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Polarographic Behavior of Oxovanadium (IV) Complex of Mercaptopyridine N-Oxide

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The redox properties of 2-mercaptopyridine N-oxide (mpno) and its oxovanadium complex, VO $(mpno)_2$ have been studied by the use of polarography and cyclic voltammetry. The radical anion of mpno is generated in acetone and is adsorbed to the electrode to form an adsorption wave at -0.21 V vs Ag/AgCl electrode. The normal wave appeared at -0.50 V is attributed to the formation of radical anion. The VO $(mpno)_2$ exhibits one oxidation wave at +0.57 V, and two reduction waves at -1.07 V and -1.76 V vs. Ag/AgCl electrode; the oxidation is fully reversible one-electron process ($VO(mpno)_2 \rightleftharpoons VO(mpno)_2^+ + e$). The reduction wave at -1.07 V is quasireversible and is arised from the formation of VO $(mpno)_2^-$. The second reduction wave at -1.76 V is irreversible and this reduction process consists of two one-electron steps. The sulfur containing ligands seem to enhance the stability of lower oxidation state of vanadium while the oxygen or nitrogen donor of the ligands stabilize the higher oxidation state of vanadium when comparisons are made among several oxovanadium complexes.

Introduction

Although the chemistry of vanadium is now quite well understood, its biological role in some living species still remains uncertain. In seawater, vanadium exists as the vanadium anion, $H_2VO_4^-$ (+5), at a concentration of 5×10^{-8} M[1]. In vanadium containing blood cell of some axcidian, the concentration of vanadium can be as high as 0.1M[2], and the intracellular vanadium is mainly in the V (III) state, with about 10% in V (IV) state[3,4]. Accumulation of vanadium occurs in some sort of ascidian and it is believed that accumulation appears to be driven by the redox processes in a specific vanadate transport system of the blood cells of ascidian[5]. It seems to be essential to understand the electrochemical behavior of vanadium to elucidate its biological role and accumulation mechanism in living species. However, a few electrochemical studies in vanadium (IV) or vanadium (III) complexes have been made.[6-11] This may be attributed to the fact that oxovanadium (IV) complexes do not seem to warrant an electrochemical investigation since most oxovanadium (IV) complexes are unstable and/or insoluble in most organic solvent as well as in water. Eventhough previous works have been carried out on some oxovanadium complexes with bidentate ligands[6-9], any informative electrochemical results have not been reported on the vanadium complexes having both sulfur and oxygen as donor atoms. During the preliminary polarogrphic investigation of several oxovanadium complexes of type VO $(L)_2$ (L: bidentate ligand), oxovanadium complex of 2-mercaptopyridine N-oxide ($VO(mpno)_2$) was found to be proper for complete electrochemical study, and seemed to provide a better understanding of redox chemistry of vanadium. This study was carried out in aprotic solvent mainly due to the poor solubility of this complex in water.

Experimental

Preperation of Complexes. 2-mercaptopyridine N-oxide (mpno) was obtained from Aldrich Co. and was used without further purification. $VOSO_4 \cdot 3H_2O$ was also purchased from Aldrich Co. and was recrystalized from water before use. Oxovanadium (IV) complex of 2-mercaptopyridine N-oxide ($VO(mpno)_2$) was prepared by adding aqueous solution of sodium salt of 2-mercaptopyridine N-oxide (obtained by neutralizing the ligand) dropwise to a stoichiometric amount of vanadyl sulfate in warm water. Violet 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 recrystalized. Anal. Calcd.

for VO $(C_5H_4NOS)_2$; C, 37.38%; H, 3.14%; N, 8.76%. Found: C, 37.5%; H, 3.13%; N, 8.91%.

