

## Physico-Chemical Studies on Vanadium(V), Niobium(V) and Tantalum(V) Complexes with Eriochrome cyanine-R and Methylene Blue

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The complexation of V(V), Nb(V) and Ta(V) with methylene blue (MB) and eriochrome cyanine-R (ECR) was investigated by conductometric titrations, conductometric measurements and spectrophotometric methods. The stoichiometry, formation constants and thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H$  and  $\Delta S$ ) of the complexes were investigated. Effect of pH on the absorption spectra of complexes, effect of time and temperature on the stability of metal chelates were also studied. Vanadium, niobium and tantalum form complexes at pH 8.0 ( $\lambda = 660$  nm), 3 ( $\lambda = 665$ ) and 7 ( $\lambda = 670$  nm) with methylene blue and at pH 3.5 ( $\lambda = 540$  nm), 4.53 ( $\lambda = 520$  nm) and 4.6 ( $\lambda = 520$  nm) with ECR for V, Nb and Ta-complexes, respectively. The complexes reach maximum development immediately and at  $60^\circ$  in the case of V-MB, immediately and at  $50^\circ$  in the case of Nb-MB, immediately and at  $80^\circ$  in the case of Ta-MB, after 30 min and at  $30^\circ$  in the case of Ta-ECR complexes.

### INTRODUCTION

Our earlier studies on metal complexes of V(V), Nb(V) and Ta(V)-2,2 dipiryridyl<sup>1,2</sup>, haematoxylin and murexide<sup>3</sup>, -violurates<sup>4</sup>, Nb(V) and Ta(V)-oxine<sup>5</sup>, -AIRS, and QuS<sup>6,7</sup>, Nb(V)<sup>8</sup>, Ta(V)<sup>9</sup>, Nb(V)-, Ta(V)-QuS<sup>10,11</sup>, and Nb(V)- and Ta(V)-QuS<sup>12</sup> by different techniques were reported. Methylene blue (tetra-methyl diaminodiphenazthionium chloride, MB) and eriochrome cyanine R (tri (3-5-dimethyl, 4-hydroxy, 3,6-disodium carboxylate 2-sodium sulphate) aryl mono methylene dye, ECR) are good organic dyes acts as potential chelating agents for numerous metals. In addition, methylene blue is utilised as potential biochemical therapeutic reagent and as pigment in biology. The present paper describes the conductometric and spectro-photometric studies of V(V), Nb(V) and Ta(V)-MB and ECR complexes the determination of their compositions  $K_f$ ,  $\Delta G^\circ$ ,  $\Delta H$ ,  $\Delta S$  and in analytical chemistry for the microdetermination of the elements.

### EXPERIMENTAL

All the chemical used were of AnalaR grade (99.9%, Riedel de Haën, BDH or E. Merck).

#### Preparation of Solutions

$1 \times 10^{-3}$  M-V(V) solution was prepared by treating the accurately weighed appropriate amount of  $V_2O_5$  with few ml of concentrated HCl.

The solution was heated followed by the addition of few drops of concentrated  $\text{HNO}_3$ . The solution was transferred into 500 ml measuring flask and completed to the mark using bidistilled water.  $1 \times 10^{-3}$  M-Nb(V) or Ta(V) solution was prepared by fusing the appropriate amount of  $\text{Nb}_2\text{O}_5$  or  $\text{Ta}_2\text{O}_5$  with  $\text{K}_2\text{S}_2\text{O}_7$  in a platinum crucible at relatively low heat in order to achieve complete attack, then the temperature was raised. The melt was swirled during fusion and spread around the sides of the crucible in a thin layer, then allowed to cool and solidify into a thick cake. The melt after cooling, was leached with 20% tartaric acid, transferred into a small beaker with hot tartaric acid and water, and heated to ensure complete dissolution. Niobium or tantalum solution was transferred into 500 ml volumetric flask and completed with 2% tartaric acid to the mark. The vanadium, niobium and tantalum solutions were standardised following recommended methods<sup>13</sup>.  $1 \times 10^{-2}$  M-MB or ECR was prepared by dissolving the accurately weighed amount of methylene blue ( $\text{C}_{16}\text{H}_{18}\text{N}_3\text{Cl} \cdot 3\text{H}_2\text{O}$ ) or eriochrome cyanine R ( $\text{C}_{23}\text{H}_{15}\text{NO}_3\text{O}_9 \cdot \text{S}$ ) dye in redistilled water<sup>14</sup>. Universal and Thiel, Schulz and Coch buffer solutions were prepared following the scheme given by Britton<sup>15</sup>. Buffer solutions were standardised on Pye Unicam-2-pH Meter Model 290 MK.

