Spectrophotometric Studies and Analytical Applications of Vanadium(IV) Chelates with 4-(2-Pyridylazo)resorcinol and 1-(2-Pyridylazo)-2-naphthol

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Oxovanadium(IV), VO^{2+}, gives sensitive colour reactions with 4-(2-pyridylazo)resorcinol ($\varepsilon=2.54\times10^4$ at λ_{max} 550 nm) and 1-(2-pyridylazo)-2-naphthol ($\varepsilon=1.02\times10^4$ at λ_{max} 560 nm). The composition of the complexes VO^{2+}: PAN or PAR was established by the continuous variations, mole ratio, and Asmus straight line methods. Lambert-Beer's law range, Ringbom optimum range, pH stability range, photometric error, and stability constant values were also evaluated.

The formation of coloured chelates of VO^{2+} with Alizarin red S,[1] chrome azurol S,[2] Pyrocatechol violet,[3] and Pyrogallol red[4] have recently been reported. Pyridylazo dyes particularly 4-(2-pyridylazo)resorcinol (PAR) and 1-(2-pyridylazo)-2-naphthol (PAN) have assumed importance in analytical chemistry as metallochromic indicators and colorimetric reagents for the microdetermination of a number of metal ions.[5-8] The present paper describes spectrophotometric studies on the composition, stability and analytical applications of VO^{2+} chelates with PAR and PAN.

Experimental

The metal salt ($VOSO_4\cdot H_2O$, Anala R. B.D.H.) solution prepared in water was standardized by titration with permanganate. The solution was flushed with pure nitrogen to check aerial oxidation of the metal ion. The solutions of PAR and PAN (E. Merck) were prepared in doubly distilled water and ethanol, respectively. Acetate buffer of pH 5.0 and 4.4 was used in VO^{2+}-PAR and VO^{2+}-PAN systems, respectively. Ionic strength was adjusted to 0.1 in VO^{2+}-PAR system and 0.05 in VO^{2+}-PAN system by the addition of sodium perchlorate solution.

A Beckman (DU) spectrophotometer with 10 mm^2 quartz cells was used for all absorbance measurements. For pH measurements a Leeds and Northrup direct reading pH meter with glass-calomel electrode assembly was used.

All mixtures were flushed with pure nitrogen and kept at 12°C in a water bath for 15 minutes and then absorbance was recorded. The total volume was kept at 25 m*l*. The VO^{2+}-PAR system was studied in aqueous medium and VO^{2+}-PAN system in 30% ethanol.

Results and Discussion

At pH>3 a water soluble red VO^{2+}-PAR chelate is formed and at pH 5—7 the colour of the chelate is red-violet and is intensified by the addition of excess of metal ion. The VO^{2+}-PAN chelate formation starts at pH>2 and a red violet chelate is formed at pH>3.5. The reagents are coloured yellow under these conditions. The pH *versus* λ_{max} plots (Fig. 1) show that the VO^{2+}-PAR system is stable at pH 5—7 and VO^{2+}-PAN at pH 4.7.

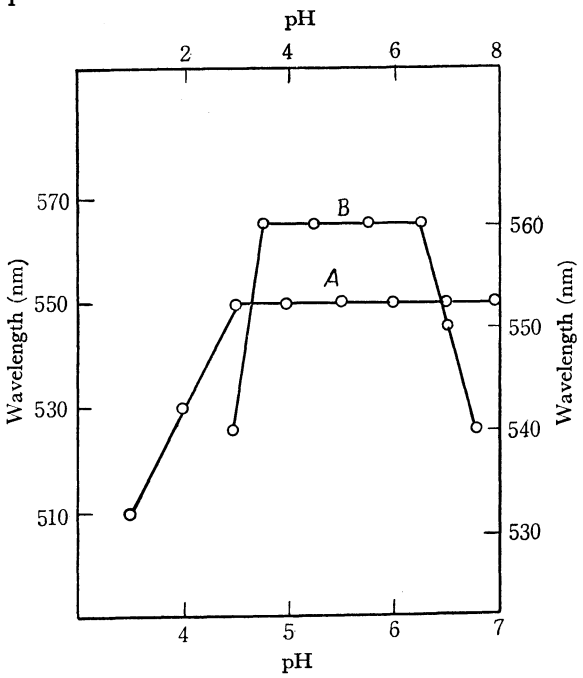

Fig. 1. Variation of λ_{max} of the chelates with pH; A, VO^{2+}-PAN chelate; B, VO^{2+}-PAR chelate.