Polarographic Measurement. Conventional dc polarograms of free ligand and metal complex in acetone were recorded with a Yanaco P-8 type polarograph using 0.1 M tetraethylammonium perchlorate as supporting electrolyte. A three electrode system using a Yanaco PT-8 type was employed for all conventional dc measurements. The reference electrode, constructed in our laboratory, was Ag/AgCl electrode (0.1 M LiCl in acetone). 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 height was 67cm in open circuit, flow rate of mercury,m was 1.645mg/s, drop time,t was 4.60sec and $m^{2/3}t^{1/6}$ was 1.797. The dropping mercury electrode (DME) has responsed quite accurately in the acetone/0.1M Et_4NClO_4 medium, and exihibited the useful measurable rang starting from +0.8V vs. Ag/AgCl electrode. This range observed is in good agreement with previous results.[12]

All test solutions were throughly degassed with nitrogen gas saturated with acetone and a continuous stream of nitrogen was passed over the solution while measurements were being taken. Test solutions were thermostated at 25 ± 0.1 C and an H-type cell was used.

Cyclic Voltammetric and Coulometric Measurements. Cyclic voltammetric measurements were made with a three-electrode potentiostat, composed of solid state operational amplifiers which were constructed in our laboratory. The voltammograms were recorded with an X-Y recorder (Watanabe Instruments Corp. model 451). The working electrode used for cyclic voltammetry was a glassy carbon electrode (Yanaco, GC-P2 type, diameter: 3mm). The auxiliary electrode was made of platinum wire. The reference electrode with glass frit tip was Ag/AgCl electrode (0.1 M LiCl in acetone). All test solutions were also degassed using nitrogen gas saturated with acetone. The scanning rate of cyclic voltammetric apparatus was fixed at 40 mV/sec. The working electrode used for controlled potential electrolysis was a cylindrical platinum-mesh electrode and mercury pool electrode. Coulometric determination of the number of electrons was undertaken by the use of Potentiostat/Galvanostat Model 273 of EG&G PAR.

Conductance Measurements. Contuctance measerments were made to determine pka of free ligand and equivalant conductance of VO $(mpno)_2$ in acetone. The conduct meter used was TOA model CM-2A (Tokyo TOA Electronics) and the cell constant of the electrode was 0.0995. The pka of mpno in 6.55 at 20°C and the equivalant conductance of VO $(mpno)_2$ (0.1 mM) in acetone is 0.795 cm^2/ohm equiv.. Conductance measurements indicate that the mpno and VO $(mpno)_2$ exist predominantly as neutral species in acetone solvent.

Results and Discussion

Polarographic and cyclovoltammetric behavior of 2-mercaptopyridine N-oxide. Figure 1 shows typical polarogram of the mpno ligand. The mpno ligand exihibits a small wave at -0.21 V vs. Ag/AgCl electrode and one well-defined polarographic reduction wave at a potential of -0.50 V vs. Ag/AgCl electrode. The height and the limiting current of prewave appeared at -0.21 V is independent of the concentration in the range of 1×10^{-4}-1×10^{-3}M. Also the maximum of the electrocapillary curve of mpno ligand shifted to more negative potentials than that of supporting electrolyte (see Figure 2). This type of shift usually occurs in many other sulfur containing organic compounds which exihibit and adsorption wave.[13] So the prewave is considered to be an adsorption wave.

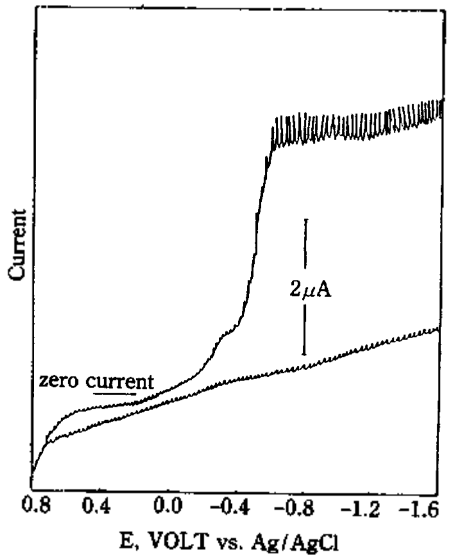


Figure 1. The dc polrarogram of mpno in 0.1 M tetraethylammonium perchlorate/aceton solution at 25°C.