## WORKING PROCEDURE

### Conductometry

Conductometric titrations were carried out by placing 25 ml of  $1 \times 10^{-3}$  M-V(V), Nb(V) or Ta(V) in a 100 ml graduated cylinder, then titrating these solutions at room temperature with 0.5 ml incremental addition of  $1 \times 10^{-2}$  M-MB or ECR solution from a fine division standard burette. The conductance values of these solutions, after each addition and stirring the solutions magnetically for three minutes, were measured. The specific conductivity values were corrected by the factor:  $(V_1 + V_2)/V_1$ , where  $V_1$  is the volume of metal ion and  $V_2$ , the volume of ligand. Conductometric measurements were performed by measuring the conductance values of a series of V(V)-, Nb(V)- and Ta(V)-MB and ECR solutions in which the metal ion was kept constant at  $4 \times 10^{-4}$  M and the ligand was varied from  $1 \times 10^{-4}$  to  $4 \times 10^{-3}$  M, after thermostating the solutions at  $35^\circ$  for two hours. Conductance values were measured using conductance bridge, REG. U, PAT. OFF. RD B 15.

### Spectrophotometric Measurements

Spectrophotometric measurements were done on Pye Unicam SP 450 spectrophotometer by measuring the spectral absorbance values of V(V)-, Nb(V)-, or Ta(V)-MB and ECR solutions, against blank solution containing the same ligand concentration as in the case of metal-ligand solutions, at  $\lambda = 200\text{-}800$  nm.

## RESULTS AND DISCUSSION

### Conductivity Experiments

The conductance values obtained during the course of titrations of V(V), Nb(V), and Ta(V) with MB and ECR and measurements of V(V)-, Nb(V)- and Ta(V)-MB and ECR solutions increase with the increase of [MB] or [ECR]. The gradual increase in conductance values may be as a result of the liberation of H<sup>+</sup> ions from the hydroxyl and carboxylic groups of the eriochrome cyanine R which increase the diffusion coefficient of the diffusing particles and hence increases the conducting power of the solutions leading to complex formation<sup>16, 17</sup>.



On the other hand, the small increase of conductance in the case of MB complexes suggests a formation of coordinate bonds between metal ion and each of -S-and-N-of the diphenathionium ring giving sandwich structure  $(M^{5+} + nMB \rightarrow [M-(MB)_n]^{5+})$ . The results of the conductometric titrations and conductometric measurements give the mole ratios: (2 : 1) V(V)-, (1 : 1) V(V)-, (1 : 2) V(V)-, (1 : 3) V(V)- and (1 : 4) V(V)-MB complexes, (2 : 1) Nb(V)-, (1 : 2) Nb(V)-, (1 : 3) Nb(V)-, (1 : 4) Nb(V)- and (1 : 5) Nb(V)-MB complexes, (1 : 1) Ta(V)-, (1:2) Ta(V). (1 : 3) Ta(V) and (1 : 5) Ta(V)-MB complexes, (1 : 1) V(V)-, (1-2) V(V)-, (1 : 3) V(V)-ECR, (2 : 1) Nb(V), (1 : 1) Nb(V)-, (1 : 2) Nb(V)- and (1 : 4) Nb(V)-ECR complexes and (2 : 1) Ta(V)-, (1 : 1) Ta(V)-, (1 : 2) Ta(V)- and (1 : 3) Ta(V)-ECR complexes.

#### Spectrophotometric measurements:

In order to find out the factors affecting the complex formation and on the spectral absorbance of the coordination compounds, effect of pH, effect of times, effect of temperature, effect of ligand concentration, and effect of metal ion concentrations were studied. The spectrograms of V(V), Nb(V) and Ta(V)-methylene blue and eriochrome cyanine R complexes are characterised by one apparent maximum peak. The factors influencing the spectral absorbance of the complexes are as follows:

