November, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *54, 3387—3390 (1981)* 3387

Studies on Electronic Spectrum and Electron Spin Resonance of Vanadium(IV) Complexes with Organophosphorus Compounds and High Molecular Weight Amines

Taichi SATO* and Takato NAKAMURA

Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu 432

(Received March 5, 1981)

In the extraction of vanadium(IV) from aqueous solutions containing hydrochloric acid and/or a mixture of hydrochloric acid and lithium chloride by bis(2-ethylhexyl) hydrogenphosphate (DEHPA; HX), trioctylmethylammonium chloride (Aliquat-336), trioctylamine (TOA), trioctylphosphine oxide (TOPO) and tributyl phosphate (TBP), the complexes formed in the organic phases have been examined by spectrophotometry and electron spin resonance spectroscopy. It is found that in the extraction by DEHPA, the vanadium in the organic phase exists as the monomeric species, $VO(X_2H)_2$, or the polymeric one, $(VOX_2)_n$, and that in the extractions by Aliquat-336, TOA, TOPO, and TBP, tetravalent vanadium complexes are stable in the organic phases extracted from a mixed solution of hydrochloric acid and lithium chloride, while complexes containing pentavalent vanadium and VOV^{4+} ions are formed in the organic phases extracted from hydrochloric acid solutions.

For the extraction of vanadium(IV) from hydrochloric acid solutions by trioctylmethylammonium chloride (Aliquat-336; $R_3R'NCl$), trioctylamine (TOA, R_3N), trioctylphosphine oxide (TOPO; R_3PO), and tributyl phosphate (TBP; $(RO)_3PO$), the spectral properties of the organic phases have been discussed in a previous paper.[1] The present paper extends the work to the extraction by bis(2-ethylhexyl) hydrogenphosphate (DEHPA; HX; $(RO)_2POOH$), and observations on the difference in the structure among the complexes formed in the organic phase with those acid, basic, and neutral extractants are reported on the basis of the results obtained by spectrophotometry and electron spin resonance (ESR) measurement.

Experimental

Chemicals. DEHPA (Daihachi Chemical Industry Co., Ltd.), Aliquat-336 (General Mills) and TBP (Daihachi Chemical Industry Co., Ltd.) were purified by the usual methods,[2–4] and diluted with hexane or benzene. TOA (Kao Soap Co., Ltd.) and TOPO (Hokko Chemical Industry Co., Ltd.) were used without purification. The vanadium(IV) chloride oxide solutions were prepared by dissolving vanadium(IV) chloride oxide, VCl_2O, in hydrochloric acid solutions of the required concentration. The chemicals used were of analytical reagent grade.

Extraction Procedures. Equal volumes (15 cm³ each) of the aqueous and organic phases were shaken for 10 min in 50 cm³ stoppered conical flasks in a thermostated water bath at 20 °C. The mixture was centrifuged and separated, and then the concentrations of vanadium in both phases were determined by edta titration as described already.[5] (In this case vanadium in the organic phase was stripped with 0.1 mol dm^{-3} hydrochloric acid). The complexes were isolated by drying the organic phases *in vacuo* at 50—60 °C.

Spectrophotometrical and ESR Measurements. The electronic spectra were obtained on a Shimadzu Model QV-50 spectrometer, using matched 1.00 cm fused silica cells. ESR spectra were recorded at 20 °C with a high sensitivity X-band spectrometer, designed in the Research Institute of Electronics, Shizuoka University, and at −30 °C with a JEOL JES-PE-3X X-band spectrometer, which operated at about 9.3 GHz using 100 kHz field modulation. Field calibration was checked by using DPPH and MnO doped in MgO. The calculation of ESR derivative line shape was made by using the computers of FACOM 230-45S and MELCOM COSMO 500.[6]

