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Abstract. Speciation has been determined in aqueous oxovanadium, glycylvaline and imidazoles at $25 \pm 1°C$ and $\boldsymbol{m} = 0.1M$ $NaClO_4$ using a combination of potentiometry, and visible and EPR spectroscopy. Results of potentiometric and spectroscopic methods are consistent. Calculations of stability constants have been made using the SCOGS computer program.

Keywords. Oxovanadium (IV); glycylvaline; imidazoles.

1. Introduction

The aqueous chemistry of vanadium has been attracting interest for many years. Solution equilibria involving oxovanadium can be followed very conveniently using potentiometry and EPR spectroscopy. The importance of histidyl residues makes imidazole a relevant target for metal binding studies in biomolecules. Further, only limited information is available on oxovanadium(IV) ternary complexes[1–4] and oxovanadium (IV) complexes with peptides[5,6], aminoacids[7–15] and imidazoles[16]. There are also examples[17–20] with other simple molecules containing this type of donor groups. With this view in mind, we have studied oxovanadium (IV) ternary systems using glycylvaline (A) (I) and three imidazoles (B) (II) viz., imidazole (ImH), 2-methylimidazole (M-ImH) and 2-ethylimidazole (E-ImH), using three different techniques in aqueous solution.

## 2. Experimental

2.1 *Chemicals*

Vanadyl sulphate (Aldrich), glycylvaline (Aldrich) and imidazoles (s.d. Fine Chem.) were used as received. All other chemicals used were of reagent grade. Solutions were prepared using double distilled water.

2.2 *Potentiometric measurements*

Values of pH were determined with a Systronics pH meter, model 335 (accuracy ± 0.01 pH units) using special glass electrodes (pH 1–14) and saturated calomel electrodes.

*For correspondence

$$NH_3 — CH_2 — \overset{\overset{\textstyle O}{\|}}{C} — NH — \overset{\overset{\textstyle (CH_3)_2}{|}}{CH} — COO^-$$

(I)
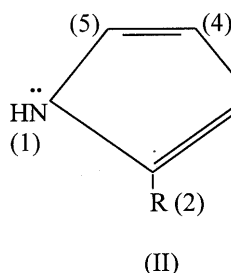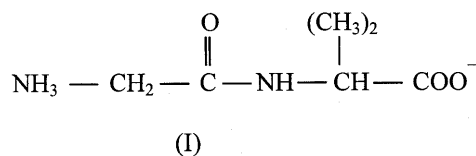
(a) R = H, Imidazole (ImH)
(b) R = −CH$_3$, 2-methylimidazole (M-ImH)
(c) R = −CH$_2$CH$_3$, 2-ethylimidazole (E-ImH)

(II)

Titration procedures were the same as described in our earlier work[21–26]. The following metal–ligand mixtures were prepared for the *p*H-potentiometric study:

(i)   0·03 M perchloric acid + 0·1 M NaClO$_4$;
(ii)   0·03 M perchloric acid + 0·003 M A + 0·1 M NaClO$_4$;
(iii)   0·03 M perchloric acid + 0·003 M B + 0·1 M NaClO$_4$;
(iv)   0·03 M perchloric acid + 0·003 M VO^{2+} + 0·003 M A + 0·1 M NaClO$_4$;
(v)   0·03 M perchloric acid + 0·003 M VO^{2+} + 0·003 M B + 0·1 M NaClO$_4$;
(vi)   0·03 M perchloric acid + 0·003 M VO^{2+} + 0·003 M A + 0·003 M B + 0·1 M NaClO$_4$.

Here A = glycylvaline and B = imidazoles. The initial volume of all the solutions was 50 ml and the required amount of NaClO$_4$ was added to each solution to maintain the ionic strength ($m = 0·1$ M NaClO$_4$). All the solutions were allowed to attain equilibrium at $25 \pm 1°C$ and were titrated with 1 M NaOH.

2.3 *Spectrophotometric measurements*

Visible absorption spectra were recorded as functions of *p*H in aqueous solution using a Systronics UV-Vis 117 spectrophotometer and 1 cm quartz cells.