(i) *Effect of pH*: The spectral absorbances of  $2 \times 10^{-6}M$ -V(V) and  $5 \times 10^{-5}M$ -MB,  $3 \times 10^{-6}M$ -Nb(V) and  $1 \times 10^{-5}M$ -MB,  $4 \times 10^{-5}M$ -Ta(V) and  $1 \times 10^{-4}M$ -MB,  $5 \times 10^{-5}M$ -V(V), Nb(V), Ta(V) and  $1 \times 10^{-4}M$ -ECR solutions were prepared in a series of buffer solutions of pH 2.0–11.0 and measured at 200–800 nm. The absorbances of these solutions increase with the increase of pH reaching maximum at pH 8.0 ( $\lambda_{max} = 660$  nm) in the case of V(V)-MB, 3.0 ( $\lambda_{max} = 670$  nm) in the case of Nb(V)-MB, 7.0 ( $\lambda_{max} = 665$  nm) in the case of Ta(V)-MB, 3.5 ( $\lambda_{max} = 540$  nm) in the case of V(V)-ECR, 4.53 ( $\lambda_{max} = 520$  nm) in the case of Nb(V)-ECR and 4.6 ( $\lambda_{max} = 520$  nm) in the case of Ta(V)-ECR complexes, thereafter, they decrease. The V(V)-MB spectrograms exhibit one characteristic band at

660 (pH = 2,4,5,8), 665 (pH = 3.0) and 630 nm (pH = 6,7,9,10 and 11). Nb(V)-MB spectrograms show one maximum at  $\lambda = 610$  (pH = 2,4-6) and 670 nm (pH=3), and at  $\lambda = 660$  (pH=6,9-12), 665 (pH 8) and 670 nm (pH 7) in the case of Ta(V)-MB solutions. In the case of V(V)-ECR, the solutions of pH 2.1,3.0 and 3.5-9.0 show one band at  $\lambda = 440, 480$  and 540 nm, respectively, while the Nb(V)-ECR solutions show one maximum at  $\lambda = 460$  (pH = 3), 500 (pH = 4.0) and 520 nm (pH = 4.53-9.0). The Ta(V)-ECR spectrograms exhibit one peak at  $\lambda = 435$  (pH = 2.0), 470 (pH = 3.08) and 520 nm (pH = 4.2-9.0). These spectral changes with pH may be due to the progressive and continuous formation of different convertible species of complexes. The increase of absorbance with pH may be due to the increased tendency for complex formation, whereas the decrease of absorbance may be ascribed to dissociation, or to the formation of hydroxy complexes or convertible species. Shift to longer wavelength may be attributed to the formation of complexes absorbing lesser amounts of energy than these appearing at shorter wavelength (absorbing large amounts of energy). Shift to shorter wavelength (hypsochromic shift) may be due to a shift in ionisation ( $H_2L \rightarrow L^{2-} + 2H^+$  and  $LCl \rightarrow L^+ + Cl^-$ ) which denotes that the  $\pi - \pi^*$  transitions are influenced by inter and intramolecular charge transfer while the shift to longer wavelength (bathochromic shift) may be due to d-d transition ( $\nu V(V)$ -MB = 15151.5,  $\nu Nb(V)$ -MB = 14925.4,  $\nu Ta(V)$ -MB = 15039,  $\nu V(V)$ -ECR = 18518.5,  $\nu Nb(V)$ - and Ta(V)-ECR = 19230.7  $cm^{-1}$ ) in solution.

(ii) *Effect of time:* The concentrations of V(V), Nb(V), Ta(V)-MB and ECR were kept constant ( $[V(V)] = 5 \times 10^{-6}M$  &  $[MB] = 1 \times 10^{-5}M$ ,  $[Nb(V)] = 3 \times 10^{-6}M$  &  $[MB] = 1 \times 10^{-5}M$ ,  $[Ta(V)] = 1 \times 10^{-6}M$  &  $[MB] = 5 \times 10^{-5}M$ ,  $[V(V)] = [Nb(V)] = [Ta(V)] = 5 \times 10^{-5}M$  and  $[ECR] = 1 \times 10^{-4}M$ ) and the absorbance values were measured after different (10 min) time intervals (0.0-40 min). The spectral absorbance, in the case of V(V)-, Nb(V)- and Ta(V)-MB complexes, decrease with the increase of time. Therefore, the spectral absorbance of the solutions should be measured immediately just beyond the preparation of the solutions. In the case of V(V)-, Nb(V)- and Ta(V)-ECR complexes, the spectral absorbance values should be measured after 30 minutes.

