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A New Spectrophotometric Determination of Vanadium (V) in Pharmaceutical and Steel Samples

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Vanadium(V) is quantitatively extracted into nitrobenzene as a ternary complex in the presence of 8-hydroxyquinoline (HR) and chlorosubstituted acetic acids, namely monochloroacetic acid (MCA), dichloroacetic acid (DCA) and trichloroacetic acid (TCA). The optimum experimental conditions for the quantitative recovery of vanadium and also the composition of the extracted ternary species have been determined. The effectiveness of these chlorosubstituted acetic acids as synergists for the extraction of vanadium is found to have the order TCA > DCA > MCA. A sensitive analytical procedure for vanadium is developed based on the formation of the ternary complex with HR and TCA which is highly suitable for its determination in pharmaceutical and standard steel samples.

INTRODUCTION

Binary vanadium(V)-8-hydroquinoline (HR) complex which is extractable into organic solvents has been extensively studied[1]. Rao *et al.*[2–6] and Sriramam *et al.*[7] reported that some anions present in buffer components and inert electrolytes to maintain ionic strength constant in the extraction of vandium-HR system into nitrobenzene interfere through the formation of ternary complexes giving various coloured extracts. However, when certain other solvents are used; only magenta black binary vanadium-HR complex is extracted even in the presence of these anions. Blair and Pantony[8] reported a spot test for the identification of TCA, a usual buffer component using vanadium-HR complex as a reagent. No detailed investigation of this colour reaction has been studied so far. This communication presents a detailed study on the ternary complex formation of vanadium(V)-HR with chloro-substituted acetic acids *viz.*, MCA, DCA and TCA as synergists and extraction of these complexes into nitrobenzene.

Of these ternary complexes studied, the one between V(V)–HR and TCA has higher sensitivity for vanadium and basing on this a spectrophotometric procedure for its determination in pharmaceutical and standard steel samples has been reported.

EXPERIMENTAL

A Beckman-DU 40 Spectrophotometer with Epson Printer and Eltop 3030 pH meter with a glass electrode combination were used.

A 0.01 M vanadium(V) solution was prepared by dissolving ammonium metavanadate (GR E. Merk) in distilled water and standardized potentiometrically using standard iron(II) solution. Suitable dilutions were made as when needed. A 0.2 M solution of 8-hydroquinoline was prepared by dissolving 8-hydroxy quinoline (AnalaR, BDH) in minimum amount of dilute sulphuric acid. Required concentration of 8-hydroquinoline was obtained by suitable dilution of the stock solution with dilute sulphuric acid. 2.0 M solutions of sodium salts of MCA, DCA and TCA were prepared by reacting required amount of the acid HA (Riedel, Germany) with equivalent amount of sodium hydroxide (AnalaR, BDH).

All other chemicals used were of analytical grade reagents. The solvents were distilled before use.

General extraction procedure

5.0 mL of 4.0×10^{-4} M vanadium(V) solution (*ca.* 100 μg) along with the required amounts of HR solution (5 mL of 0.2 M HR) and of the salt solutions (5 mL of 2 M MCA/DCA/TCA) were taken in a 125 mL separating funnel. The total volume of the aqueous phase was made up to 20 mL, the pH being adjusted to required value with dilute sulphuric acid or sodium hydroxide. The ionic strength of the aqueous phase is maintained at 0.5 with sodium sulphate as the inert electrolyte. The aqueous phase was then equilibrated for 2 min with 20 mL of nitrobenzene. The organic phase was separated and dried over anhydrous sodium sulphate and its absorbance was measured at 630 nm aganist a respective reagent blank. The pH of the aqueous phase was checked up. The mass balance and hence the distribution ratio for vanadium was calculated by determining the vanadium content in the aqueous phase also using the procedure described elsewhere[9].