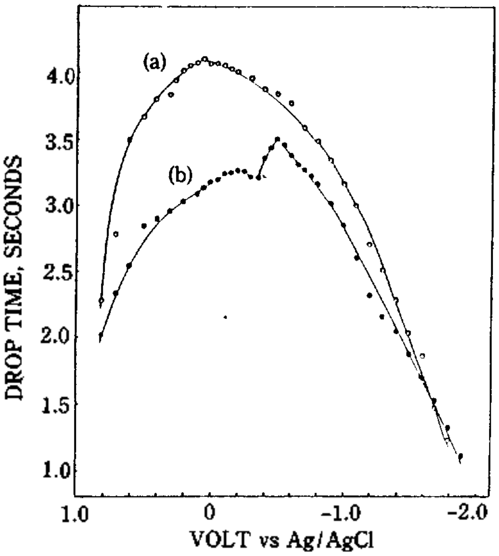


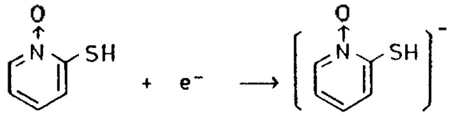
Figure 2. The electrocapillary curves (DME at h = 68 cm) of (a) 0.1 M Et_4NClO_4 in acetone (o) and (b) soultion (a) plus 10^{-3}M mpno (●).

For the normal reduction wave appeared at -0.50 V vs. Ag/AgCl electrode, a plot of diffusion current i_d vs. concentration is linear, and a plot of i_d vs. the square root of the mercury column height, $h^{1/2}$ is also linear. These indicate that the wave at -0.50 V vs. Ag/AgCl is diffusion controlled. The plot of $E_{1/2}$ vs. log $i/(i_d$-$i)$ of the wave is linear and the slope of the plot is 65 ± 2 mV, indicating the electrode reaction is reversible. The $(E_{1/4}$-$E_{3/4})$ value is indenpendent of DME

Table 1. Variation of $E_{1/2}$ and ($E_{1/4}$-$E_{3/4}$) Values with Drop-time for the Mpno Ligand

drop time (sec)	concentration (M)	$E_{1/2}$ (V vs.Ag/AgCl)	i_d (μA)	$E_{1/4}$-$E_{3/4}$ (mV)
0.26	5×10^{-4}	-0.50	1.7	70
1.06	5×10^{-4}	-0.49	2.1	70
2.13	5×10^{-4}	-0.51	2.6	75
4.26	5×10^{-4}	-0.49	2.7	70

drop time. This value equals to 70 ± 5 mV (see Table 1), also indicating reversible nature of the electrode reaction. The height of this normal wave, which is diffusion controlled, decreases as the concentration of mpno ligand decreases. In aprotic solvents many aromatic hydrocarbons and their derivatives are reported to be reduced electrolytically in two successive one electron steps;[12] the first step is the formation of radical anions and the second step produces the dianion. As a result, a polarogram of such hydrocarbon usually consists of two one electron waves, and the second wave generally occurs at potential about 0.5 V more negative than the first.[12] Although we observed two waves for the mpno ligand, the redox processes seem not to occur via above mechanism; the first wave observed at -0.20 V vs. Ag/AgCl is found to be an adsorption wave. The normal wave observed at -0.50 V seems to be attributed to the formation of radical anion. This reduction process is diffusion controlled and is found to be an one electron process based on the result of the coulometric measurement.



When water is added, the adsorption wave gradually disappears, and it is completely eliminated when the content of water reaches to 5%. It is well known that some aromatic derivatives are reduced to its radical anions in aprotic solvent but the reduction of those compounds involve two electrons in water, not producing radical anions.[14] So we can conclude that the prewave at -0.21 V vs. Ag/AgCl is formed when radical anion of mpno is adsorbed on mercury surface. The presence of water molecule inhibits the formation of radical anion, resulting in the disappearence of the adsorption wave. Relatively large difference in halfwave potentials between the adsorption wave and the normal reduction wave implies that this radical anion generated in acetone by electrolysis is stable relative to the life time of mercury drop. Also cyclovoltammograms of the mpno were obtained by the use of glassy carbon electrode and HMDE (see Table 2). The peak seperation between cathodic and anodic peaks for the wave of mpno is about 60 mV. The reduction is found reversible and is one electron transfer process (see Figure 3).