(iii) *Effect of temperature:* For studying this factor,  $[V(V)] = [Ta(V)] = 5 \times 10^{-6}M$ .  $[Nb(V)] = 3 \times 10^{-6}M$  &  $[MB] = 1 \times 10^{-5}M$  and  $[V(V)] = [Nb(V)] = [Ta(V)] = 5 \times 10^{-5}M$  and  $[ECR] = 1 \times 10^{-4}M$  were kept constant while the temperature was varied from 10-90° and the absorbance values were measured. Absorbances increase with the increase of temperature reaching maximum after 70,50 and 80° in the case of V(V)-, Nb(V)- and Ta(V)-MB complexes, respectively, thereafter, absorbances of V(V)- and Nb(V)-MB complexes slow down due to dissociation, while those of Ta(V)-MB complexes maintain stable. The spectral absorbance of V(V)-, Nb(V)- and Ta(V)-ECR complexes increase with the increase

TABLE 1  
EFFECT OF pH ON THE ABSORPTION SPECTRA OF V(V)-, Nb(V)- AND Ta(V)-MB AND ECR COMPLEXES  
[M(V)] =  $5 \times 10^{-5}$ M, [L] =  $1 \times 10^{-4}$ M, pH = 2.0 - 11.0,  $\lambda$  = 200 - 750 nm

		V(V)-MB complexes, $\lambda$ = 660 nm										V(V)-ECR complexes, $\lambda$ = 540 nm									
pH		5.0	6.0	7.0	8.0	9.0	10.0	11.0	2.10	3.0	3.5	4.2	5.1	6.0	7.1	8.1	9.0				
A		0.04	0.04	0.08	0.10	0.08	0.07	0.06	0.100	0.150	0.350	0.120	0.118	0.049	0.046	0.00	0.00				
Nb(V)-MB complexes, $\lambda$ = 665 nm																					
pH		2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	1.80	3.05	4.08	4.53	5.00	5.50	6.0	7.0	8.0	9.0		
A		0.073	0.120	0.062	0.056	0.043	0.043	0.043	0.043	0.00	0.23	0.38	0.54	0.50	0.46	0.42	0.27	0.17	0.0		
Ta(V)-MB complexes, $\lambda$ = 670 nm																					
pH		5.0	6.0	7.0	8.0	9.0	10.0	11.0	12.0	2.0	3.1	3.7	4.2	4.6	5.3	6.0	7.3	8.4	9.0		
A		0.052	0.098	0.123	0.108	0.080	0.073	0.044	0.03	0.07	0.29	0.54	0.57	0.67	0.56	0.42	0.37	0.08	0.0		
Ta(V)-ECR complexes, $\lambda$ = 520 nm																					

TABLE 2  
EFFECT OF TIME ON THE STABILITY OF V(V)-, Nb(V)- AND Ta(V)-MB AND ECR COMPLEXES

		V(V)-MB complexes										V(V)-ECR complexes									
		[V(V)] = 5 × 10 <sup>-6</sup> M, [MB] = 1 × 10 <sup>-3</sup> M, pH = 8.0, λ = 660 nm										[V(V)] = 5 × 10 <sup>-5</sup> M, [ECR] = 1 × 10 <sup>-4</sup> M, pH = 3.5, λ = 540 nm									
		blank = same [L]										blank = same [ECR]									
Time		0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0		
A		0.034	0.032	0.031	0.030	0.028	0.027	0.027	0.027	0.027	0.0110	0.170	0.230	0.300	0.350	0.375	0.380	0.380	0.380	0.380	
		Nb(V)-MB complexes										Nb(V)-ECR complexes									
		[Nb(V)] = 3 × 10 <sup>-6</sup> M, [MB] = 1 × 10 <sup>-3</sup> M, pH = 3.0, λ = 665 nm										[Nb(V)] = 5 × 10 <sup>-5</sup> M, [ECR] = 1 × 10 <sup>-4</sup> M, pH = 4.53, λ = 520 nm									
Time		0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0		
A		0.090	0.085	0.083	0.083	0.083	0.083	0.083	0.083	0.083	0.15	0.37	0.52	0.60	0.66	0.70	0.70	0.70	0.70	0.70	
		Ta(V)-MB complexes										Ta(V)-ECR complexes									
		[Ta(V)] = 1 × 10 <sup>-6</sup> M, [MB] = 5 × 10 <sup>-3</sup> M, pH = 7.0, λ = 670 nm										[Ta(V)] = 5 × 10 <sup>-5</sup> M, [ECR] = 1 × 10 <sup>-4</sup> M, pH = 4.6, λ = 520 nm									
Time		0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0		
A		0.090	0.088	0.085	0.082	0.082	0.082	0.082	0.082	0.082	0.13	0.46	0.63	0.70	0.81	0.82	0.82	0.82	0.82	0.82	