Results and Discussion

Electronic Spectra. The representative electronic spectra of organic phases for the extraction from aqueous hydrochloric acid solutions containing 0.036 mol dm^{-3} vanadium(IV) chloride oxide with 0.05 mol dm^{-3} DEHPA, 0.05 mol dm^{-3} Aliquat-336, 0.05 mol dm^{-3} TOA, 0.05 mol dm^{-3} TOPO, and 0.5 mol dm^{-3} TBP at 20 °C are shown in Fig. 1. The blue organic phase is obtained in the extraction by DEHPA. In the extractions by Aliquat-336, TOA, TOPO, and TBP,

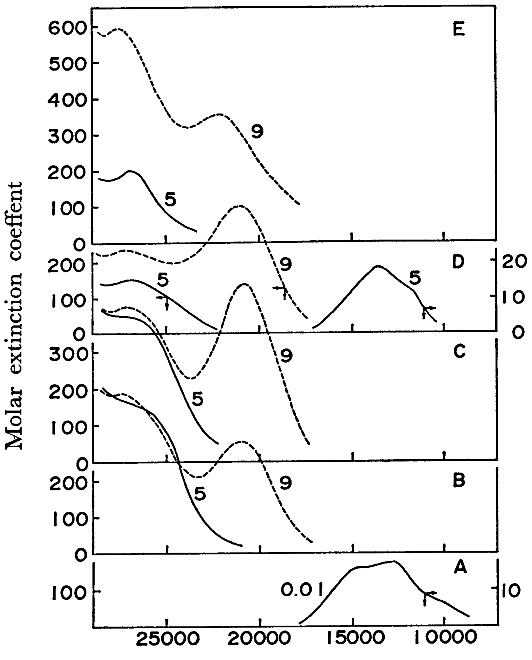


Fig. 1. Electronic spectra of organic phases from the extraction of aqueous solutions containing vanadium (IV) chloride oxide of 0.0036 mol dm^{-3} in hydrochloric acid with 0.05 mol dm^{-3} DEHPA (A), 0.05 mol dm^{-3} Aliquat-336 (B), 0.05 mol dm^{-3} TOA (C), 0.05 mol dm^{-3} TOPO (D), and 0.5 mol dm^{-3} TBP (E) (numerals on curves are hydrochloric acid concentrations in aqueous phase, mol dm^{-3}).

the organic phases depend on the kind of extractants in colour (yellow for Aliquat-336 and TOA, greenish yellow for TOPO, and pale yellow for TBP) at the aqueous hydrochloric acid concentration below 7 mol dm^{-3}, but at higher acidity above 8 mol dm^{-3} redish orange colour is developed in these organic extracts.

The spectra of the organic phases from the extraction by DEHPA, classified as acid extractant, show the d-d bands at 14700 and 12700 cm^{-1} accompanied by a shoulder around 9530 cm^{-1}. From the results obtained previously,[7] it is deduced that their bands rise from those of monomeric species VOX_4H_2 and/or polymeric one $(VOX_2)_n$. In both the complexes, the X^- group is bound to vanadium ion through the oxygen atoms which occupy the corner of a square, implying that the ligand field effect to vanadium ion resemble each other. Assuming that the extracted species is in a point group C_{4v} symmetry, the absorption bands at 14700 and 12700 cm^{-1} are assigned to the transitions $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E(I)$, respectively.

In the extractions by Aliquat-336 and TOA, classified as basic extractant, the spectra of yellow organic solutions exhibit no band due to the d-d transition of tetravalent vanadium ion but a band at 26000—27000 cm^{-1}. These organic solutions do not reveal a signal in the ESR experiment. In the extraction from 9 mol dm^{-3} hydrochloric acid solution, the absorption at about 21000 cm^{-1} appears in the spectra of redish orange organic solutions. This band probably arises from binuclear ion VOV^{4+}, which is an intermediate in the reaction between di- and tetravalent vanadium ions.[8] Accordingly it is considered that in the extractions by Aliquat-336 and TOA at the aqueous hydrochloric acid concentration below 7 mol dm^{-3}, the vanadium is oxidized during the extraction process, while the species formed in the extraction at higher acidity exists as a polymer containing ion such as VOV^{4+}.