Table 2. The Peak Potential Values (E_p) vs. Ag/AgCl Electrode in Cyclic Voltammograms for VO $(mpno)_2$ and Mpno[a]

	Glassy carbon electrode		HMDE	
	E_{pc}	E_{pa}	E_{pc}	E_{pa}
$VO(mpno)_2$ peak 1	+1.06V	+1.12V	+0.49V	+0.55V
peak 2	-1.22 V		-1.08V	
peak 3	-1.4~-1.8V		-1.2~-1.7V	
mpno peak 1		+0.95V	-0.45V	-0.38V
peak 2	-1.45V			

[a] Cyclic voltammetric peak potential was obtained in acetone with tetraethylammonium perchlorate as supporting electrolyte. the scan rate was 50 mV S^{-1} at all measurements.

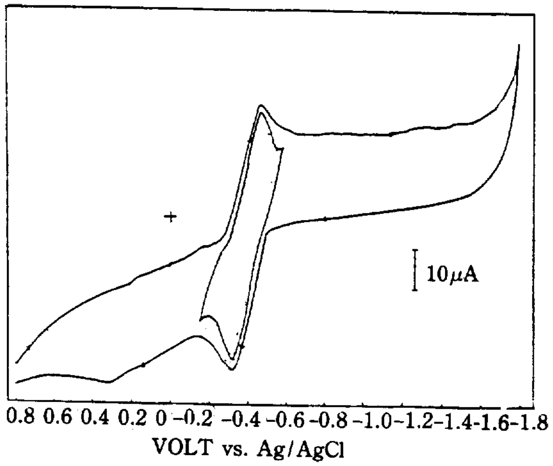


Figure 3. Cyclic voltammogram of mpno with HMDE (in acetone/0.1M tetraethyl ammonium perchlorate).

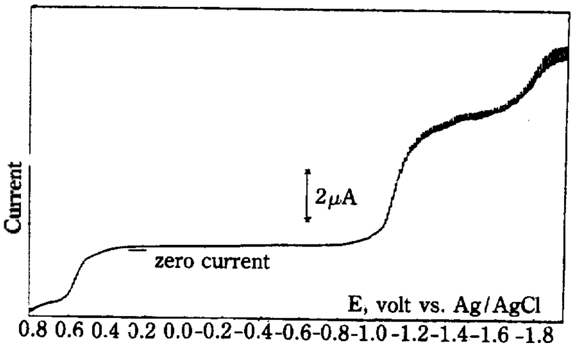


Figure 4. The dc polarogram of $VO(mpno)_2$ in 0.1 M tetraethylammonium perchlorate/acetone solution at 25°C.

Polarographic and Cyclovoltammetric Behavior of (2-Mercaptopyridine-N-oxo) Oxovanadium (IV). The polarogram of oxovanadium complex shows three polarographic waves in Fig. 4, i.e., one oxidation wave (wave 1; +0.57 V vs. Ag/AgCl electrode) and two reduction waves (wave 2; -1.09 V and wave 3; -1.76 V vs. Ag/AgCl electrode). The plot of diffusion current, i_d vs. concentration, C is linear in the range of 1×10^{-3} - 1×10^{-4} M both for wave 1 and wave 2. The plot of i_d vs. the square root of the mercury column height, $h^{1/2}$ is linear. Therefore the wave 1, wave 2 and wave 3 are controlled by diffusion. The plot of $E_{1/2}$ vs. log $i/(i_d\text{-}i)$ is also linear for wave 1 and wave 2. However, the plot of wave 3 showes slight deviation from linearity at both ends of the wave. The slopes of these plots are 57 ± 2 mV, 67 ± 2 mV and 92 ± 2 mV respectively. These results indicate that the electrode reaction of wave 1 is a reversible one-electron process while that of wave 2 is quasi-reversible and that of wave 3 is irreversible. The number of electrons involved in the redox processes was also determined by the coulometric measurements. the reversible nature of the elec-