TABLE 3  
EFFECT OF TEMPERATURE ON THE STABILITY OF V(V)-, Nb(V)- AND Ta(V)-MB AND ECR COMPLEXES

Temp.	V(V)-MB complexes [V(V)] = $5 \times 10^{-6}$ M, [MB] = $1 \times 10^{-5}$ M, pH = 8.0, $\lambda = 660$ nm										V(V)-ECR complexes [V(V)] = $5 \times 10^{-5}$ M, [ECR] = $1 \times 10^{-4}$ M, pH = 3.5, $\lambda = 450$ nm									
	10	20	30	40	50	60	70	80	90	10	20	30	40	50	60	70	80	90		
A	0.050	0.053	0.060	0.090	0.125	0.135	0.132	0.130	0.130	0.150	0.41	0.55	0.52	0.50	0.49	0.48	0.48			
Temp.	Nb(V)-MB complexes [Nb(V)] = $3 \times 10^{-6}$ M, [MB] = $1 \times 10^{-5}$ M, pH = 3.0, $\lambda = 660$ nm										Nb(V)-ECR complexes [Nb(V)] = $5 \times 10^{-5}$ M, [ECR] = $1 \times 10^{-4}$ M, pH = 4.53, $\lambda = 520$ nm									
	10	20	30	40	50	60	70	80	90	10	20	30	40	50	60	70	80	90		
A	0.015	0.020	0.050	0.053	0.055	0.050	0.040	0.040	0.040	0.18	0.24	0.35	0.60	0.72	0.80	0.80	0.80			
Temp.	Ta(V)-MB complexes [Ta(V)] = $1 \times 10^{-3}$ M, [MB] = $5 \times 10^{-6}$ M, pH = 7.0, $\lambda = 670$ nm										Ta(V)-ECR complexes [Ta(V)] = $5 \times 10^{-5}$ M, [ECR] = $1 \times 10^{-4}$ M, pH = 4.6, $\lambda = 520$ nm									
	10	20	30	40	50	60	70	80	90	10	20	30	40	50	60	70	80	90		
A	0.070	0.080	0.100	0.115	0.130	0.136	0.139	0.140	0.140	0.50	0.70	0.83	0.87	0.92	0.96	0.86	0.82			

of temperature upto  $30^\circ$  in the case of V(V)-ECR and  $60^\circ$  in the case of Nb(V)-and Ta(V)-ECR complexes, then absorbance decrease (due to the formation of other complex species) and becomes constant due to equilibrium attainment. The reaction between V(V), Nb(V) and Ta(V) with MB and ECR is temperature dependent (endothermic). Effect of pH, effect of time and effect of temperature on stability of complexes are reported in Tables 1-3 and represented graphically in Figures 1-3.

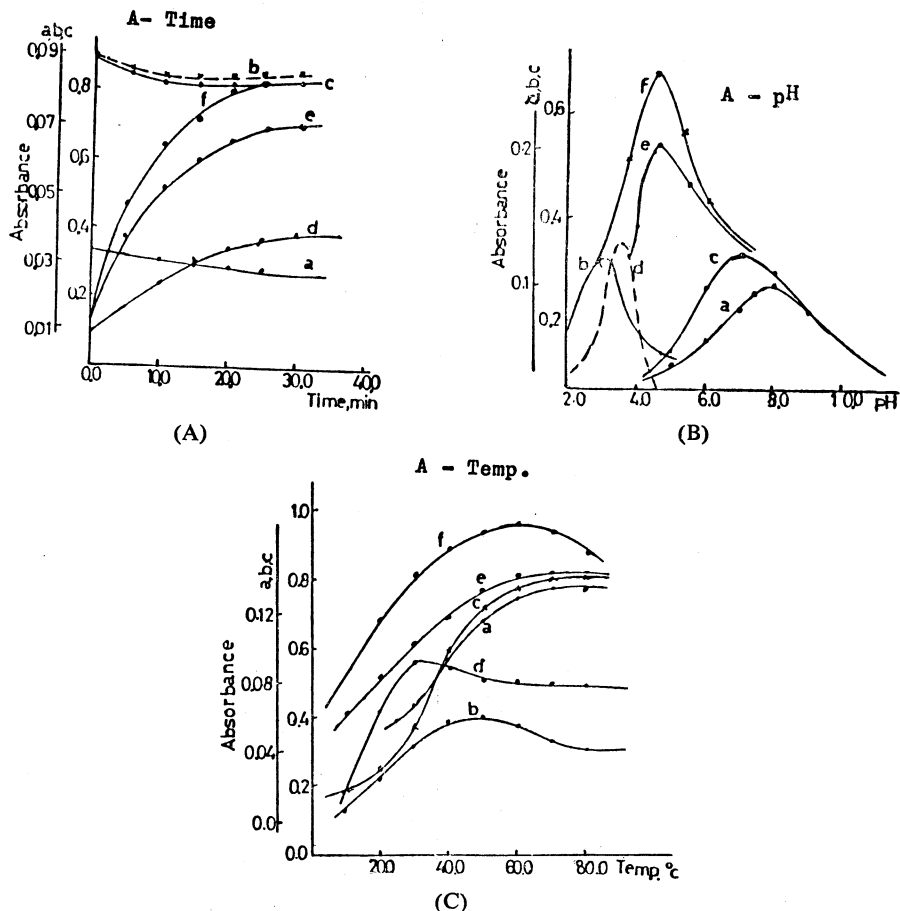


Fig. 1. (A) Absorbance—Time relationship  
(B) Absorbance—pH relationship  
(C) Absorbance—Temperature relationship

