CHEMISTRY LETTERS, pp. 1071-1074, 1975. Published by the Chemical Society of Japan

STUDIES ON ELECTRODE PROCESSES OF OXOVANADIUM(IV). III. SOLVENT EFFECT ON REDUCTION POTENTIAL OF VANADYL ACETYLACETONATE

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The correspondence of the reduction potential of vanadyl acetylacetonate and the wavelength of the optical absorption band was well recognized from the solvent effect on the ligand configuration. However, the noticeable deviation of the data in the aqueous solution was observed. The corelation to the donor number is also discussed.

The purpose of this investigation is to study the solvent effect on the reduction potential of vanadyl acetylacetonate (VA), [VO(acac)$_2$], and to clarify its electrochemical significance in relation to the ligand structure of the complex.

The electrolytic reduction of VA at the dropping mercury electrode (DME) involves complication associated with the irreversible electron transfer process and the coupled chemical reactions. However, the half-wave potential corresponding to the reversible electron transfer process can be estimated by the logarithmic analysis of the polarographic current-potential curve developed in the presence of excess acetylacetone (Hacac) as reported in the preceding paper.[1)] This value of the half-wave potential, $E^r_{1/2}$, for the reversible one-electron transfer process was estimated by the extrapolation of the initial portion of $\log[i/(i_d-i)]$ versus E plot, where i_d was approximated by one half of the overall limiting current corresponding to n=2 (i: the current at E, i_d: the diffusion-controlled current, E: the electrode potential, n: the number of electrons transferred per an ion or molecule). The half-wave potential thus estimated is intrinsically an imaginary value, nevertheless it bears a thermodynamic consideration.

The first electron transfer to VA results in the formation of the V(III) entity coupled with the breaking of the V-O bond as shown in Eqs. (1) and (2), where * denotes an intermediate state (cf. Ref. 1)):

$$[\mathrm{VO(acac)_2}] + \mathrm{Hacac} + e^- \rightarrow ([\mathrm{V(acac)_2\cdots O\cdots Hacac}]^-)^* \qquad (1)$$

$$([\mathrm{V(acac)_2\cdots O\cdots Hacac}]^-)^* \rightarrow [\mathrm{V(acac)_3}] + \mathrm{OH}^- \qquad (2)$$

Since the reduction of +4 to +3 vanadium (Reaction (1)) proceeds slightly irreversibly but +3 to +2 reduction, which proceeds following the rearrangement of the ligand configuration (Reaction (2)), proceeds at the less negative potential than the first electron transfer by about 0.15 V, the current-potential curve is fairly distorted in comparison with a simple quasi-reversible process. In the acetonitrile solution these two processes were clearly separated in the logarithmic plot, and the inclination of its initial portion was 58 mV. In the dimethylsulfoxide solution, however, the initial linear portion was not clear and its inclination was about 44 mV as shown in Fig. 1. The value of 44 mV is much smaller than the theoretical value of 58 mV for a reversible one-electron transfer process.

The reason is supposedly due to the predominant coupled chemical reactions in this medium (cf. Ref. 1)). In the acetonitrile solution (AN), propylene carbonate solution (PC), dimethylformamide solution (DMF) and aqueous solution (H_2O) the inclination of the logarithmic plot was approximately equal to 58 mV. Only these four cases are taken into consideration in the following discussion.

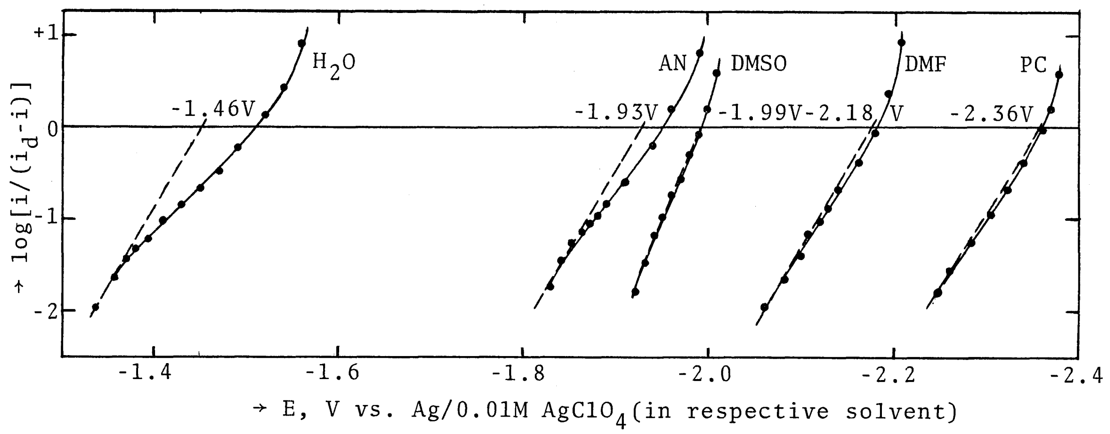

Fig. 1. Logarithmic plots of current-potential curves of VA in various solvents.

