

Spectrophotometrical and Thermal studies on Vanadium-Pyrocatechol Complexes and their Application for Vanadium Ions Determination.

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Abstract

Pyrocatechol (P.C.) is proposed as a spectrophotometric reagent for some metal ions determination. It reacts with vanadium ions to give stable coloured complexes in two stoichiometric ratios 1:2 and 1:3. The composition, stability and spectrophotometric characteristics of the formed complexes are reported. The solid V-P.C. complexes are separated and characterized using elemental analysis, IR spectra and thermal analysis (DTA and TG) in order to outline their structures and thermal stability. Determination of vanadium in some deposits are also outlined spectrophotometrically.

Keywords: Vanadium pyrocatechol complexes, spectrophotometrically, thermal analysis.

Introduction

Vanadium forms number of complexes with some phenolic ligands and have been studied spectrophotometry¹⁻⁴. Charney et al⁵. and others⁶⁻⁷ reported interesting investigation on the polyhydric phenols containing two ortho OH groups as excellent analytical reagents. On the discriminating and stability increasing properties of pyrocatechol-vanadium complexes, many works were published elsewhere⁸⁻¹⁰. Unfortunately, the publication on studying the effect of temperature on such complexes are scanty. Therefore, this work is devoted to throw more light on the thermal stability of the formed solid complexes and the use of the coloured V-P.C. chelates in the microdetermination of vanadium of some deposits. Also, it is aimed to study the capability of using these complexes as dye stuff.

Experimental

Reagents

All chemical used were of analytical-reagent grade and doubly distilled water from alkaline permanganate solutions was used for preparation of solutions. Pyrocatechol stock solution, 1.0×10^{-2} M of

ammonium metavanadate solution was prepared by dissolving the appropriate amount in 250ml of distilled water. 1.0M and 0.1M solutions of HCl and carbonate free-NaOH were prepared and used for adjusting the pH-values. All stock solutions were diluted as necessary to produce working standard solutions.

Apparatus

The absorption spectra of solutions to be tested were recorded on spectronic 601 instrument (from Milton Roy Company, USA). The IR spectra of the prepared complexes were also recorded as KBr discs on a Beckmann Infrared spectrophotometer (Inc, fullation. California USA) in the wave number range 250-4000 cm^{-1} . Thermal analysis (DTA. TG) were performed by using Shimadzu 30 series thermal analysis instrument in the temperature range 20-520 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{min}^{-1}$. under a nitrogen atmosphere.

Solid complexes

The solid V-P.C. complexes (1:2 and 1:3) were prepared as the method mentioned elsewhere¹¹. The microanalyses of separated complexes were carried out in the Micro Analytical Unit, Cairo University.

Spectrophotometric Determination of Vanadium in its Deposits

The sample deposits were used to test the possibility of using P.C. as a selective indicator for the spectrophotometric determination of vanadium (V). Nine samples of vanadium deposits were collected from boilers of the electrical generating station of South Cairo. The samples were dissolved and prepared for analysis as given before¹¹. $1.0 \times 10^{-2}\text{M}$ of P.C. was added to 0.1-0.7ml of the previously prepared vanadium deposit solutions. The pH was adjusted at 5.5 and the absorbance was measured at $\approx 550\text{nm}$ after waiting 1min., 1hrs., 3hrs. or 5hrs. for colour development.

Results and Discussion

Absorption Spectra

The absorption spectra of $2 \times 10^{-4}\text{M}$ P.C. ligand as shown in Fig. (1) exhibit two absorption bands at pH 2.0-12.0 and λ 220-230nm ($\epsilon = 1.46 \times 10^4$) and 250nm ($\epsilon = 5 \times 10^5$). The pKa values of P.C. calculated by the limiting absorbance method¹² were $\text{pK}_1 = 7.15$ and $\text{pK}_2 = 10.75$ respectively. The spectrum of the reaction of ($1 \times 10^{-2}\text{M}$) with V(V) ($2 \times 10^{-3}\text{M}$) solution against a reagent blank similarly prepared but containing no vanadium exhibits a new band at $\lambda = 550\text{nm}$ and pH = 4-8 (Fig.2). The band is unambiguously due to the formation of V-P.C. binary complex.