In the extractions by neutral extractants, the spectra of organic phases for the extraction from 9 mol dm^{-3} hydrochloric acid solution are analogous to those with the basic extractants. In contrast, the spectrum of organic phase from 5 mol dm^{-3} hydrochloric acid solution with TOPO exhibits the absorption bands at 11600, 13500, and 26700 cm^{-1} due to $^2B_2 \rightarrow {}^2B_1$, $^2B_2 \rightarrow {}^2E(I)$, and $^2B_2 \rightarrow {}^2A_1$, respectively, indicating that the complex formed in the organic phase contains tetravalent vanadium ion. In addition the spectrum of the organic phase with TBP reveals a trace of band at about 14000 cm^{-1} similar to that with TOPO, although those absorption bands are hard to assign because of its low extractability.

On the other hand, the spectra of organic phase for the extraction from aqueous solution containing 0.036 mol dm^{-3} vanadium (IV) chloride oxide in a mixture of 0.06 mol dm^{-3} hydrochloric acid and 10 mol dm^{-3} lithium chloride by Aliquat-336, TOA, TOPO, and TBP exhibit the d-d bands in the range of 10000—14000 cm^{-1} (Fig. 2), which are characteristic bands of VO^{2+} ion. In the extraction by TOPO, the spectrum of the organic phase from mixed solution of hydrochloric acid and lithium chloride is similar to that from 5 mol dm^{-3} hydrochloric acid solution except that the former molar extinction coefficient of the band at 13500 cm^{-1} is larger than the latter one. This implies that the tetra- and pentavalent vanadium complexes coexist in the latter organic phase. In other spectra, the bands are assigned as follows: for Aliquat-336 26500, 14300, and 12800 cm^{-1} to $^2B_2 \rightarrow {}^2A_1$, $^2B_2 \rightarrow {}^2E(I)$, and $^2B_2 \rightarrow {}^2B_1$, respectively; for TOA 26700, 12300, and 10600 cm^{-1} to $^2B_2 \rightarrow {}^2A_1$, $^2B_2 \rightarrow {}^2B_1$, and $^2B_2 \rightarrow {}^2E(I)$, respectively; for TBP 27000, 13500, and 11800 cm^{-1} to $^2B_2 \rightarrow {}^2A_1$, $^2B_2 \rightarrow {}^2E(I)$, and $^2B_2 \rightarrow {}^2B_1$, respectively. As the complexes contained in these organic solutions could be formulated as $VOCl_2 \cdot R_3R'NCl \cdot xH_2O$, $VO(OH)Cl \cdot R_3NHCl$, $VO(OH)Cl \cdot 2R_3PO$, and $VO(OH)Cl \cdot 2(RO)_3PO$, respectively,[1] the following structures are presumed to satisfy an octahedral or square pyramidal coordination:

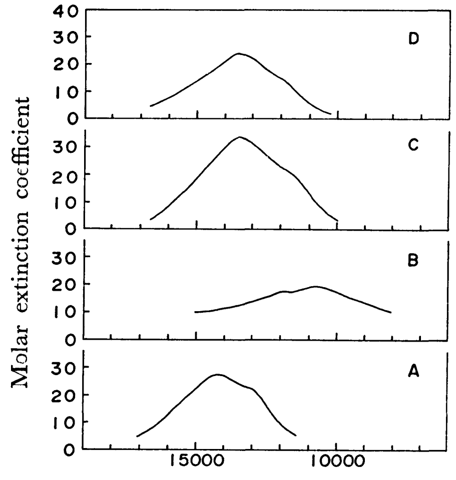
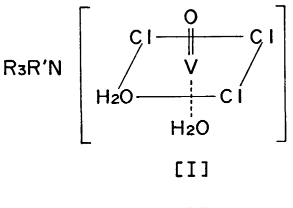
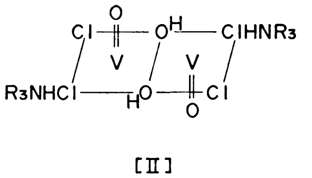