The electrode composed of Ag/0.01M $AgClO_4$ in respective solvent was used as the reference, so that the junction potential could be avoided in the mutual comparison of the p.d. But the difference of the Ag^+ activities in different solvents necessitates the calibration. In order to standardize the potential values the half-wave potential of the Rb^+ ion in each solvent was measured and used for the correction. This simple correction, however, will result in a misleading conclusion because the difference of the solvation energies of the Rb^+ ion is not taken into account properly. This correction can be achieved theoretically by using the data calculated by a modified Born equation.[2)]

The logarithmic plots in each case are shown in Fig. 1. The values of $E^r_{1/2}$ directly estimated from the logarithmic analyses (Column (1)), the values of the half-wave potential, $E_{1/2}$, of the Rb^+ ion in each solvent (Column (2)), the relative solvation energies of the Rb^+ in each solvent referred to the aqueous solution (Column (3)) and the values of $E^r_{1/2}$ corrected tentatively by using the data in Columns (2) and (3) (Column (4)) are given in Table I.

TABLE I. SOLVENT EFFECT ON HALF-WAVE POTENTIAL OF VANADYL ACETYLACETONATE

Solvent	H_2O	DMF	PC	AN
(1) $E^r_{1/2}$ of VA, V vs. Ag/0.01M $AgClO_4$ electrode	-1.46	-2.18	-2.36	-1.93
(2) $E_{1/2}$ of Rb^+, "	-2.55	-2.50	-2.73	-2.28
(3) Relative solvation energy of Rb^+, eV	0	$+0.00_5$*	+0.15*	+0.15*
(4) $E^r_{1/2}$ corrected, V vs. Ag/0.01M $AgClO_4$ in H_2O	-1.46	-2.24	-2.33	-2.35
ΔE, V		0.78	0.09	0.02

[VA]=1mM, [Hacac]=20mM in H_2O, PC and AN, 10mM in DMF, Tetraethylammonium perchlorate, [TEAP]=0.1M, Temp.=20°C, DME: h=36cm, m=0.69_7mg/s, t=4.00s (controlled with a hammer). In the aqueous solution VA developed a pre-wave at -1.15 V, the wave-height being about 6% of the main-wave (cf. Ref. 3)). This pre-wave disappeared by the addition of excess Hacac (*vide infra*). * The data evaluated by Matsuura et al. (Ref. 4)) are reproduced here.

In Table I Column (4) the corrected values of $E^r_{1/2}$ are in the order of H_2O> DMF>PC>AN, while the order is upset in the uncorrected data. This result shows that the electron transfer, in other words the breaking of the V-O bond, is more feasible in the order of the H_2O, DMF, PC and AN solutions.

According to Dodge, Templeton and Zalkin$^{5)}$ the structure of anhydrous VA is given as a five coordinated complex with the VO^{2+} group perpendicular to the oxygen base of a square pyramid. The complex presumably retains its original ligand configuration in solution as Bernal and Rieger $^{6)}$ have pointed out, i.e., the two Hacac ligands lie flat in the equatorial plane and provide four oxygen ligands to the V^{4+} ion, the fifth ligand is the vanadyl oxygen and the sixth position, trans to the vanadyl oxygen, is sterically unhindered and may be coordinated by solvent molecules to complete a distorted octahedral array. The solvent molecule thus coordinated in the axial direction of the complex will show a marked perturbation effect on the V-O linkage, and reduces the V-O interaction. Accordingly, it is easily understood why the more strongly coordinated solvent molecule shows the less negative reduction potential.

The above-mentioned trend was also substantiated by the optical absorption spectrum. The absorption bands in each solvent are illustrated in Fig. 2, and the data are shown in Table II. The most noticeable band shift was observed in the first absorption band, while the solvent effect was rather small in the second and third absorption bands. According to the molecular orbital calculation by Ballhausen and Gray$^{7)}$ the b_2-orbital, which corresponds to the ground state, is an almost pure vanadium $3d_{xy}$ orbital, the $e\pi^*$ orbital is made up of a linear combination of vanadium $3d_{xz}$ and $3d_{yz}$ orbitals with $2p_x$ and $2p_y$ orbitals of vanadyl oxygen, and the energy of the $e\pi^*$ level is sensitive to any perturbation which changes the axial compression.