Table 3. Variation of $E_{1/2}$ and ($E_{1/4}$-$E_{3/4}$) Values with Drop-time for VO $(mpno)_2$

drop time (sec)	$E_{1/2}$(V vs.Ag/AgCl)		i_d(uA)		$E_{1/4}$-$E_{3/4}$(mV)	
	wave 1	wave 2	wave 1	wave 2	wave 1	wave 2
3.20	0.58	-1.09	2.83	1.70	60	60
1.60	0.58	-1.08	2.53	1.70	60	65
0.80	0.58	-1.14	2.02	1.85	60	60
0.40	0.58	-1.16	1.72	1.72	65	60
0.20	0.58	-1.15	1.93	1.93	60	65

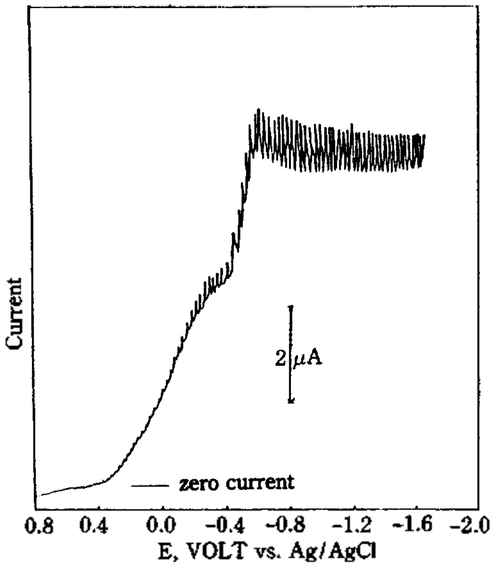


Figure 5. Conventional dc polarogram of $Hg(mpno)_2$ complex in 0.1 M tetraethylammonium perchlorate/acetone solution at 25°C.

trode reaction of wave 1 is evidenced further by the fact that ($E_{1/4}$-$E_{3/4}$) value of wave 1 is 60 ± 2 mV and is independent of DME drop time. The variation of $E_{1/2}$ and ($E_{1/4}$-$E_{3/4}$) values against drop time are summaried in Table 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 suggest the following electrode reaction might take place in the VO $(mpno)_2$ complex;

$$VO(mpno)_2 \rightleftharpoons VO(mpno)_2^+ + e^- \qquad (\text{Wave 1})$$

The VO $(mpno)_2$ exhibits an oxidation wave with $E_{1/2}$ value of + 0.57 V vs. Ag/AgCl electrode while the free ligand does not exhibit any oxidation wave. This clearly indicate that the oxidation wave is attributed to the oxidation of vanadium complex. Also the polarogram of Hg $(mpno)_2$ does not exhibit oxidative wave but only shows reductive waves (Figure 5). Moreover, the $E_{1/2}$ and i_d values of wave 1 are not affected by the presence of excess free ligand (see Figure 6). Resultantly, the oxidation wave of VO $(mpno)_2$ seems not to be associated with the ligand dissociation.

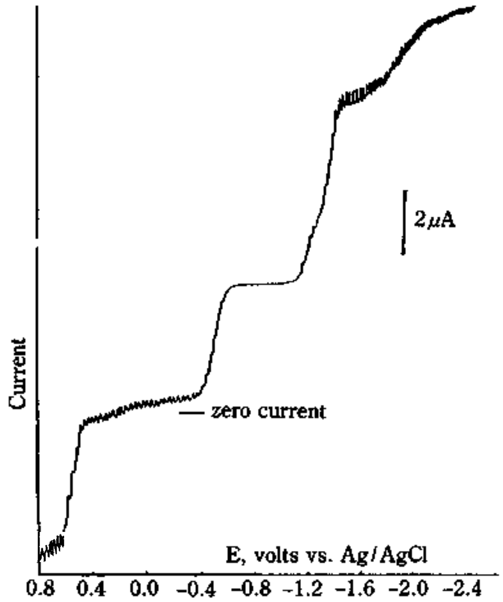


Figure 6. The polarogram of $VO(mpno)_2$ obtained after adding the mpno ligand in exess in 0.1 M tetraethylammonium perchlorate/acetone solution at 25°C.