This band undergoes bathochromic and hypochromic shifts on increasing the pH. This may be attributed to the formation of more than one complex species of different maximum absorbances. The intensity of the colour of the formed complex increases with time, so it is preferable to leave the excess ligand in contact with V(V) ions at the suitable pH (5.5) for some times (15min.) to allow the colour development.

Stoichiometry of the Complexes

The stoichiometry of the formed complexes between V(V) and P.C. indicator was studied spectrophotometrically by applying the familiar molar ratio (M.R.) and continuous variation (C.V.) methods. The results revealed the formation of 1:3; M:L, complex at pH = 2.0 - 10.0 and $\lambda_{\max} = 550\text{nm}$ but the absorbance vs pH graph for solutions containing excess ligand to V(V) ions show two inflections at the aforementioned pH range indicating the existence of two ratios of the complexes in solution. This is probably due to a stepwise transition of the two complexes (Fig.2). This result was also confirmed by microanalysis for the separated solid complexes. The stability constants of the complexes were evaluated by the method of Taneija¹³ and are given in Table 1. The average value of the stability constant for 1:3 complex was 8.76. These conditions allow the spectrophotometric determination of V(V) as an alternative to ICP-OES.

Table 1. Stability constant of V(V) P.C. complex at pH=5.0 - 7.0; $\lambda_{\max}=550\text{nm}$ $T_L = 1 \times 10^{-2}\text{M}$; $T_M = 2 \times 10^{-3}\text{M}$; $\text{p}K_1 = 7.10$ and $\text{p}K_2 = 10.75$

pH	A	A_{\max}	n	pL	Log K
5.0	1.228	1.875	0.655	9.966	10.24
5.2	1.260	1.875	0.675	9.57	9.94
5.4	1.290	1.875	0.688	9.42	9.76
5.6	1.340	1.875	0.715	8.77	9.17
5.8	1.390	1.875	0.741	8.30	8.17
6.0	1.490	1.875	0.768	7.97	8.75
6.2	1.500	1.875	0.800	7.58	8.49
6.4	1.570	1.875	0.837	7.18	8.18
6.6	1.650	1.875	0.880	6.79	7.89
6.8	1.760	1.875	0.938	6.39	7.66
7.0	1.875	1.875	1.000	6.00	7.55

Log K av = 8.75, T_L = The stoichiometric concentration of the ligand, T_M = The stoichiometric concentration of the metal.

Spectrophotometric Determination of Vanadium in Some Deposits Using P.C. as Indicator

Nine vanadium deposits were made as very fine powder and digested by microwave computerized system as given before¹¹. The analysis was conducted by ICP-OES instrument connected to auto sampler device. This was performed in the Institute Fur Siedlungs, Wasserbau Wassergut, Stuttgart University, Germany. Vanadium and other elements such as alkali (Na, K), alkaline earths (Mg, Ca, Ba) and heavy metals (Cr, Mn, Fe, Co, Zn, W) were analyzed four times in four weights of each sample. The average content of V in each sample, the standard deviation and the relative standard deviation were $1488 \times 10^2 \text{ mg/kg}$, 0.32-3.3 and 0.16-0.8% respectively. These results refer to the high accuracy of ICP-OES analysis of the given deposits.

The deposits in our laboratory was opened using 1, 2, 3 or 18M NaOH, 0.5, 1, 2 or 12.5M HNO₃ and a mixture of 2ml HF, 5ml HNO₃ and 50ml H₂SO₄. All samples were filtered off and solutions were prepared in 100ml deionized water. Various volumes of each prepared solution (0.1-0.7ml) were added to 5ml 0.05M solution of P.C ligand and the pH was adjusted at 5.5 and the absorbance was measured at 550 nm after leaving the mixture to develop its colour for 1 min., 1hr., 3hrs. and 5hrs. Respectively using water as a blank. From the measured absorbance, the vanadium concentration was determined using the calibration curves (Fig 3).

Table 2. Spectrophotometric determination of vanadium in its deposits by using P.C. as indicator H₂O as a blank at pH = 5.5 and $\lambda_{\text{max}} = 550\text{nm}$.