The optimum experimental conditions for the formation of these ternary complexes, their absorption characteristics, stability constants and synergistic coefficient values are presented in Table-1. The absorption spectra of these ternary complexes along with the binary complex in nitrobenzene are depicted in Fig. 1. The colour of the extract is stable for more than 12 h provided care is taken to prevent loss of the solvent. Experiments based on the graphical method of Coleman *et al.*[10] indicate that a single individual absorbing species is present throughout in all the systems (corresponding to the three HA species)

The composition of these ternary complexes in all the systems were determined by distribution studies. Plots of log q vs $[HR]_{total}$ (Fig. 2) in the presence of constant excess of corresponding [HA] gave straight lines with slope two indicating that two molecules of HR are associated with vanadium in the extracted ternary complex. The ratio of vanadium to the respective HA in the extracted ternary complex is determined by Hiskey-Meloche's method[11], the absorbance being measured at 800 nm, where the binary V-HR complex has negligible absorbance. Fig. 3 is the plot between log q and pH in the presence of constant

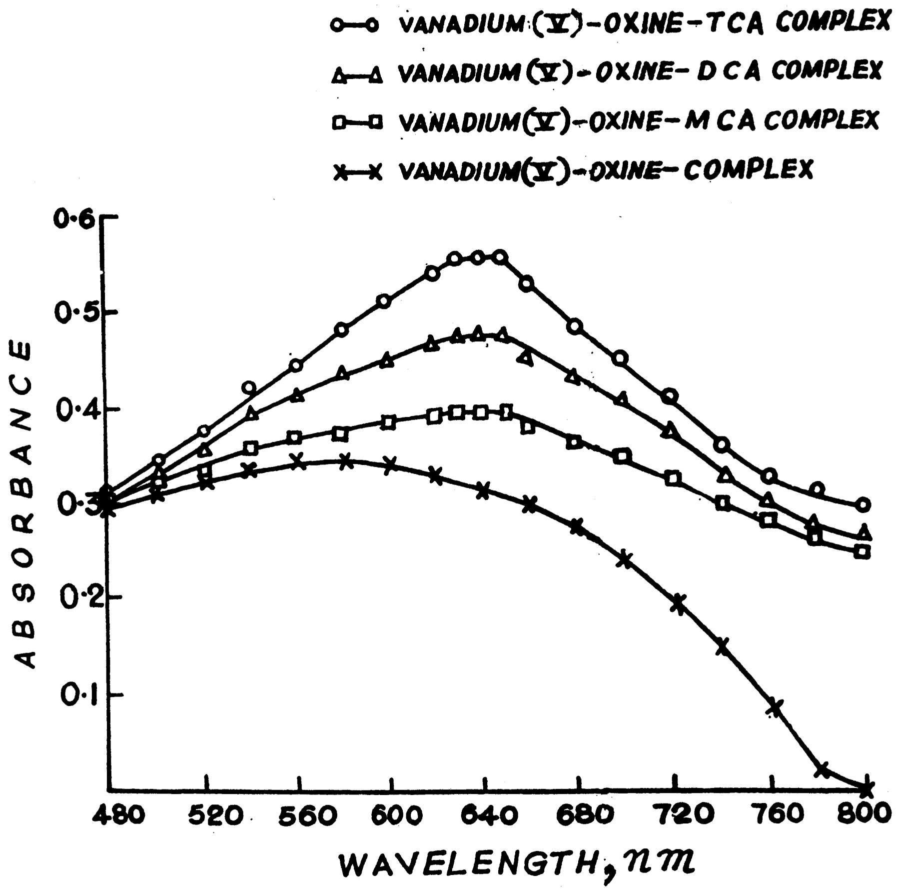

Fig. 1. Plot of absorbance vs wavelength.
Aqueous phase: [vanadium] = 1.0×10^{-4} M, [oxine] = 5.0×10^{-2} M, [TCA/DCA/MCA] = 5.0×10^{-1} M
Aqueous phase = 20 mL, Organic phase = 20.0 mL of nitrobenzene

excess of HR and HA for the ternary system which are linear with slope one indicating the release of one proton during the ternary complex formation enabling us to assume that of the two HR molecules in the ternary complex, one is ionized to associate as a chelate while the other is attached as a monodentate adduct. Based on these findings, the composition of the ternary complex in the extracted species can be represented as $[VO(R)(HR)(A)_2]$ which satisfies hexa-coordination for vanadium[12] and is also being hydrophobic in its nature which explains the quantitative recovery of vanadium. Marked synergism in the extraction of vanadium has been extracts to a small extent. There is no extraction of vanadium in the presence of these chlorosubstituted acetic acids alone under the experimental conditions. The synergistic coefficient data presented in Table-1. sugests the order of synergism (effectiveness of HA (MCA/DCA/TCA) as a synergist for the extraction of vanadium as the ternary complex) to be TCA >