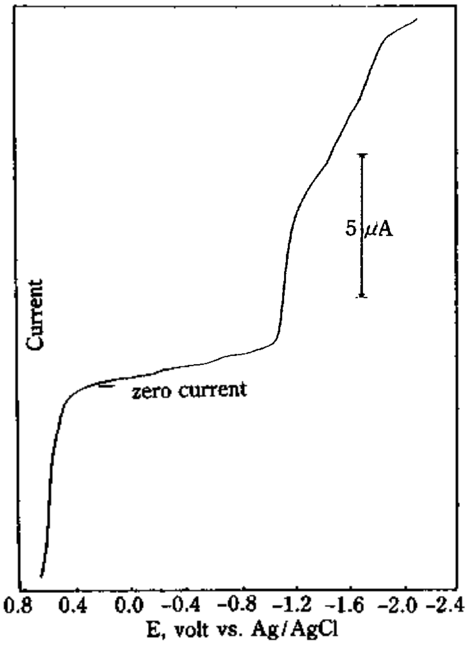


Figure 7. Rapid dc polarogram of $VO(mpno)_2$ complex in 0.1 M tetraethylammonium perchlorate/acetone solution at 25°C.

Under rapid polarographic condition, with short controlled drop time of 0.40 sec or less, polarographic parameters remain unalterd and the heights of the wave 1 and the wave 2 are equal (see Table 3). Since two waves have the same diffusion current constant, the same number of electrons must be involved in both electrode processes. This indicates that electroreduction reaction of wave 2 is one electron process. The reduced form should essentially have the same five or six coordiante structure like VO $(mpno)_2$. If the reduction causes gross structural change such as the loss of a ligand, this reduction would not occur rapidly within the polarographic time scale. The electroreduction reaction of VO $(mpno)_2$ for wave 2 can be described by the following;

$$VO(mpno)_2 + e^- \rightleftharpoons VO(mpno)_2^- \qquad (\text{Wave 2})$$

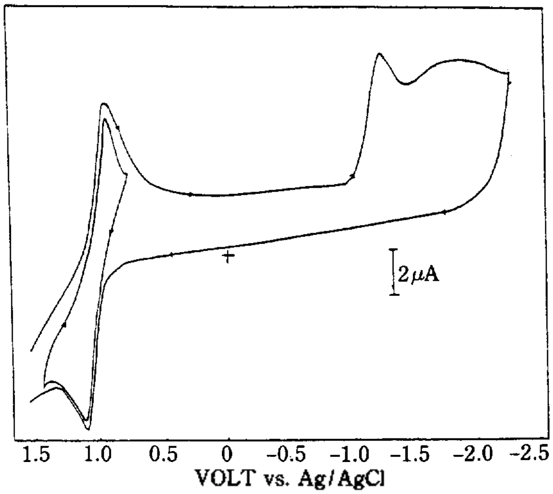


Figure 8. Cyclic voltammogram of VO(mpno)$_2$ with glassy carbon electrode in 0.1M tetraethylammonium perchlorate/acetone solution at 25°C.