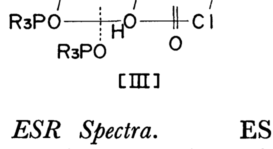
Fig. 2. Electronic spectra of organic phases from the extraction of aqueous solutions containing vanadium (IV) chloride oxide of 0.036 mol dm^{-3} in a mixture of 0.06 mol dm^{-3} hydrochloric acid and 10 mol dm^{-3} lithium chloride with 0.05 mol dm^{-3} Aliquat-336 (A), 0.05 mol dm^{-3} TOA (B), 0.05 mol dm^{-3} TOPO (C), and 0.5 mol dm^{-3} TBP (D) in benzene.



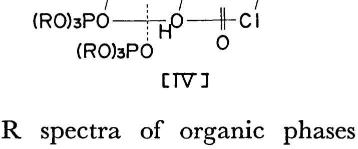
[I]



[II]



[III]



[IV]

ESR Spectra. ESR spectra of organic phases from the extraction of aqueous solutions containing vanadium(IV) chloride oxide in 0.01 mol dm^{-3} hydrochloric acid with 0.05 mol dm^{-3} DEHPA in hexane at 20 °C are shown in Fig. 3. The well resolved hyperfine line with eight components is observed in the spectrum at the molar ratio of $[DEHPA]/[V]_{org} = 10.2$, which is assigned to that of the monomeric species

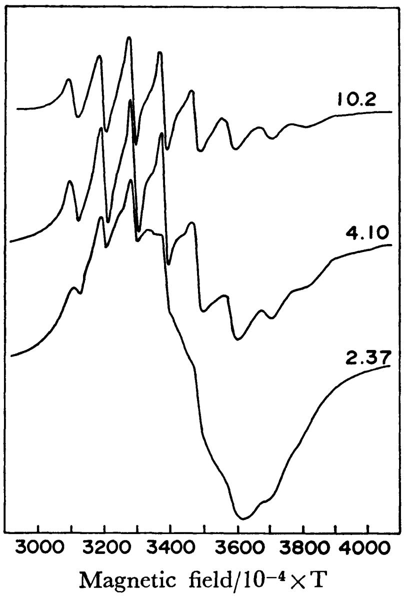
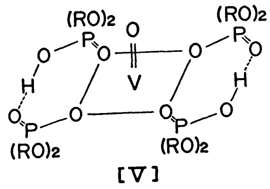


Fig. 3. ESR spectra of the organic phases from the extraction of vanadium(IV) by 0.05 mol dm^{-3} DEHPA in hexane (numerals on curves are the molar ratio of $[HX]/[V]_{org}$).

VOX_4H_2. On the one hand, the spectrum at the molar ratio of $[DEHPA]/[V]_{org}=4.10$ contains the broad line showing no hyperfine structure, and that at the molar ratio of $[DEHPA]/[V]_{org}=2.37$ is so broadened that the hyperfine structure is unresolved, although the spectra of aqueous solutions exhibit hyperfine structure, indicating that the vanadium ion concentration in the aqueous phases before extraction is magnetically diluted. This broadening is probably due to the exchange interaction among the unpaired electrons of vanadium ions, suggesting that the polymeric species is formed in the organic phase by substituting the hydrogen ions of the monomeric species VOX_4H_2 for VO^{2+} ion in the aqueous phase. It is thus considered that the anisotropy in ESR spectrum of the organic extract prepared by drying the organic phase for the extraction of 0.0072 mol dm^{-3} vanadium(IV) chloride oxide solution containing 0.01 mol dm^{-3} hydrochloric acid with 0.05 mol dm^{-3} DEHPA in hexane is due to that of the monomeric species



[V]

because of the molar ratio of $[DEHPA]/[V]_{org}=7.14>4$.