2.4 *EPR measurements*

EPR spectra were recorded with a Varian E-line Century Series EPR spectrometer equipped with dual cavity and operating with X-band with 100 kHz modulation frequency. TCNE ($g_e = 2·00277$) was used as the field marker.

3. Results and discussion

Protonation constants of ligands were determined by Calvin–Bjerrum's[27,28] technique as adopted by Irving and Rossotti[29]. The formation constants of different binary and ternary complexes were evaluated using the SCOGS computer program[30]. Protonation constants

$$[\{VO(OH)\}_2]^{2+} + 2H^+. \tag{2}$$

The equilibrium constants of the above equations are given in table 1. These hydroxo species are not seen in the species distribution curves (figures 1 and 2) as their percentage is less than 1%.

Table 1. Proton–ligand and metal–ligand binary and ternary constants at $25 \pm 1°C$ in aqueous solution, ionic strength $I = 0.1$ M NaClO$_4$ (standard deviations are ± 0.02 in log unit).

(a) *Proton–ligand constants*

Ligand	pK_2^H	pK_1^H
Glycylvaline (AH$_2$)	3·15	8·25
Imidazole (BH$^+$)	–	7·10
2-Methylimidazole (BH$^+$)	–	8·00
2-Ethylimidazole (BH$^+$)	–	8·00

(b) *Hydrolytic constants of VO^{2+} aq. ions*

log b_{VO}^H	-6.00
log b_{VO}^{2H}	-12.88

(c) *Stability constants (log$b$) of binary complexes*

	GlyVal	ImH	2-M-ImH	2-E-ImH
VO(AH)	7.82	–	–	–
VO(AH$_{-1}$)	3.70	–	–	–
VO(B)	–	5.77	6.66	6.66

(d) *Stability constants (log$b^{VO}_{VO(A)(B)}$) of ternary complexes*

A	B	log$b^{VO}_{VO(A)(B)}$	Δlog K_{VO}
GlyVal	ImH	15·47	+ 1·88
	2-M-ImH	15·02	+ 0·54
	2-E-ImH	15·00	+ 0·52
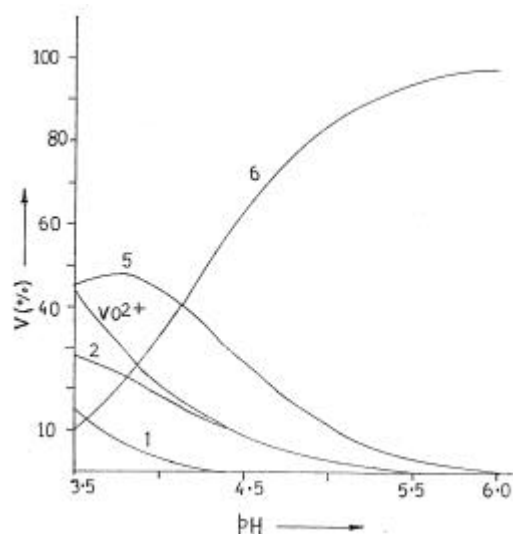
Figure 1. Species distribution curves of M:AH (1:1) binary system: (1) AH_2, (2) AH, (3) $M(OH)^+$, (4) $M(OH)_2$, (5) MAH and (6) MAH_{-1}.
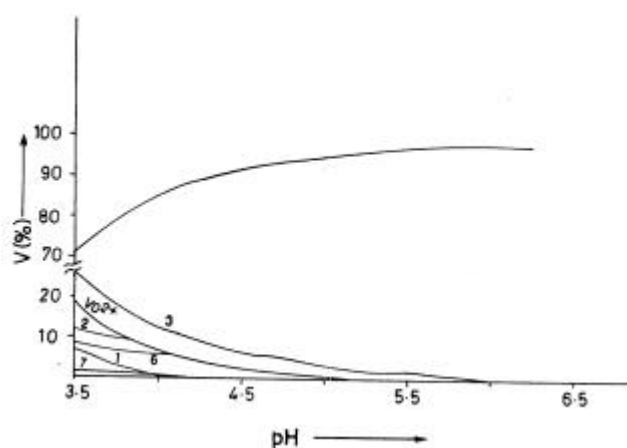
Figure 2. Species distribution curves of M:AH:BH (1:1:1) ternary system: (1) AH_2, (2) AH, (3) BH^+, (4) $M(OH)^+$, (5) $M(OH)_2$, (6) MAH, (7) MB, (8) MAB and (9) $MABH_{-1}$.