(iv) *Effect of ligand concentration:* The concentration of V(V) ( $3 \times 10^{-6}$ M), Nb(V) and Ta(V) ( $5 \times 10^{-5}$ M) was kept constant and [MB] varied from  $1 \times 10^{-6}$ M to  $1 \times 10^{-5}$ M [V(V)],  $1 \times 10^{-6}$ M to  $1.1 \times 10^{-5}$ M [Nb(V)] and  $1 \times 10^{-6}$ M to  $1.2 \times 10^{-5}$ M [Ta(V)]. Also, in the case of V(V)-, Nb(V)- and Ta(V)-ECR, [V(V)], [Nb(V)] and [Ta(V)] were kept constant at  $5 \times 10^{-5}$  while that of ECR was varied from  $1 \times 10^{-5}$ M to



$3 \times 10^{-4}M$ . The spectral absorbances increase gradually with the increase of [MB] and [ECR] due to gradual complex formation having large [MB] or [ECR], then reaches a limiting value. As [MB] and [ECR] increase,  $\lambda_{\max}$  does not change. This may be ascribed that the complexes of the same metal having different compositions, absorb at the same wavelength (d-d transition).

(v) *Effect of metal ion concentration:* The [MB] was kept constant at  $3 \times 10^{-5}M$  in the case of V(V) and at  $5 \times 10^{-6}M$  in the case of Nb(V) and Ta(V), whereas [V(V)] changed from  $1 \times 10^{-6}M$ , [Nb(V)] and [Ta(V)] from  $1 \times 10^{-6}M$  to  $1 \times 10^{-5}M$ . In the case of V(V)-, Nb(V)- and Ta (V)-ECR, [ECR] was maintained constant at  $5 \times 10^{-5}M$  whereas [V(V)], [Nb(V)] or [Ta(V)] varied from  $1 \times 10^{-5}M$  to  $1.5 \times 10^{-4}M$ . The increasing of metal ions concentration, increase the spectral absorbance apparently. This may be attributed to the tendency of V(V), Nb(V) and Ta(V), characters of MB and ECR towards the formation of complex compounds having high stoichiometric ratios.

*Validity fo Beer's law:* Beer's law is valid making possible using methylene blue and eriochrome cyanine R as analytical reagents for the microdetermination of 0.05-0.41 ppm V( $\epsilon = 1.103 \times 10^4$ ), 0.19-1.30 ppm Nb ( $\epsilon = 1.014 \times 10^4$ ) and 0.72-2.46 ppm Ta ( $\epsilon = 4.44 \times 10^3 \text{ cm}^2 \text{ mole}^{-1}$ ) on using MB, and 0.51-2.65 ppm V( $\epsilon = 7.3 \times 10^3$ ), 0.46-2.42 ppm Nb ( $\epsilon = 2.2 \times 10^4$ ) and 1.44-9.05 ppm Ta( $\epsilon = 2.048 \times 10^4 \text{ cm}^2 \text{ mole}^{-1}$ ) on using ECR.

*Stoichiometry of the complexes:* The stoichiometric composition of V(V)-, Nb(V)- and Ta(V)-MB and ECR complexes were determined by conductometric studies and spectrophotometric methods (molar ratio<sup>18</sup>, (M.R.); straight line<sup>19, 20</sup>, (S.L.), continuous variation<sup>21-23</sup>, (C.V.); slope ratio<sup>24</sup>, (S.R.), limiting logarithmic<sup>25</sup>, (L.L). The results reveal the formation of 2 : 1, 1 : 1, 1 : 2, 1 : 3 and 1 : 4 (M : L) ratios. This is an agreement with the conductometric titration results.