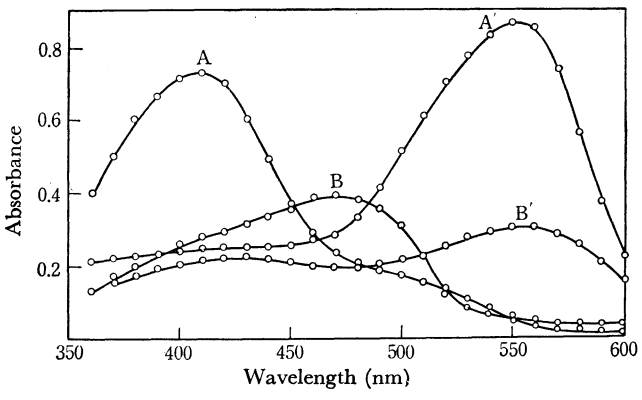

Fig. 2. Absorption spectra A, PAR (4.0×10^{-5}M); A', VO^{2+}-PAR chelate (CM=CR=4.0×10^{-5}M); B, PAN (4.0×10^{-5}M) B', VO^{2+}-PAN chelate (CM=CR=4.0×10^{-5}M).

1) P. Sanyal and S.P. Mushran, *Anal. Chim. Acta*, **35**, 400 (1966).
2) P. Sanyal and S. P. Mushran, *Mikrochim. Acta*, **5**, 959 (1965).
3) S. P. Mushran, O. Prakash, and J. N. Awasthi, *Anal. Chem.*, **39**, 1307 (1967).
4) S. P. Mushran, O. Prakash, and J. N. Awasthi, *Microchem. J.*, **14**, 29 (1969).
5) K. L. Cheng and R. H. Bray, *Anal. Chem.*, **27**, 782 (1955).
6) R. Pueschel, E. Lassner, and K. Katzengruber, *Z. Anal. Chem.*, **223**, 414 (1966).
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8) F. J. Langmyhr and H. Kritiansen, *Anal. Chim. Acta*, **20**, 524 (1959).

The absorption curves for the reagents PAR and PAN and their chelates with VO^{2+} were obtained by the method of Vosburgh and Cooper[9] (Fig. 2). At pH 5.0 λ_{max} of PAR is 410 nm and of VO^{2+}-PAR chelate 550 nm. The λ_{max} of PAN and VO^{2+}-PAN chelate at pH 4.4 are 470 nm and 560 nm, respectively. The λ_{max} of the chelates remain unchanged in small excess of reagent or large excess of metal concentrations showing the existence of only one chelate.

The composition of the chelate was studied by continuous variations (Fig. 3), mole ratio (Fig. 4) methods. The composition 1: 1 (VO^{2+}: PAR or PAN) was established by the above methods. Application of Asmus[10] straight line method as extended by Klausen and Langmyhr[11] shows straight line at $m=1$ and $n=1$ (Figs. 5 and 6, where m and n are the number of metal atoms and ligand molecules, respectively, in a chelate molecule) establishing the formation of only one mononuclear chelate in each system having the composition 1: 1 (VO^{2+}: PAR or PAN).

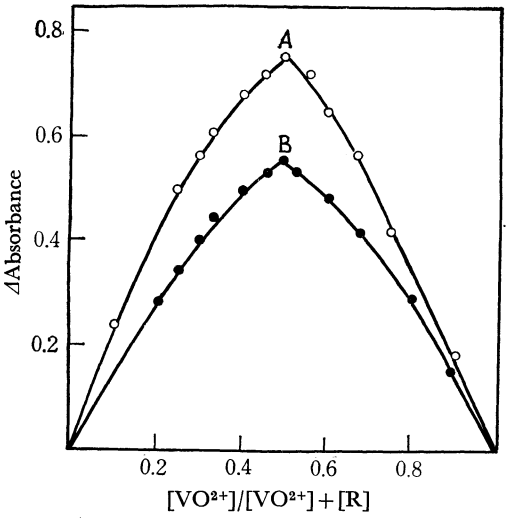

Fig. 3. Continuous variation plots, A, VO^{2+}-PAR chelate at pH 5.0, λ_{max} 550 nm (CM=CR=1.33×10^{-4}M); B, VO^{2+}-PAN chelate at pH 4.0, λ_{max} 560 nm (CM=CR=1.67×10^{-4}M).