Stability constants (table 1) and speciation curves (figures 1 and 2) were obtained from the SCOGS (stability constants of generalized species) computer program. Complex formation equilibria have been illustrated on the basis of the concentration distributions of the complexes formed in the VO^{2+}: A binary and VO^{2+}: A:B ternary systems in aqueous solutions. Stability of the ternary VO(A)(B) complex was generally characterized on the basis of $\Delta \log K_{VO}$ values (table 1) calculated using relation [32–34],

$$\Delta \log K_{VO} = \log b^{VO}_{VO(A)(B)} - \log b^{VO}_{VO(A)} - \log b^{VO}_{VO(B)}. \tag{3}$$

$$VO(A)(B) + H^+. \tag{6}$$

3.1 *Stability constants with respect to imidazoles*

Stability constants of ternary VO(A)(B) complexes were found to be in the order: imidazole<2-methylimidazole<2-ethylimidazole. As we pass from imidazole to 2-ethylimidaozle, an increase in log$\boldsymbol{b}$ value is observed, which is due to increase in the basicity of the alkyl-substituted imidazoles. From steric considerations, the log$\boldsymbol{b}$ values in case of complexes with substituted imidazoles should be smaller than that for imidazole complexes. The increase in basicity of substituted imidazoles thus compensates for the negative contribution of the steric effect and further enhances the values of log$\boldsymbol{b}$ in all the cases. Among the methyl- and ethylimidazoles, there is not much difference either in ligand basicities or in steric effects so that both methyl- and ethylimidazole give almost similar logβ values.

3.2 *EPR studies*

X-band EPR spectra at liquid nitrogen temperature may be simulated as axial spectra[35]. The field region[7] corresponding to $A_{\parallel}$ and $M_I = 5/2$ and $7/2$ gives more information about the type and number of species. We have recorded the EPR spectra of binary and ternary systems as functions of pH. The derived EPR parameters are collected in table 2. Some representative EPR spectra are shown in figure 3. In the case of binary systems, the spectrum at pH 2·50 is characteristic of aquo vanadium. When pH is increased from 2·50 to 3·50 the peaks shift slightly to lower fields, hence more than one species contributes to each spectrum. At higher pH values, distinct species are detected, and signal intensity weakens significantly. In the case of ternary systems, at the lowest pH (i.e. pH 2·50) studied the spectrum is not due to aquo VO^{2+} ion. It could be due to the binary species VO(AH), as its EPR parameters resemble that of the binary species detected in $VO^{2+} + A(1:1)$ systems. When pH is increased from 2·50 to 3·50 the peak again shifts to lower fields, hence more than one species contributes to each spectrum. At higher pH values, signal intensities differ from that of binary high pH spectra. Change in signal intensity could be due to ternary species formation.