The apparent conditional formation constant: the apparent conditional stability constant ( $K_f$ ), free energy changes ( $\Delta G^\circ$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of V(V)-, Nb(V)- and Ta(V)-MB and ECR complexes are evaluated making use of the results of spectrophotometric methods<sup>18-20, 24, 25</sup>

$$K_f = \frac{A/Am}{(1 - A/Am)^{n+1}n^2[L]^2}$$

$K_f = 1/kc^{-1}/kd$ ,  $\beta_n = \log (A/\epsilon n) - [m \log [M^{n+}] + n \log [L]]$  and the analytical ( $pH = \log (A/A_1 - A) + pK_f + npk_i \cdot n \log [H]$ ) method<sup>26</sup>. The free energy changes ( $\Delta G^\circ$ ) of the complexes can be evaluated using the equation:  $\Delta G^\circ = -RT \ln k$  values of the heat content (enthalpy;  $\Delta H$ ) and entropy ( $\Delta S$ ) of the complexes can be calculated applying the following equations

$$\Delta H = \frac{2T_1T_2}{T_2 - T_1} \ln k \quad \text{and} \quad \Delta S = \frac{\Delta H - \Delta G^\circ}{T_1}$$

TABLE 4

RESULTS OF STOICHIOMETRY, APPARENT FORMATION CONSTANTS ( $K_f$ ), FREE ENERGY CHANGES ( $\Delta^{\circ}G$ , 25°, kcal. mol<sup>-1</sup>, deg<sup>-1</sup>), ENTHALPY ( $\Delta H$ , 25°-30°, kcal. deg<sup>-1</sup>) AND ENTROPY ( $\Delta S$ , 25-30, kcal. mol<sup>-1</sup>, deg.) FOR V(V)-, Nb(V)- AND Ta(V)-MB AND ECR COMPLEXES

## (A) M(V)-MB complexes

Method	Ratio	V(V)-MB complexes			Nb(V)-MB complexes			Ta(V)-MB complexes					
		$K_f$	$\Delta^{\circ}G$	$-\Delta H$	$-\Delta S$	$K_f$	$\Delta^{\circ}G$	$-\Delta H$	$-\Delta S$	$K_f$	$\Delta^{\circ}G$	$-\Delta H$	$-\Delta S$
M.R.	2:1	$2.56 \times 10^5$	7.42	449.81	1.53	$1.18 \times 10^6$	8.34	505.13	1.72	—	—	—	—
	1:1	$1.09 \times 10^8$	11.03	668.28	2.28	$3.61 \times 10^8$	11.74	711.69	2.43	$9.24 \times 10^7$	10.93	666.39	2.28
	1:2	$8.33 \times 10^{14}$	20.48	1240.83	4.23	$8.45 \times 10^{14}$	20.49	1241.38	4.23	—	—	—	—
C.V.	2:1	$3.31 \times 10^5$	7.58	459.06	1.57	—	—	—	—	—	—	—	—
	1:1	—	—	—	—	$1.01 \times 10^8$	10.99	665.74	2.27	$1.86 \times 10^8$	—	—	—
S.L.	1:2	$2.06 \times 10^{15}$	21.02	1273.53	4.34	$4.50 \times 10^{15}$	18.74	1135.45	3.87	—	—	—	—
	1:1	—	—	—	—	$6.59 \times 10^4$	6.61	400.78	1.37	$1.97 \times 10^4$	5.89	357.11	1.22
	1:2	$1.27 \times 10^{14}$	19.35	1172.80	4.00	—	—	—	—	—	—	—	—
L.L.	1:3	—	—	—	—	—	—	—	—	—	—	—	—
	1:4	—	—	—	—	—	—	—	—	—	—	—	—
pH	1:1	—	—	—	—	—	—	—	—	—	—	—	—
	1:1	—	—	—	—	—	—	—	—	—	—	—	—
pH	1:1	$7.41 \times 10^4$	6.68	404.98	1.38	$9.60 \times 10^9$	13.70	830.16	2.83	$1.36 \times 10^6$	8.42	509.97	1.74