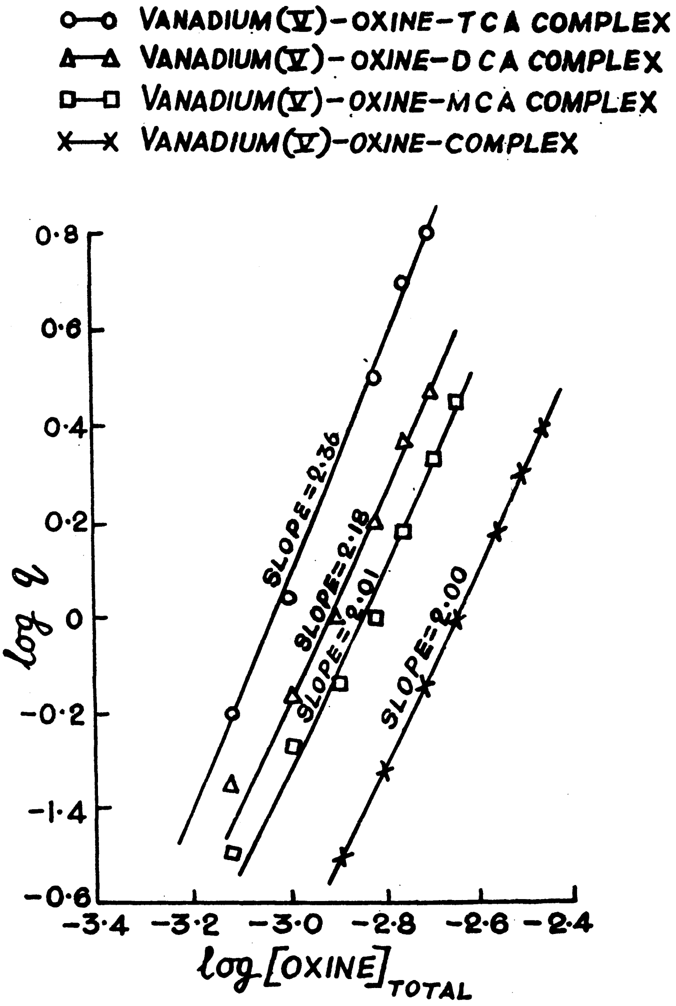

Fig. 2. Plot of log q vs log [oxine]$_{\text{total}}$

Aqueous phase: [vanadium] = 1.0×10^{-4} M, [oxine] = 6.0×10^{-4} to 4.0×10^{-3} M, [TCA/DCA/MCA] = 5.0×10^{-1} M.

Aqueous phase: 20.0 mL, Organic phase: 20.0 mL of nitrobenzene

DCA > MCA. The extraction constants (K_{ex}) of these ternary complexes and that of the binary determined by using distribution data are presented in Table-1 and the data suggests that the order of the effectiveness of these chloro-substituted acetic acids as synergists for the extraction of vanadium as a ternary complex correlates well with the corresponding increasing trend in the log K_{ex} value. It is also observed from the data in Table-1 that there is a linear relationship between the dissociation constant (pK_a) of the chloro-substituted acetic acids[13] and the extraction constant [K_{ex}] of the respective ternary complex as is graphically shown in Fig. 4