In the extraction of aqueous solution containing 0.036 mol dm^{-3} vanadium(IV) chloride oxide in a mixture of 0.06 mol dm^{-3} hydrochloric acid and 10 mol dm^{-3} lithium chloride with 0.05 mol dm^{-3} Aliquat-336, 0.05 mol dm^{-3} TOA, 0.05 mol dm^{-3} TOPO, and 0.5 mol dm^{-3} TBP in benzene, the ESR spectra of the frozen organic phases were measured at −30 °C in order to estimate ESR parameters (Fig. 4), because apparent change in the colour of organic phases was observed during the evaporation of benzene to isolate the complexes by drying. As the transition due to $S_1 \cdot S_2$ is not observed in the spectra of the organic solutions extracted with TOA, TOPO, and TBP, the exchange interaction between vanadium ion in the complexes [II], [III], and [IV] is presumed to be weak and/or less anisotropic. In addition the difference to be expected in the x, y components is not resolved in the spectra. Therefore those spectra can be described by the axially symmetric spin Hamiltonian including the terms of Zeeman and nuclear-electron hyperfine interactions:

$$\mathbf{H} = \beta H(g_{/\!/}S_z\cos\theta + 2g_{\perp}S_x\sin\theta) + A_zS_z + B(S_xI_x + S_yI_y) \tag{1}$$

where β is the Bohr magneton, H the applied magnetic field, $g_{/\!/}$ and $g_{\perp}$ the g-tensor values parallel and perpendicular, respectively, to z-axis corresponding to the V=O bond direction, θ the angle between H and z-axis, $S_{x,y,z}$ and $I_{x,y,z}$ the components of the electron and nuclear spin vectors, respectively, and A and B the hyperfine splitting constants for vanadium nucleus. Computer simulation method described in an earlier paper[6] is used for determining the ESR parameters of VO^{2+} complexes with DEHPA, Aliquat-336, TOA, TOPO, and TBP. The resulting parameters are shown in Table 1.

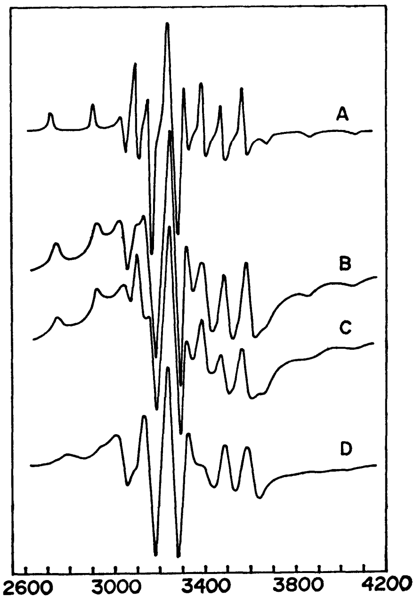


Fig. 4. ESR spectra of frozen organic phases from the extraction of aqueous solutions containing vanadium (IV) chloride oxide of 0.036 mol dm^{-3} in a mixture of 0.06 mol dm^{-3} hydrochloric acid and 10 mol dm^{-3} lithium chloride with 0.05 mol dm^{-3} Aliquat-336 (A), 0.05 mol dm^{-3} TOA (B), 0.05 mol dm^{-3} TOPO (C), and 0.5 mol dm^{-3} TBP (D) in benzene.

The g-values and hyperfine splitting constants are related to the energy levels and bonding parameters. For the purpose of estimating approximate bonding parameters, it is assumed that the complexes are approximately in a point group C_{4v} symmetry, because the parameters indicating the difference in bonding between two perpendicular directions can not be obtained, and that the b_2 orbital is a non-bonding orbital. This leads to the following relationship:

$$\Delta g_{//} = 8\lambda_v\beta_1{}^{*2}/\Delta_{//}, \tag{2}$$

$$\Delta g_{\perp} = 2\lambda_v\varepsilon_\pi{}^{*2}/\Delta_{\perp}, \tag{3}$$

$$A = P[-(4/7+\kappa_v) - 8(\lambda_v\beta_1{}^{*2}/\Delta_{//}) - 6/7(\lambda_v\varepsilon_\pi{}^{*2}/\Delta_{\perp})], \tag{4}$$