No.	Vanadium deposits dissolved in	Dissolution %	Time before measuring absorbance			
			1min.	1hr.	3hrs	5hrs
			[V] x 10 ² in mg/kg			
1	18M NaOH	36.3	4442	3837	2976	2761
2	3M NaOH	40.9	5758	5662	3930	4743
3	2M NaOH	36.5	4361	4347	3095	3944
4	1M NaOH	35.2	5188	5262	3482	3628
5	12.5 HNO ₃	41.2	4220	3994	3332	3379
6	2 HNO ₃	60.2	8019	8780	7029	7388
7	1 HNO ₃	49.0	5726	6807	5063	4962
8	0.5 HNO ₃	38.4	3987	4517	3538	3972
9	HF + HNO ₃ + H ₂ SO ₄	95.0	3596	4227	3472	3914

The results recorded in Table (2) show a much deviation of V concentration in comparison to its average value measured by ICP-OES method (1488×10^2 mg/kg). Therefore, we have been studied the interference of the coherent elements present in V deposits. In this concentration we use these metals in concentration similar to that given by ICP-OES mixed with the used concentration of P.C as blank. The results presented in Table (3) indicates that the value of V concentration in deposits which was opened by 3M NaOH, 0.5 or 2M HNO₃ or mixture of HF+HNO₃ + H₂SO₄ (0.4:1:10) are 1323×10^2 , 1374×10^2 , 1400×10^2 and 1577×10^2 mg/kg respectively which are near to the average value of V obtained by ICP-OES (1488×10^2 mg/kg). It is worth mentioning that, the deposit is not completely digested by microwave system and values obtained here are for the digested part of the deposits only.

Table 3. Spectrophotometric determination of vanadium in its deposit using P.C. as indicator and a blank solution containing the same concentration of the interfering metal ion at pH = 5.5 and $\lambda_{\max} = 550\text{nm}$

Sample	V deposit dissolved in	[V] in mg/kg
1	18M NaOH	1120.0×10^2
2	3M NaOH	$1323.4.0 \times 10^2$
3	2M NaOH	1221.6×10^2
4	1M NaOH	534.5×10^2
5	12.5 HNO ₃	1043.5×10^2
6	2 HNO ₃	1400.0×10^2
7	1 HNO ₃	2074.2×10^2
8	0.5 HNO ₃	1374×10^2
9	HF + HNO ₃ + H ₂ SO ₄	1577.9×10^2

Comparison With Other Methods

The proposed method is simple and yields a dark blue complex which is stable for 12hrs. Therefore, V(V) can be determined directly in aqueous solution without the need for extraction into organic solvents. The method described here is highly sensitive and is comparable to other methods for direct spectrophotometric determination of V. The sensitivity of other methods are listed in Table (4).

Table 4. Comparison of Spectrophotometric reagents used for determination of V (V).

Reagent	[V] mg/ml	ϵ , mol ⁻¹ cm ⁻¹	pH	λ nm	Ref.
3.5 diamino 4- (o-hydroxyphenyl)azole pyrazole	0.2	3.5x10 ³	4.0	450	14
8-Hydroxyquinoline (chloroform extract)	3.0	3.4x10 ³	3.5 4.5	550	15
Catechol-pyridine N-oxide (solvent extraction)	0.1	7.0x10 ⁴	3.0	720	16
Pyrocatechol-4-aminoanti-pyridine	2.04	5.3x10 ⁴	4.0	340	17
Catechol	1.4	9.0x10 ⁴	5.5	550	This work

Solid Vanadium P.C Complexes.

The above study of V(V) P.C. complexes in solution by CVM and MRM proved the formation of 1:3 complex and proved also that they can be utilized as dyes but they need a long time to develop their stable colour. This study encouraged us to isolate these complexes in deep blue solid complexes. The results obtained by elemental analysis of the solid vanadium complexes are in an agreement with the formation of 1:2 and 1:3 complex types having a molecular formula $L_1=VC_{12}H_{22}O_{14}N$ (M.W.454.4), $L_2=VC_{18}H_{24}O_{14}N$ (M.W.528.9) respectively.


To understand the nature of the bonding in pyrocatechol and its complexes, assignment of IR bands¹⁸ is necessary, Table (5). The ligand spectra are characterized by a broad band at 3320-3470cm⁻¹ may be assigned to ν OH of both free and hydrogen bonded phenolic groups of P.C. the bands at 1180, 1470 and 1600-1620 cm⁻¹ may be attributed to the aromatic ring vibrations of the ligand.