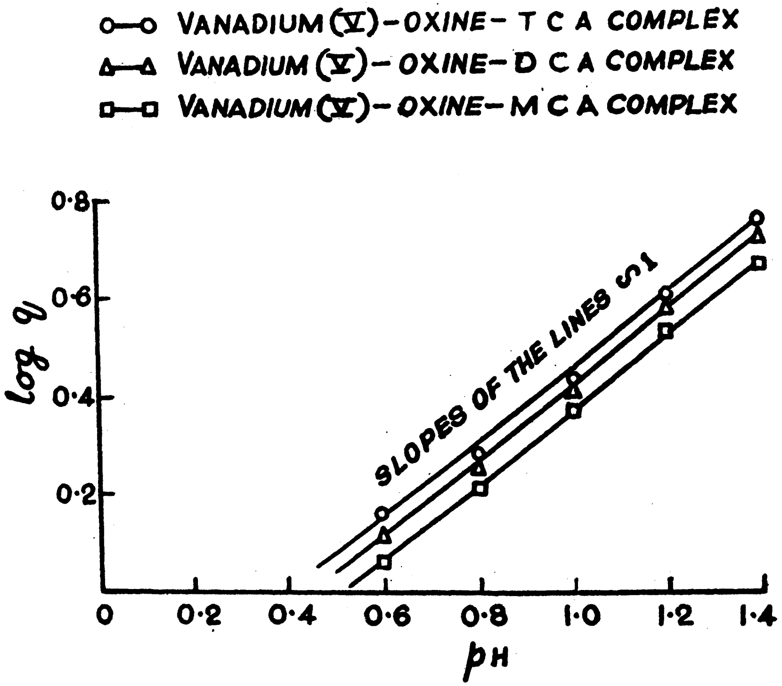

Fig. 3. Plot of log q vs pH
Aqueous phase: [vanadium] = 1.0×10^{-4} M, [oxine] = 5.0×10^{-2} M, [TCA/DCA/MCA] = 5.0×10^{-1} M.
Aqueous phase: 20.0 mL, organic phase = 20.0 mL of nitrobenzene

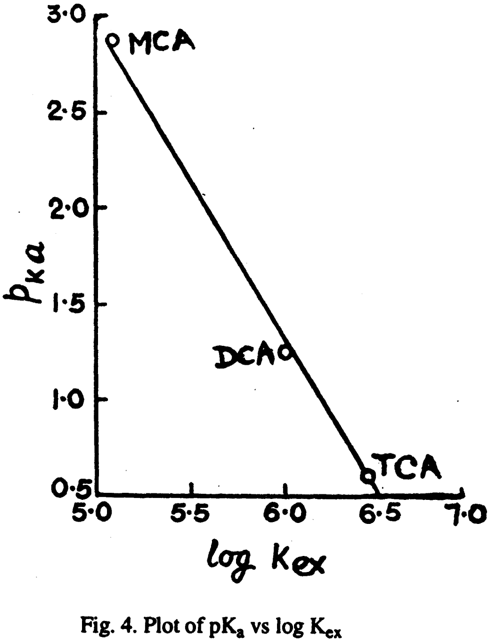

Fig. 4. Plot of pK$_a$ vs log K$_{ex}$

TABLE-1
OPTIMUM CONDITIONS AND ABSORPTION/EXTRACTION CHARACTERISTICS FOR VANADIUM(V)-OXINE-(MCA/DCA/TCA) TERNARY COMPLEX SYSTEMS.

Anion	Optimal pH	Minimum molarity		max (nm)	l mol^{-1} cm^{-1}	log K_{ex} at 30 ± 0.1°C	pk_a	Synergistic coefficient
		HR	HA*					
None	3.0–4.5	0.10	—	540–580	3460	3.4†	—	—
SO_4^{2-}	3.0–4.5	0.10	1.0	540–580	3460	—	—	—
CH_3COO^-	3.0–4.5	0.10	1.0	540–580	3460	—	—	—
CH_2ClCOO^-	1.5–4.0	0.10	0.5	610–640	3950	5.2	2.85	0.61
$CHCl_2COO^-$	1.5–3.5	0.02	0.3	610–640	4700	6.0	1.25	0.93
CCl_3COO^-	1.0–3.0	0.01	0.2	610–640	5800	6.4	0.66	1.15

*Taken as sodium salt

†Determined and found to be agreeing with the value reported by Rao *et al.*[5]