By applying the additivity relationship[36] to the species assumed to be present at different pH values, the $A_{z,i}$ values for different coordinate sites were calculated and are given in table 2. These calculated values for the equatorial sites are almost identical to the experimental values. Holyk[37] plotted the relation (figure 4) between $A_{\parallel}$ and $g_{\parallel}$ values for vanadyl complexes and defined zones for complexes having different equatorial donor atom sites, such as $VO(N_4)$, $VO(N_2O_2)$ and $VO(O_4)$. In this plot, our data points shift from the main domains. This kind of shifting relative to the reference data implies that
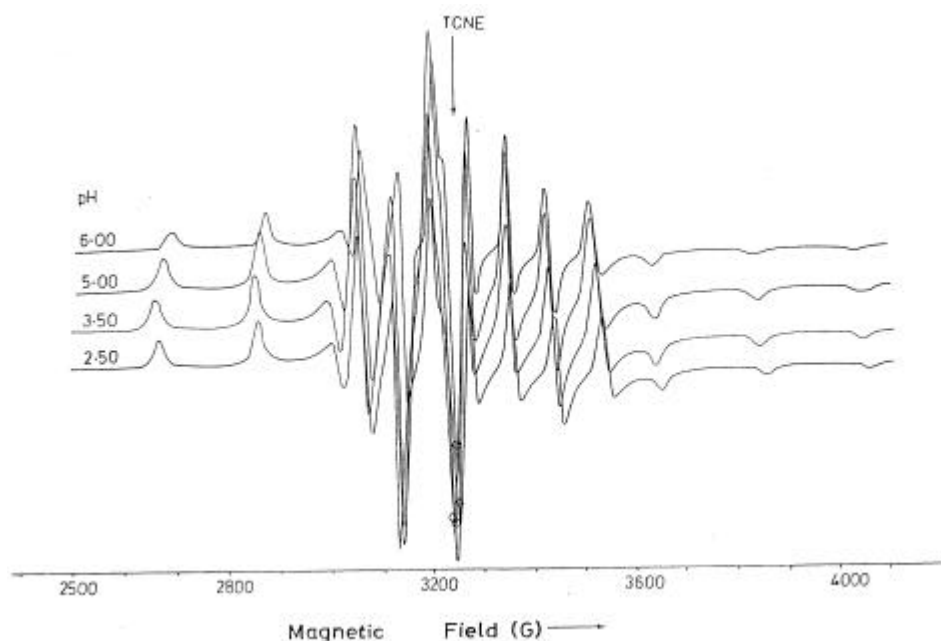
Table 2. EPR parameters, proposed equatorial coordination and λ_{max} for different binary and ternary oxovanadium (IV) systems.

Composition	Complex	pH	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (10^{-4}cm^{-1})	$A_{\perp}$ (10^{-4}cm^{-1})	Proposed equatorial coordination	$A_{z,i}$ (10^{-4} cm^{-1}) Calc. value	Lit. value	λ_{max} (nm)
VO^{2+}:A (1:1)	VO^{2+} aq.	2·50	1·931	1·972	183	72	4H$_2$O	45·9	45·7	–, 772
	VO(AH)	3·50	1·928	1·976	174	62	R–NH$_2$	39·9	40·1	–, 760
							R–CO$_2$	42·5	42·7	
	VO(AH$_{-1}$)	5·50	1·931	1·978	160	49	2H$_2$O	45·5	45·7	ill-defined
							R–NH$_2$	39·6	40·1	
							R–CO$_2$	42·2	42·7	
							H$_2$O	45·2	45·7	
							CONH	31·5	32·0	
VO^{2+}:A:ImH (1:1:1)	VO(AH)	2·50	1·933	1·981	174	63	R–NH$_2$	39·9	40·1	–, 760
							R–CO$_2$	42·5	42·7	
							2H$_2$O	45·5	45·7	
	VO(A)(B)(H$_2$O)	3·50	1·937	1·987	167	58	R–NH$_2$	40·3	40·1	–, 766
							R–CO$_2$	42·9	42·7	
							=N–	38·5	38·3	
							H$_2$O	45·9	45·7	
	VO(A)(B)	5·00	1·935	1·984	153	41	R–NH$_2$	40·0	40·1	ill-defined
							R–CO$_2$	42·6	42·7	
							=N–	38·2	38·3	
							CONH	31·9	32·0	
	VO(A)(B)	6·00	1·932	1·980	153	40	R–NH$_2$	40·0	40·1	580, –
							R–CO$_2$	42·6	42·7	
							=N–	38·2	38·3	
							CONH	31·9	32·0	

(continued)

Table 2. (*Continued*).