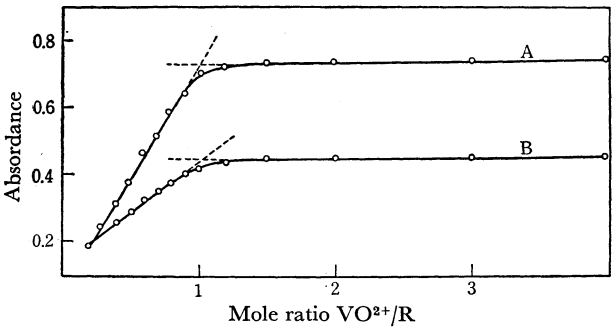

Fig. 4. Mole ratio plots, A, VO^{2+}-PAR chelate at pH 5.0, λ_{max}, 550 nm (CR=3.33×10^{-5}M); B, VO^{2+}-PAN chelate at pH 4.4, λ_{max} 560 nm (CR=5.0×10^{-5}M).

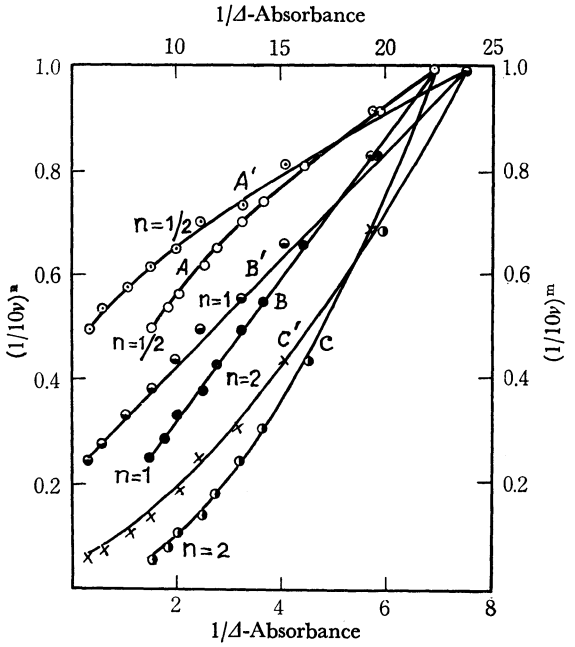

Fig. 5. Straight line plots, A, B, and C, VO^{2+}-PAR chelate in excess of $VOSO_4$ at pH 5.0, λ_{max} 550 nm, CM=2.0×10^{-3}M (1.0 m*l*), CR=2.0×10^{-3}M (0.1 —0.4 m*l*); A′, B′, and C′, VO^{2+}-PAN chelate in excess of $VOSO_4$ at pH 4.4, λ_{max} 560 nm, CM=1.0×10^{-3}M (1.0 m*l*), CR=1.0×10^{-3}M (0.1—0.4 m*l*).

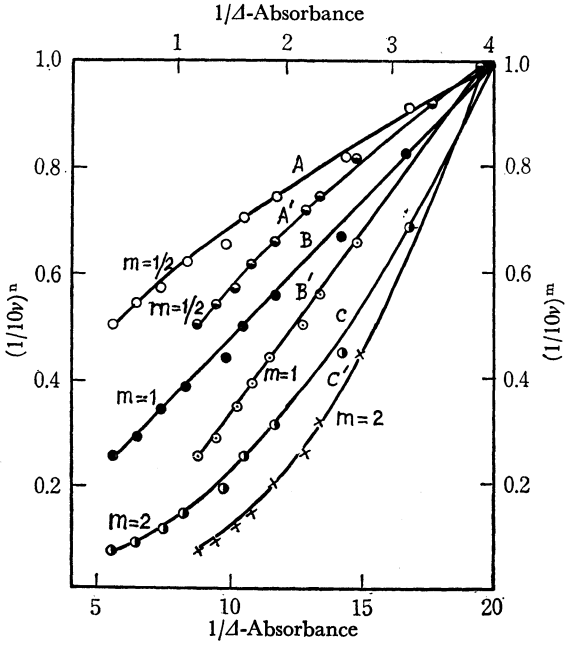

Fig. 6. Straight line plots, A, B, and C, VO^{2+}-PAR chelate in excess of $VOSO_4$ at pH 5.0, λ_{max} 550 nm, CR=2.0×10^{-3}M (1.0 m*l*), CM=2.0×10^{-3}M (0.1 —0.4 m*l*); A′, B′, and C′, VO^{2+}-PAN chelate in excess of $VOSO_4$ at pH 4.4, λ_{max} 560 nm, CM=1.0×10^{-3}M (1.0 m*l*), CR=1.0×10^{-3}M (0.1—0.4 m*l*).