The conventional polarogram shows that wave 3 has an slight inflection near the midpoint, indicating some complexity of the electrode process. The overall wave has apparent ($E_{1/4}$-$E_{3/4}$) value of about 120 mV. The apparent large ($E_{1/4}$-$E_{3/4}$) value indicates the possible presences of two separate but incompletely resolved, reduction steps. The large ($E_{1/4}$-$E_{3/4}$) value also suggests the irreversible nature of the process. Fortunately, the use of rapid dc polarography of short controlled drop time enabled us to resolve wave 3 into two waves (see Figure 7) which are of equal diffusion current. Thus the electrode process for wave 3 involves two one-electron reductions. The following two mechanisms can be postulated for the electroreduction of wave 3;

$$(1)\ \mathrm{VO\,(mpno)_2^-} \xrightarrow{e} \mathrm{V\,(III)} \xrightarrow{e} \mathrm{V\,(II)} \xrightarrow{e} \mathrm{V\,(I)}$$

$$(2)\ \mathrm{VO\,(mpno)_2^-} \xrightarrow{2e} \mathrm{V\,(II)} \qquad (\text{Wave } 3)$$

$$\mathrm{VO\,(mpno)_2^-} \xrightarrow{e} \mathrm{V(III)} \xrightarrow{e} \mathrm{V\,(II)}$$

The dissociation of metal-ligand bonds as in the first step of mechanism (1) was previously suggested both by Kitamura[9-a] and Asri Nawi[9-b] for the similar redox process of VO (acac)$_2$ in acetonitrile and dimethylsulfoxide. However, oxidation state of +1 for vanadium is quite uncommon except for some organometallic compound and the generation of V (I) species is quite unlikely. The mechanism (2) involves parallel one electron transfer processes and seems to be more plausible. If reduction potentials of two parallel processes of similar values, then it will complicate the wave form and so is true for wave 3. Polarographic experimental evidences that favor mechanism (2) are the followings; firstly, the diffusion current of wave 3 is smaller than that of wave 1 or wave 2. Secondly, wave 2 is shifted negatively in the presence of exess free ligand and some degree of dissociation of coordinated ligand seems to follow the reduction process of wave 2. However, we can not eliminate the possible reduction of dissociated ligand mpno for wave 3. The cyclic voltammetric results for wave 1 and wave 2 of the complex is consistent with the dc polarographic results. The cyclic voltammogram of VO (mpno)$_2$ is shown in figure 8. The first peak of voltammogram exhibits its reversible nature, but the 3rd peak does clearly exhibit their irreversibility. The peak potential values of cathodic and anoidic peak (Epc and Epa) are summarized in Table 2.

Table 4. Polarographic Data for Oxidation and Reduction of some Oxovanadium Complexes

Compound	$E_{1/2}$ (V vs.Ag/AgCl)[e]			Remark
	wave 1	wave 2	wave 3	
VO(mpno)$_2$	+0.57(ox, R)	−1.09	−1.76(I)	acetone
mpno	−0.21	−0.50		
VO(mpno)$_2$	+0.32(ox)	−0.50	−1.55	acetone/H_2O
V(dtc)$_3$[a]	+0.35(ox,I)	−1.08(R)		DMF
VQ$_3$[a]	+0.45(ox, I)	−1.48(R)		DMF
VO(dtc)$_2$[a]		−1.35(I)		DMF
VOQ$_2$[b]	+0.76(ox, I)			DMF
VO(salene)$_2$[c]	+0.3(ox, R)	−1.55(R)		acetone
VO(acac)$_2$[d]	+0.81(ox, R)	−1.90(R)		DMSO

[a] reference 6. [b] reference 7. [c] reference 10. [d] reference 9-(b) [e] R = reversible, I = irreversible, ox = oxidation Q = 8-quinolinol. dtc. = dithiocarbamate.