The IR spectra of L_1 show the disappearance of ν OH of the phenolic groups of two P.C. molecules which are strongly bonded to vanadium ion. The appearance of a new band at 1370-1390 characteristic to ν N=O refers to the non sharing of nitrate anion in complex formation and present in the outer sphere in the moiety of the complex¹⁹. The broad weak band appeared at 3000-3600cm⁻¹ substantiates the presence of the water in coordination sphere of this complex.

The IR spectra of L_2 show a broad weak band at 3300-3450cm⁻¹ which may be attributed to water molecule and/or OH groups. The sharp

band appear at 500-600cm⁻¹ in both complexes indicates the bonding of either phenolate anions to metal (M-O)¹⁹.

Table 5. Assignment of the fundamental group vibration of p. c. and vanadium P. C. complexes (L₁ and L₂).

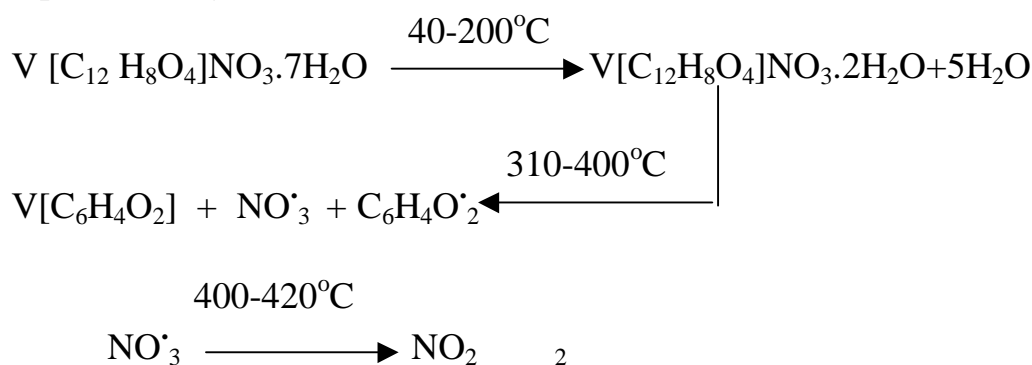
Comp.	Mode					
	ν 	ν (C=C) aromatic	ν (C H) aromatic	ν (C H) aromatic	ν (OH)	ν (NO ₂)
P. C.	1180 sh 1470 sh	1600- 1620 sh	730- 770sh	3050 s	3330 b 3470 b	-----
L ₁	1450 s	1600 w,b	870 s,b	3150 s,b	3000- 3600 b	1370- 1390 s,b
L ₂	1470 s,b	1600 b	820 s, sh 880 s, sh	3150 s,b	3300- 3450 b	1370 s,b

b= broad, S= small, sh= sharp and w = weak.

Thermal Analysis

The DTA and TG of L₁ and L₂ complexes were studied aiming to check their thermal stability. The resulting data are shown in Fig. 4 and represented in Table (6). The DTA of L₁ shows one very large big endotherm at 40-200°C which refers to the loss of five water molecules of hydration and/or crystallization (calcd. mass loss = 19.8 and found = 20%) as given by TG of L₁. This is followed immediately by a broad exthotherm at 200-310°C which may be attributed to the increase in heat capacity of the remaining part of the complex. The second endotherm at 310-400°C refers to the loss of the pyrocatechol molecule together with NO₃ group (calcd. mass loss = 37.6 and found = 37.5%).

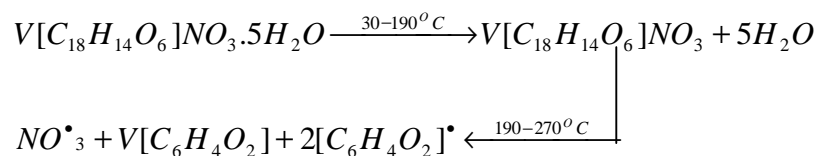
The decomposition of NO₃ radical into NO₂ gas or radical appears as a vigorous sharp exotherm at 400-420°C. these changes can be represented by



Scheme (1)

This scheme indicates no loss of phenolic radical which means that vanadium is strongly bounded to P.C molecules. Therefore this complex can be used as dye ink or painting agent at high temperature.