VO²⁺:A:M-ImH (1:1:1)	VO(AH)	2·50	1·928	1·980	174	64	$R-NH_2$ $R-CO_2$ $2H_2O$	39·9　40·1 42·5　42·7 45·5　45·7	632, 768
	VO(A)(B)(H₂O)	3·50	1·928	1·978	167	57	$R-NH_2$ $R-CO_2$ $=N-$ H_2O	40·3　40·1 42·9　42·7 38·5　38·3 45·9　45·7	–, 760
	VO(A)(B)	5·00	1·930	1·950	153	45	$R-NH_2$ $R-CO_2$ $=N-$ CONH	40·0　40·1 42·6　42·7 38·2　38·3 31·9　32·0	ill-defined
	VO(A)(B)	6·00	1·928	1·967	153	42	$R-NH_2$ $R-CO_2$ $=N-$ CONH	40·0　40·1 42·6　42·7 38·2　38·3 31·9　32·0	ill-defined
VO²⁺:A:E-ImH (1:1:1)	VO(AH)	2·50	1·928	1·967	174	64	$R-NH_2$ $R-CO_2$ $2H_2O$	39·9　40·1 42·5　42·7 45·5　45·7	635, 765
	VO(A)(B)(H₂O)	3·50	1·930	1·950	167	58	$R-NH_2$ $R-CO_2$ $=N-$ H_2O	40·3　40·1 42·9　42·7 38·5　38·3 45·9　45·7	–, 762
	VO(A)(B)	5·00	1·928	1·980	153	41	$R-NH_2$ $R-CO_2$ $=N-$ CONH	40·0　40·1 42·6　42·7 38·2　38·3 31·9　32·0	ill-defined
	VO(A)(B)	6·00	1·928	1·978	153	42	$R-NH_2$ $R-CO_2$ $=N-$ CONH	40·0　40·1 42·6　42·7 38·2　38·3 31·9　32·0	ill-defined

Figure 3.   X-band EPR spectra of M:AH:ImH (1:1:1) ternary system as a function of *p*H.
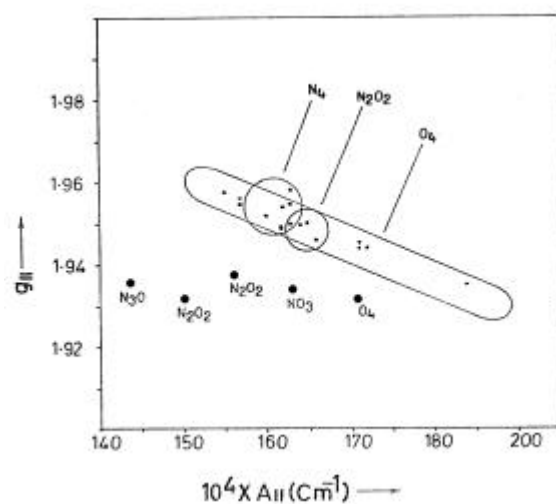
Figure 4.   A correlation plot of $A_{\parallel}$ vs. $g_{\parallel}$ for the VO^{2+} complexes: for (●)N_3O, N_2O_2, NO_3, O_4 (points of the present study) and (.) in various domains for a series of oxovanadium (IV) complexes with different donor atoms [22].

the physical mechanism which determines the $A_{\parallel}$ values in our complexes is not the same as in reference compounds.

3.3 *Spectrophotometric study*

Visible absorption spectra of the oxovanadium (IV) binary and ternary systems were recorded as a function of pH. Values of $\boldsymbol{l}_{max}$ obtained are shown in table 2. Values of $\boldsymbol{l}_{max}$ are not given for all binary and ternary species owing to ill-defined band positions. Band positions of binary and ternary species differ.

4. Conclusion

In biological systems, the available ligand atoms are S, N, and O. The oxovanadium (IV) is a powerful paramagnetic probe of protein structure and therefore it is important to ascertain the nature of its aminoacid, peptide and protein complexes. $A_{z,i}$ values are identical to the literature values.

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