RESULTS AND DISCUSSION

From the data in Table-1, of the three ternary complexes studied, only V-HR-TCA system is found to be more sensitive (comparison of ε values), a procedure for the determination of vanadium with application to the analysis of pharmaceutical and standard steel samples has been undertaken. Beer's law was obeyed up to 18 μg of vanadium/mL at 630 nm while Ringbom plot[14] indicated a range of 0.5–8.0 μg of vanadium/mL as the optimum range with minimum photometric error. The sensitivity of the colour reaction as defined by Sandell[15] is found to be 0.0094 μg of vanadium per mL at 630 nm. The equation for the calibration curve for the determination of vanadium is $X = 9.0253A-0.1619A$ where 'A' is the absorbance measured and 'X' the concentration of vanadium in solution, μg/mL. The correlation coefficient of absorbance-concentration relationship for vanadium is 0.9993.

General procedure for the determination of vanadium

An aliquot of vanadium containing 10–60 μg is treated with 5 mL of 0.2 M HR solution and 5 mL of 2.0 M sodium trichloroacetate (NaTCA) in a 125 mL separatory funnel. The pH is adjusted to 2 in a total aqueous volume of 20 mL. This is equilibrated with 20 mL of nitrobenzene for 2 min. The phases are separated and the organic phase is dried over anhydrous sodium sulphate and its absorbance is measured at 630 nm against a reagent blank. The amount of vanadium is calculated from the equation for the calibration curve for the determination of vanadium. Some typical results are presented in Table-2.

The interference of various substances was studied in the determination of 100 μg of vanadium in a total aqueous volume of 20 mL. Al^{3+}, Ba^{2+}, Bi^{3+}, Ca^{2+}, Cr^{3+}, Li^+, Mg^{2+}, Zn^{2+} PO_4^{3-} and CO_3^- do not interfere when present in 100-fold excess. The tolerance limits for other substances are Ni^{2+}, 1 mg; U(VI), 4 mg; Mo(VI), 0.5 mg; Cu(II) and Co(II), 100 μg. Iron(III), oxalate and EDTA interfere seriously even when present at very low concentrations. Fluoride is tolerated up to 40-fold. The interference of tungstate even when present in 100-fold amounts can be eliminated by adding sodium pyrophosphate (overall 0.035 M). The interference of iron can be eliminated by extracting twice with IBMK from 4 M hydrochloric acid solution as an ion-association complex $H^+ : FeCl_4^-$. The general excipients and additives used in pharmaceutical preparations are found not to interfere with the procedure for the determination of vanadium.

TABLE-2
DETERMINATION OF VANADIUM

S.No.	Vanadium, μg		Relative error (%)
	Taken	Found (Mean* ± 95% confidence interval)	
1.	12.26	12.24 ± 0.02	0.16
2.	18.48	18.36 ± 0.03	0.65
3.	25.52	25.48 ± 0.02	0.16
4.	56.42	56.86 ± 0.02	0.84
5.	68.28	68.24 ± 0.02	0.05
6.	89.22	88.94 ± 0.03	0.30
7.	106.44	106.24 ± 0.03	0.20
8.	125.42	125.38 ± 0.02	0.30
9.	142.22	142.86 ± 0.02	0.45
10.	156.42	156.28 ± 0.02	0.10

*Average of five determinations

Dissolution procedure for steel samples

Transfer 0.5 g of sample A or 2.0 g of sample B (Table-3) which are accurately weighed into a 600 mL beaker and heat with 100 mL of acid mixture (320 mL of 1 : 1 sulphuric acid + 80 mL of 80% phosphoric acid + 600 mL of distilled water) until reaction ceases. Then add 10 mL of (1 : 1) nitric acid and boil to dissolve all black carbide particles and to expel nitrous fumes. Cool, dilute to 200 mL with distilled water, filter through a Gooch crucible and wash into dilute sulphuric acid (1 : 200) and make up to the mark with distilled water after transferring to a 250 mL volumetric flask.