The DTA and TG of L₂ show an exothermic sharp peak at 20-30°C which may be attributed to increase in heat capacity and vigorous internal rearrangement occur in complex. This followed by a very large broad endotherm at 30-190°C comparable to L₁ and it refers to a mass loss of five water molecules of hydration and/or crystallization (calcd. mass loss 17.0 and found 17.0). At 190-270°C a broad exotherm peak is appeared due to the mass loss of two molecules of P.C. ligand as active radicals (calcd. mass loss = 41.2 and found 41.0%) as given by TG data (Table 6). The last very sharp exotherm appears in a narrow range (280-290°C) which may be attributed to fast rearrangement occurs in the remaining part of L₂ and/or rearrangement of the loosed active P. C. radical. These changes and reactions may be tentatively given by:



Scheme (2)

The activation energy and the order process were calculated by Zayed method²⁰ and are depicted in Table (6). Comparing the activation energies of the two complexes, one can state that L₁ is more stable than L₂. Based upon the above facts, the following structural formulae for the formed complexes are proposed:

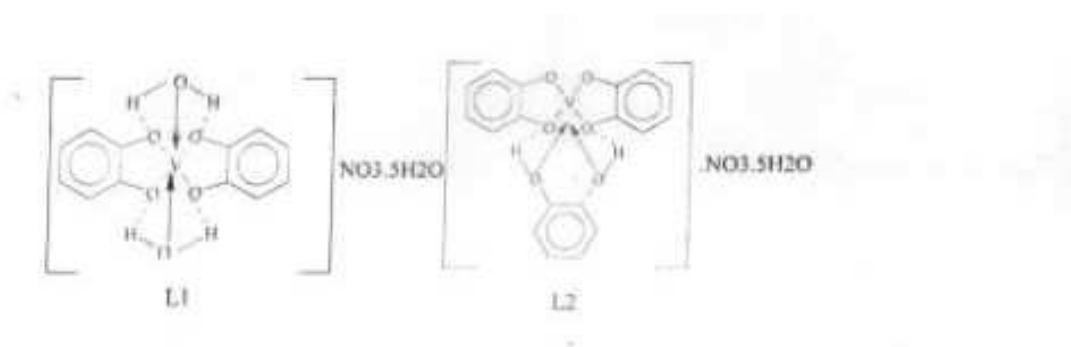


Table 6. Mass loss and activation parameters for decomposition steps of vanadium complexes (L_1 and L_2).

Comp.	Decomposition steps and temp. range ($^{\circ}\text{C}$)	Mass loss %		Decomposition Products	E^* (kg/mol)	Order
		Calcd.	found			
L_1	1 st step endo 40-200	19.8	20.0	$5\text{H}_2\text{O}$	0.022	1.0
	2 nd step exo 310-400	37.6	37.5	$\text{C}_6\text{H}_5\text{O}_2 + \text{NO}_3$	0.146	0.0
L_2	1 st step exo 20-30	-	-	-	0.565	0.667
	2 nd step endo 30-190	17.0	17.0	$5\text{H}_2\text{O}$	0.323	1.0
	3 rd step exo 190-270	41.2	41.0	$\text{C}_{12}\text{H}_{10}\text{O}_4 + \text{NO}_3$	0.253	0.0

Conclusion

Pyrocatechol is recommended as indicator for spectrophotometric determination of vanadium in its deposits with using mixture of heavy metal complexes with P. C. in the same conditions as a blank. This suggested classical procedure can be used to avoid the use of highly expensive sophisticated instruments as ICP-OES and XRF which may not be available in the field of vanadium deposit production. Also, the prepared complexes are freely soluble in water and polar organic solvents; therefore they can be used as dye, black ink or in industrial tanning processes²¹.