and

$$B = P[2(2/7-\kappa_v) - 11/7(\lambda_v\varepsilon_\pi{}^{*2}/\Delta_{\perp})], \tag{5}$$

where $\Delta g_{//}=2.002-g_{//}$, $\Delta g_{\perp}=2.002-g_{\perp}$, $\beta_1{}^{*2}$ and $\varepsilon_\pi{}^{*2}$ are the fractional contributions of the orbitals $d_{x^2-y^2}$ and d_{xz} (and/or d_{yz}) in antibonding molecular orbitals $^2B_1$ and $^2E(I)$, respectively, λ the spin-orbital coupling constant for the free ion of vanadium, κ_v the Fermi contact term for the vanadium atom, $P=2.002g_N-\beta\beta_N\langle r^{-3}\rangle$ in which r is the distance from the central nucleus to the electron and β_N the nuclear magneton, $\Delta_{\perp}$ the energy in the transition $^2B_2\rightarrow{}^2E(I)$ and $\Delta_{//}$ the energy in the transition $^2B_2\rightarrow{}^2B_1$. The molecular parameters of the VO^{2+} complexes with DEHPA, Aliquat-336, TOA, TOPO, and TBP obtained from simultaneous solution of Eqs. 3—6 are given in Table 1. The values of $\beta_1{}^{*2}$ for those complexes range from 0.50 to 0.59 except that of the complex with DEHPA being 0.78. This means that for the complexes with Aliquat-336, TOA, TOPO, and TBP the in-plane σ bonding is covalent so that the unpaired electron is delocalized, while somewhat covalent for that with DEHPA. This values of $\varepsilon_\pi{}^{*2}$ range from 0.66 to 0.98, implying that the out-of-plane π bonding is almost completely ionic for the complexes with DEHPA, Aliquat-336, and TBP, somewhat covalent for that with TOPO and covalent for that with TOA.

TABLE 1. ESTIMATED ESR PARAMETERS OF THE VANADIUM(IV) COMPLEXES WITH DEHPA, ALIQUAT-336, TOA, TOPO, AND TBP

Parameter	Vanadium(IV) complex				
	DEHPA	Aliquat-336	TOA	TOPO	TBP
$g_{//}$	1.930	1.940	1.947	1.935	1.945
$g_{\perp}$	1.976	1.979	1.980	1.980	1.978
$\lvert A\rvert/\text{cm}^{-1}$	0.0147	0.0177	0.0170	0.0170	0.0155
$\lvert B\rvert/\text{cm}^{-1}$	0.0063	0.0067	0.0069	0.0069	0.0074

Conclusion

In the extraction by DEHPA, the monomeric species, $VO(X_2H)_2$, in which central vanadium ion possesses little π bonding of coordinated oxygen atoms of DEHPA, is formed when DEHPA is present in excess, and an increase in the organic vanadium concentration involves the formation of polymeric species arising from the substitution of the hydrogen ion of coordinated anion X_2H^- by vanadium ion in aqueous phase. In the extraction by Aliquat-336, the tetravalent vanadium species, $R_3R'NVOCl_3$, which is also deduced from the extractions of other metals, exists stably in the organic phase extracted from a mixed solution of hydrochloric acid and lithium chloride, and while the hydrolytic tetravalent vanadium species, $VO(OH)Cl\cdot nL$, are found in the extractions by TOA, TOPO, and TBP.

We wish to thank Dr. Kenzo Watanabe of the Research Institute of Electronics, Shizuoka University, and Prof. Takafumi Kanazawa, Dr. Hiroshi Kawazoe, and Mr. Hideo Hosono of the Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University for the ESR spectral measurements, and also the Kao Soap Co., Ltd. for the sample of TOA, the Hokko Chemical Industry Co., Ltd. for the sample of TOPO, and the Daihachi Chemical Industry Co., Ltd. for the samples of DEHPA and TBP.

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