Dissolution procedure for ferrovanadium

About 0.1 g of sample-C (Table-3) accurately weighed is treated with 80 mL of 1 : 3 sulphuric acid and 40 mL of 1 : 1 nitric acid in a 600 mL beaker. When the reaction abates, the solution is evaporated to dense white fumes, cooled, diluted with distilled water and again heated to dissolve the salts. The solution is cooled to room temperature, transferred to a litre volumetric flask and made up to the mark with distilled water.

Sample solution preparation in the case of the pharmaceutical sample

Neogadine Elixir (Raptakos Britt and Co. Ltd., Bombay) which is used as a tonic and appetite stimulant which contains vanadium is treated as follows : 30 mL of the sample-d (Table 3) is weighed accurately and treated with 100 mL of acid mixture (200 mL of 1 : 1 sulphuric acid + 100 mL of 1 : 1 nitric acid) and heated on a sand bath to white fumes for 30 min. Then it is treated with distilled water and dried on a sand bath twice and finally transferred to a 100 mL volumetric flask and made up to the mark with distilled water. However, care should be taken to ensure before the transfer of the solution to the volumetric flask that the alcohol content of the sample is completely eliminated otherwise it may interfere with the procedure for the determination of vanadium giving a red coloured extract in the presence of HR. However, with the above recommended procedure, the authors did not encounter any such problem.

TABLE-3
DETERMINATION OF VANADIUM IN PHARMACEUTICAL AND STEEL SAMPLES

Sample	Vanadium (%)		Relative error (%)
	Certified value	Value obtained by present procedure (Mean* ± 95% confidence interval)	
(a) B.C.S. No. 220/2	1.940	1.920 ± 0.02	1.03
(b) B.C.S. No. 224/ 1 Cr-V steel	0.190	0.188 ± 0.04	1.05
(c) B.C.S. No. 205/3 Euro-standard 57-1 Ferrovanadium	50.160	49.840 ± 0.02	0.60
(d) Neogadine Elixir	0.00184	0.00183 ± 0.04	0.54

*Average of five determinations

Recommended Procedure-I

Transfer 5.0 mL of the sample solution (a or b) and 2 mL of c into a 125 mL separtory funnel. Enough concentrated hydrochloric acid (around 3.5 mL) is added to give an overall acidity of 4 N in 10 mL aqueous phase. All the iron content is removed by shaking this solution with four 10 mL portions of IBMK for two minutes each which are separated and discarded. To the separated aqueous phase 2.5 mL of 2 M sodium pyrophosphate (in the case of sample-a), 50 mL of 0.2 M HR solution and 5 mL of 2 M NaTCA are added. The pH of the solution is adjusted to around 2 with sodium hydroxide. Although the total aqueous volume at this state slightly exceeds 20 mL, it has no deleterious effect on the extraction and analytical determination of vanadium. The contents were equilibrated with 20 mL of nitrobenzene for 2 min. After separation, the organic phase is dried over anhydrous sodium sulphate and the absorbance measured at 630 nm against the corresponding reagent blank. The amount of vanadium in each case is calculated from the equation for the calibration curve for the determination of vanadium given earlier. The results of the analysis are incorporated in Table-3.

Recommended procedure-II

5 mL of the sample-d (Table 3) solution is taken in a 125 mL separatory funnel to which 5.0 mL of 0.2 M HR solution and 5.0 mL of 2 M NaTCA solution are added. The pH of the solution is maintained at around 2 by using sodium hydroxide or dilute sulphuric acid and the total aqueous volume is made up to 20 mL. The contents of the aqueous phase is equilibrated with 20 mL of nitrobenzene for 2 min. After separation of the phase, the organic phase is dried over anhydrous sodium sulphate and the absorbance measured at 630 nm against a reagent blank. The amount of vanadium is calculted from the equation for the calibration curve for the determination of vanadium given earlier. The results of the analysis are incorporated in Table-3.

The recommended procedures for the determination of vanadium have the advantage of being free from the interference of the substances usually present in pharmaceutical preparations and steels which otherwise need cumbersome and tedious procedures to eliminate them before hand. The results in Table-3 suggest that a wide variety of samples with varying vanadium contents can be successfully analyzed by the recommended procedures.

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