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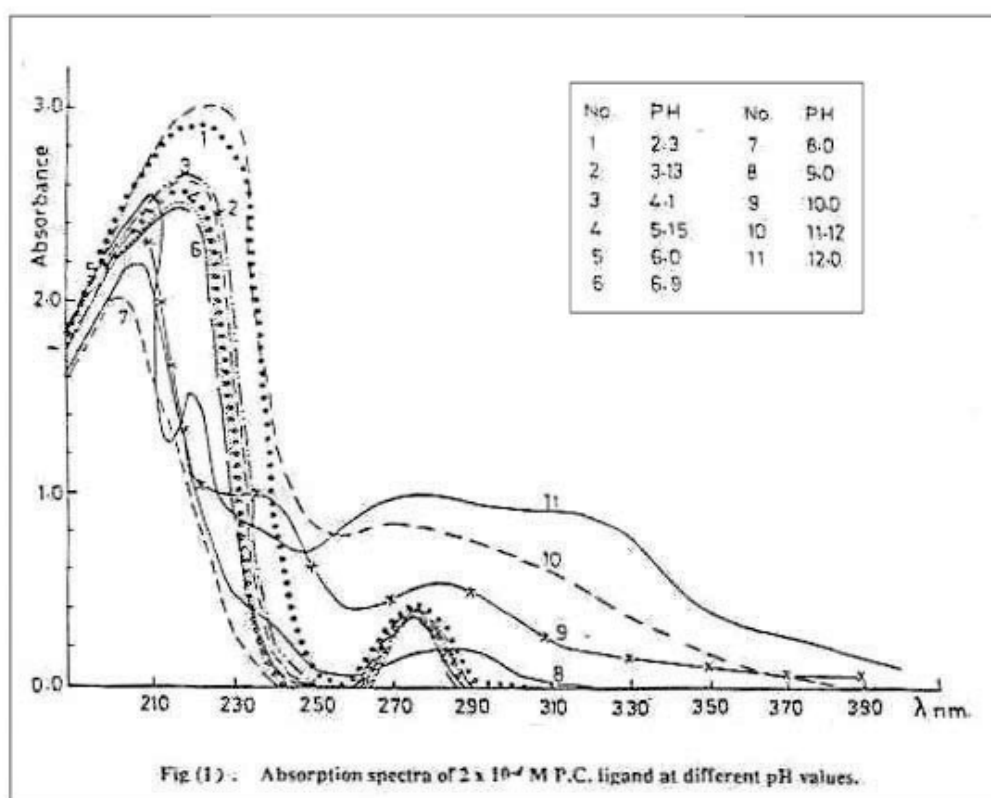


Fig (1) : Absorption spectra of 2×10^{-4} M P.C. ligand at different pH values.

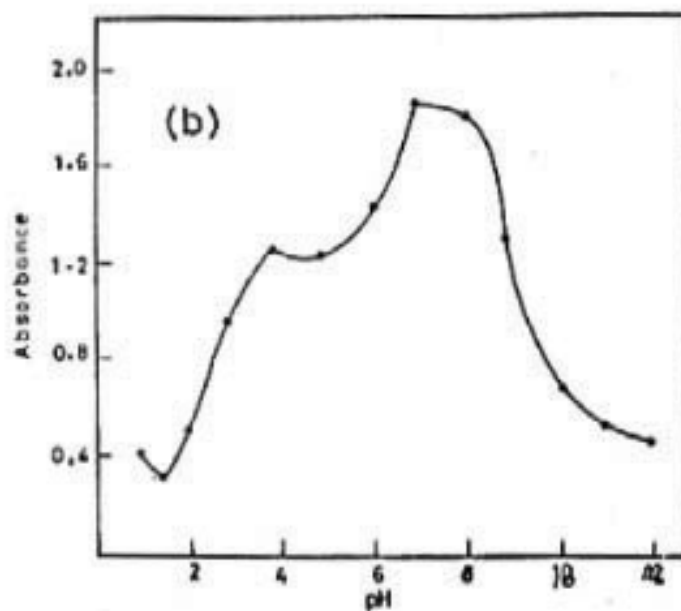
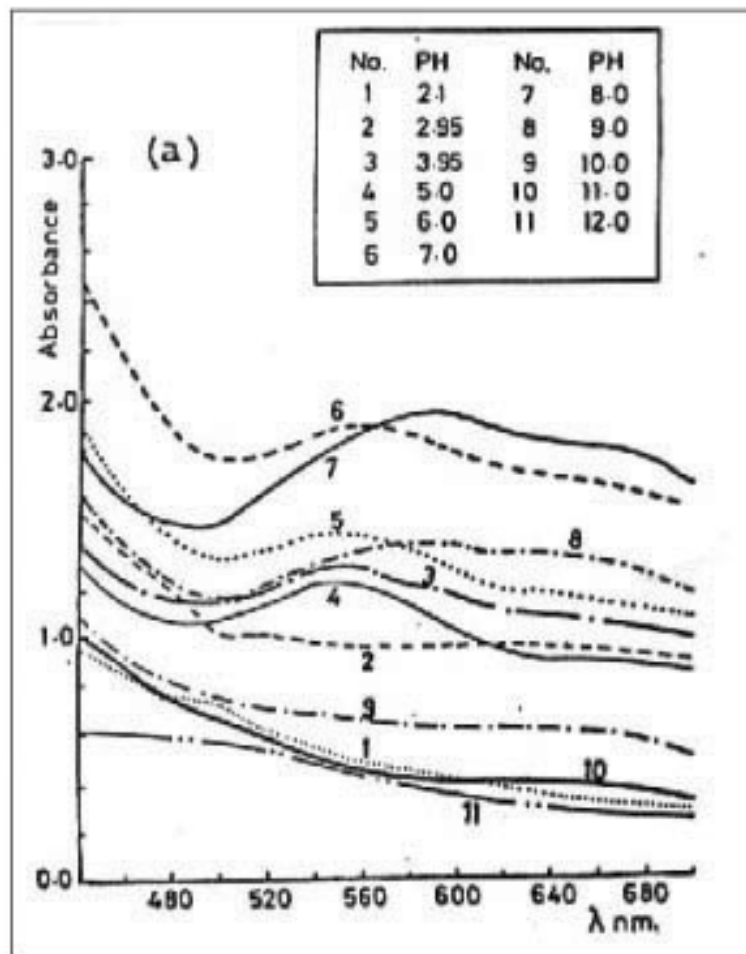


