.¹²

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