No anodic peak of reduction of VO (mpno)$_2$ were observed in cyclovoltammogram at a given scan rate of 40 mV/sec. However, anodic peak of the 2nd were observed in linear sweep voltammogram at a given scan rate of 20 mV/sec. When the excess of free ligand is added to the solution of VO (mpno)$_2$, the polarogram exhibits two more reduction waves at −0.50 V and −1.18 V vs. Ag/AgCl electrode in addition to the original polarographic waves of VO (mpno)$_2$ were not affected by the presence of free ligand (see Figure 6). The height of new wave appeared at −0.50 V increases lineary as the concentration of ligand increase. The height of wave at −1.18 V also increases but the increasing tendency is not linear and sharply drops as the concentration of free ligand increases. The wave at −0.50 V is definitely due to the formation of radical anion by the reduction of ligand. The wave at −1.18 V seems to be caused by the formation of VL$_3$ type species in the presence of excess ligand. Similar results were reported previously by Asri Nawi et. al. for VO (acac)$_2$ complex.[9-b]

In ascidian, the intracellular vanadium is mainly in the form of V (III) state and with up to 10% in the VO (IV) state. Also Dingley[15] reported that the reduction of V (V) to V (IV) is reversible and fast in the whole blood cell of ascidian, and they suggested VO^{+2} species in the acidian cell are reduced to V (III) species irreversively and this non-transportable cation species, V (III) are accumulated in the blood cell of ascidian. These results are well consistent with the electrochemical behavior of VO (mpno)$_2$. Polarographic results for oxidation and reduction of VO (mpno)$_2$ along with other oxovanadium (IV) complexes are summarized in Table 4.

The half-wave potential of the first reduction wave (wave 2) of oxovanadium (IV) complexes containing sulfur as donor atoms is more positive than those of the complexes having oxygen or nitrogen donor atoms when the comparisons are made among oxovanadium (IV) complexes.

Sulfur containing ligands seem to stabilize the lower oxidation state of vanadium while oxygen or nitrogen-containing ligands provide a better coordination sphere for reversible oxidation-reduction of higher oxidation state as suggested by Sawyer *et. al.*.[7]

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Proton Magnetic Resonance Study of the Amino Group of Thioacetamide (TA) I. Quadrupole Relaxation Effects in NH_2 of Thioacetamide

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Nitrogen-14 quadrupolar relaxation has been observed in the amino proton nmr spectra of TA in acetone and methanol solutions over the temperature range −83°C to + 35°C. The proton nmr lineshapes were analyzed to yield a ^{14}N spin lattice relaxation time $(T_1)_N$ as a function of temperature. Activation energies and correlation times at 25°C for the molecular reorientation in the two solution phases have been calculated and the results are discussed.

Introduction

Nuclei with large electric quadruple moment are relaxed so effectively by the mechanism of quadrupolar relaxation that they usually show no observable effects in the spectrum of a spin-1/2 nucleus. But if there is no or incomplete washing-out of spin-spin coupling between a spin-1/2 nucleus and spin-1 nucleus, the coupling constant can be directly observed[1-3]. It is because the fluctuating electric field gradient is either zero by symmetry or small as for isocyanides[3]. In that case, the lineshape analysis of the former nuclei gives us an alternative method to obtain an information about the quadrupolar interactions[4,5]. The theoretical basis of this method lies in the fact that under the fast exchange conditions the scalar coupling can become the second kind of scalar relaxation mechanism for spin-1/2 nuclei[6].

The ^1H-nmr spectra of amino group of TA in some solvents are split into three lines even at room temperature This means that the nitrogen nucleus of TA in those solvents has an increased symmetric environment in the electric field gradients. Therefore it is possible to obtain the ^{14}N relaxation times of TA quantitatively by analyzing the lineshapes of the proton spectra.

In the present paper we study the nuclear magnetic relaxation behavior of the amino group of TA in acetone and methanol solutions. From the lineshape analysis we obtained the reoreintational correlation times of the amino group as a function of temperature, and tried to interprete them in terms of possible structural changes in the above two systems.

Experimental

The TA (GR-grade) from Merck AG., Darmstadt was used without further purification. Deuterated acetone (d-6) and methanol (d-3) were obtained from Sharp & Dohme, Munich, and Deuterium content was more than 99 atom %. An nmr glass tube of 5-mm diameter was filled with 0.5 m*l* of liquid samples and sealed after degassing by several freeze-pump-thaw cycles. The concentration of both TA solutions was