Fig. (2) a- Absorption spectra of P.C. - V(V) complex at different pH values.
 b- Absorbance - pH curve P.C. - V(V) complex at $\lambda = 550$ nm.

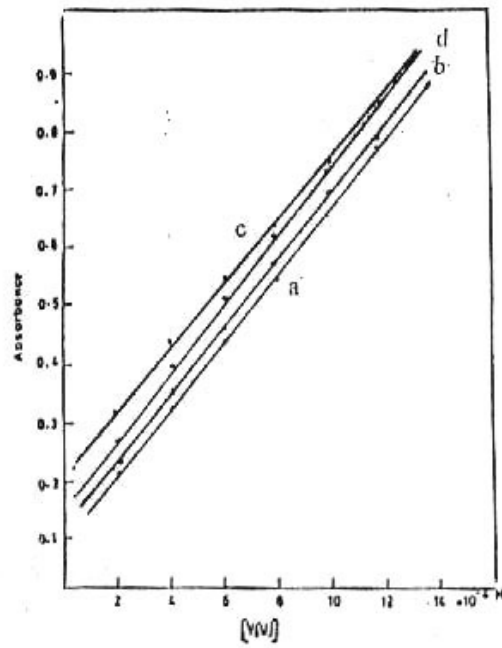


Fig.(3) Calibration curves for microdetermination of vanadium by P.C.indicator at (a) 1min., (b) 1hr., (c) 3hrs., (d) 5hrs.

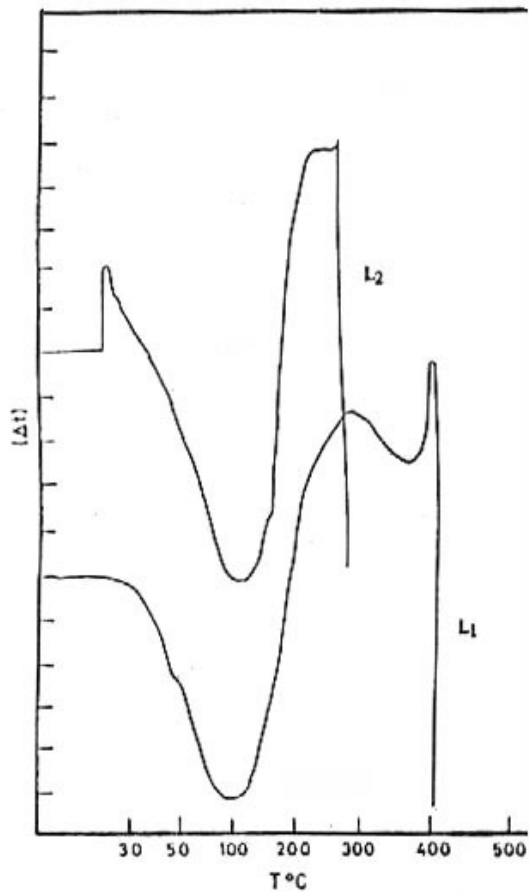


Fig. (4.) The DTA of vanadium - P.C. complexes (L₁, L₂)