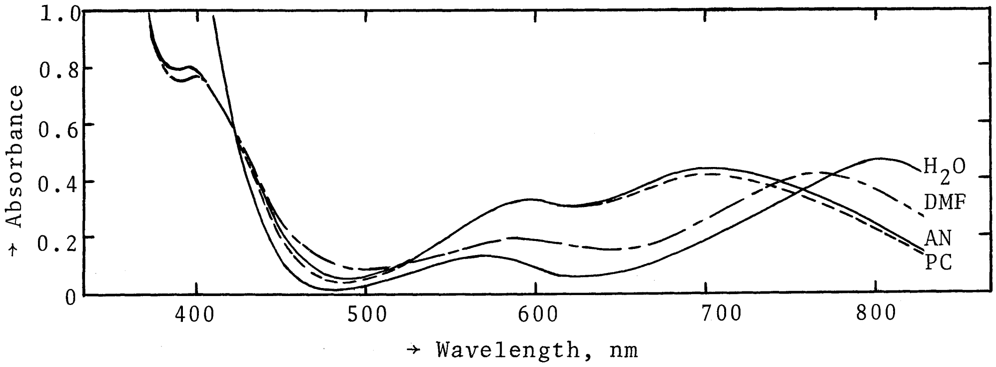

Fig. 2. Optical absorption spectra of VA in various solvents.

Therefore, the first absorption band, which corresponds to the $b_2 \rightarrow e\pi^*$ transition, is remarkably affected by the solvent molecule coordinated at the sixth position, the $e\pi^*$ level being lowered by a strong axial perturbation. The optical data denoted as $D_{II,I}$ in Table II represent the difference between the first band and the second band in each solvent. In view of the experimental error and the ambiguity involved in the standardization of the electrode potential values among varied solvents$^{8)}$ it can be concluded that the data in Tables I and II show a fairly good agreement with the molecular orbital predictions.

TABLE II. SOLVENT EFFECT ON OPTICAL ABSORPTION BAND OF VANADYL ACETYLACETONATE

	Solvent	H_2O	DMF	PC	AN
(1) λ_{max}, nm	First Band	806	770	704	710
	Second Band	564	587	590	591
	Third Band	(390)	401	392	393
(2) $D_{II,I}$, $\times 10^3$ cm^{-1}		≈ 5.5	≈ 4.1	≈ 2.7	≈ 2.8
$\Delta D_{II,I}$, $\times 10^3$ cm^{-1}		1.4	1.4	-0.1	
(3) DN($SbCl_5$) found		18.0	26.6	15.1	14.1
DN($SbCl_5$) calc.		42.3	27.5	15.1	14.6
ΔDN($SbCl_5$) calc.		14.8	12.4	0.5	

[VA]=10 mM, [Hacac]=200 mM in H_2O, PC and AN, 100 mM in DMF, [TEAP]=0.1 M. The data are slightly different from those given in the literature (cf. Ref. 9)) because of the presence of excess Hacac.

The donor number (DN) of the solvent for $SbCl_5$ is given in the last column of Table II. The order of magnitude of DN does not coincide well with the order of $D_{II,I}$. But, the correspondency among the values of $E^r_{1/2}$, $D_{II,I}$ and DN is improved, when the calculated value of DN=42.3 for H_2O is used (cf. Ref. 10)). When one compares the discrepancy denoted as Δ's between the data in each solvent, it attracts attention that the data of the aqueous solution especially the value of $E^r_{1/2}$ are anomalous. In the aqueous solution the value of pH decreased to 4.7 by the addition of 20 mM Hacac. It may be assumed that the VO^{2+} group protonated at lower pH facillitates the electron transfer, the V-O linkage being weakened.[11)] More detailed discussion on this reinforced solvent effect in the aqueous solution will be communicated in the future.

The financial support by the Science Research Fund of the Ministry of Education is gladly acknowledged.

References

1) M. Kitamura, K. Yamashita, and H. Imai, Bull. Chem. Soc. Japan, in press.
2) H. Strehlow in "The Chemistry of Non-Aqueous Solvent", J.J. Lagowski ed., Academic Press, New York and London, (1966), Chap. 4.
3) J.J. Lingane and L. Meites, Jr., J. Amer. Chem. Soc., 69, 1021 (1947).
R.L. Pecsok and R.S. Juvet, J. Amer. Chem. Soc., 75, 1202 (1953).
4) N. Matsuura, K. Umemoto, and Z. Takemoto, Preprint of XVIth Discussion on Polarography (1970, Kyoto), 1A07.
5) R.P. Dodge, D.H. Templeton, and A. Zalkin, J. Chem. Phys., 35, 55 (1961).
6) I. Bernal and P.H. Rieger, Inorg. Chem., 2, 256 (1963).
7) C.J. Ballhausen and H.B. Gray, Inorg. Chem., 1, 111 (1962).
8) N. Tanaka and T. Ogata, Inorg. Nucl. Chem. Letters, 10, 511 (1974).
M. Senda, Rev. Polarography (Japan), 20, 56 (1974).
9) J. Selbin, Chem. Rev., 65, 153 (1965).
10) V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions", Springer-Verlag, Wien・New York, (1968), p. 22.
11) A.A. Vlček in "Progress in Inorganic Chemistry", F.A. Cotton ed., Interscience Publ., New York・London, (1963), p. 361.

(Received July 28, 1975)