The conditional stability constant values were evaluated by two different methods, (a) continuous variations using non equimolar solutions and (b) mole ratio. The stability constant (K) values along with the change in free energy of formation (ΔG) are summarised in the following table.

9) W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, **63**, 437 (1941).
10) E. Asmus, *Z. Anal. Chem.*, **178**, 104 (1960).
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Table 1. Values of log K and ΔG of VO^{2+}-PAR and VO^{2+}-PAN chelates
(Temp., 12°C; μ=0.1 $NaClO_4$)

VO^{2+} complex with	Average log K	$\Delta G=-RT\log K$ (kcal/mol)	Method
PAR	6.3	−8.2	(a)
	7.2	−9.4	(b)
PAN	6.0	−7.8	(a)
	6.7	−8.7	(b)

For the photometric determination of vanadium(IV) with PAR and PAN, ranges of Beer's law were determined. These are VO^{2+}-PAR: 2.5—0.2 and VO^{2+}-PAN: 3.5—0.1 ppm of vanadium. For more accurate analysis the Ringbom[12] optimum range was determined by plotting log [V^{4+}] in ppm against % transmittance. The Ringbom optimum range of analysis for VO^{2+}-PAR system was found to be 2.0—0.3 and for VO^{2+}-PAN system it was computed as 3.0—0.6 ppm of vanadium. The photometric error was computed from the Ringbom plot using the Ayres[13] equation. The minimum % relative error per 1% photometric error was 0.3 for VO^{2+}-PAR system and 0.8 for VO^{2+}-PAN system. The sensitivity values in Sandell units are VO^{2+}-PAR 0.002 γ/cm^2 (at 550 nm) and VO^{2+}-PAN 0.005 γ/cm^2 (at 560 nm). The molar absorptivity values computed at the same wavelengths are 2.54×10^4 for the system VO^{2+}-PAR and 1.02×10^4 for the system VO^{2+}-PAN.

Procedure

For the determination of 2.0—0.3 ppm of vanadium(IV), take PAR in five times excess. Fix the pH at 5.0 using acetate buffer and flush with nitrogen. Measure the absorbance at 550 nm and compare with calibration plot. For the determination of vanadium(IV) in 3.0—0.6 ppm range, PAN is a suitable reagent. When using PAN, the mixture should contain at least-30% ethanol. The pH should be fixed at 4.4. The procedure is similar to that for PAR.

Effect of Diverse Ions

In the determination of vanadium (IV) with PAR at pH 5.0, V^{5+}, Nb^{5+}, Ta^{5+}, U^{6+}, Zr^{4+}, In^{3+}, Ga^{3+}, Al^{3+}, La^{3+}, Bi^{3+}, Y^{3+}, Sc^{3+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}, and Pb^{2+} give positive errors and Cr^{6+}, Mo^{6+}, W^{6+}, Th^{4+}, Cd^{2+}, Fe^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+} do not interfere and interferences by Zr^{4+}, Y^{3+}, Al^{3+} are masked by adding 1 m*l* 0.4% fluoride solution.

In determination with PAN at pH 4.4, Mo^{6+}, W^{6+}, Os^{8+}, Nb^{5+}, Ta^{5+}, Ti^{4+}, Zr^{4+}, Th^{4+}, Al^{3+}, La^{3+}, Sc^{3+}, Y^{3+}, Fe^{3+}, Cr^{6+}, As^{3+}, Be^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}, Pb^{2+}, Cd^{2+}, Sn^{4+}, Mg^{2+}, Tl^{+} do not interfere while U^{6+}, V^{5+}, Ga^{3+}, In^{3+}, Bi^{3+}, Co^{2+}, Ni^{2+}, Hg^{2+}, Zn^{2+}, Cu^{2+} give positive errors.

In the determination of vanadium(IV) with PAR and PAN 100 fold excess of F^-, Cl^-, Br^-, I^-, SO_3^{2-}, NO_3^-, SCN^-, IO_3^-, NO_2^-, $S_2O_8^{2-}$, PO_4^{3-}, $B_4O_7^{2-}$ do not interfere.

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12) A. Ringbom, *Z. Anal. Chem.*, **115**, 332 (1939).
13) G. H. Ayres, *Anal. Chem.*, **21**, 652 (1949).