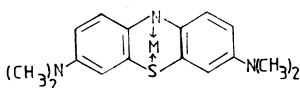
## (B) M(V)-ECR complexes

Method	Ratio	V(V)-ECR complexes			Nb(V)-ECR complexes			Ta(V)-ECR complexes					
		K <sub>t</sub>	ΔG	-ΔH	-ΔS	K <sub>t</sub>	ΔG	-ΔH	-ΔS	K <sub>t</sub>	ΔG	-ΔH	-ΔS
M.R.	2:1	—	—	—	—	3.00 × 10 <sup>5</sup>	7.52	455.50	1.55	1.69 × 10 <sup>5</sup>	7.18	434.99	1.48
	1:1	1.03 × 10 <sup>8</sup>	11.00	666.39	2.27	3.14 × 10 <sup>7</sup>	10.29	623.47	2.13	2.48 × 10 <sup>7</sup>	10.15	641.91	2.10
	1:2	—	—	—	—	4.30 × 10 <sup>12</sup>	17.34	1050.65	3.58	—	—	—	—
C.V.	1:3	9.71 × 10 <sup>18</sup>	26.07	1579.02	5.30	—	—	—	—	—	—	—	—
	2:1	7.36 × 10 <sup>4</sup>	6.68	404.46	1.38	—	—	—	—	—	—	—	—
	1:1	2.60 × 10 <sup>7</sup>	8.79	532.37	1.82	2.00 × 10 <sup>6</sup>	8.65	524.02	1.79	3.06 × 10 <sup>7</sup>	11.65	705.65	2.41
S.L.	1:2	3.80 × 10 <sup>13</sup>	18.64	1129.37	3.85	6.74 × 10 <sup>12</sup>	17.61	1066.88	3.64	1.03 × 10 <sup>13</sup>	17.86	1082.34	3.69
	1:1	2.25 × 10 <sup>4</sup>	5.97	361.50	1.23	5.03 × 10 <sup>4</sup>	6.45	390.97	1.30	—	—	—	—
	1:2	5.72 × 10 <sup>11</sup>	16.14	977.77	3.34	5.80 × 10 <sup>11</sup>	16.14	978.29	3.34	2.64 × 10 <sup>12</sup>	15.67	941.35	3.21
L.L.	1:1	5.90 × 10 <sup>4</sup>	6.55	396.78	1.35	—	—	—	—	5.27 × 10 <sup>5</sup>	7.85	475.82	1.62
	1:2	—	—	—	—	—	—	—	—	—	—	—	—
pH	1:1	3.33 × 10 <sup>3</sup>	4.83	267.86	1.00	1.52 × 10 <sup>0</sup>	13.97	846.71	2.79	—	—	—	—
	1:2	6.62 × 10 <sup>12</sup>	17.60	1066.23	3.52	—	—	—	—	1.62 × 10 <sup>12</sup>	16.50	999.96	3.41
	1:3	8.33 × 10 <sup>18</sup>	39.69	2405.17	8.20	—	—	—	—	1.33 × 10 <sup>18</sup>	38.60	2338.90	7.98
	1:4	2.64 × 10 <sup>61</sup>	84.29	5107.99	16.86	—	—	—	—	—	—	—	—

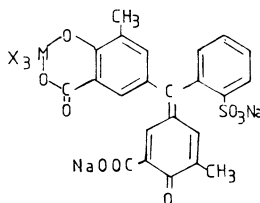
where  $R =$  gas constant,  $T = 25 + 273^\circ\text{K}$ ,  $T_1 = 25 + 273^\circ\text{K}$ ,  $T_2 = 30 + 273^\circ\text{K}$ ,  $K =$  dissociation constant of the complex.

The results of stoichiometry, formation constants, free energy changes, enthalpy and entropy of the complexes are recorded in Table 4. The  $K_f$  and  $\Delta G^\circ$  values indicate that the 1 : 3 complexes are the most stable. The order of stability constants are  $(1 : 3) \text{V(V)-ECR} > (1 : 3) \text{Ta(V)-ECR}$ . Values of  $\Delta H$  and  $\Delta S$  are negative and high, and they decrease on going from  $M_2L$  to  $ML_4$  complexes, as a result of changing ligand characters and increasing the coordination number of metal ions. The negative values of entropy may be attributed to the decrease in randomness indicating that the activated complexes are more ordered as a result of complexation.

The complexation takes place through coordinate bonds between the metal ions and -S- and -N- of diphenathionium ring with methylene blue and covalent bonds between the metal ions and hydroxy and carboxylic groups of eriochrome cyanine R. Bonding can be shown as follows:



(1:1)M(V)-MB COMPLEX



(1:1)M(V)-ECR COMPLEX

## REFERENCES

1. M. K. Sherif, R. M. Awadallah and F. S. Mohamed, *Bull. Fac. Sci., Assiut Univ.*, **7**, 461 (1978).
2. R. M. Awadallah, M. K. Sherif and F. S. Mohamed, *J. Indian Chem. Soc.*, **61**, 459 (1984).
3. M. K. Sherif, R. M. Awadallah and F. S. Mohamed, *Bull. Fac. Sci., Assiut Univ.*, **7**, 371 (1978).
4. R. M. Awadallah, *J. Indian Chem. Soc.*, **57**, 685 (1980).
5. I. M. Issa, R. M. Issa and R. M. Awadallah, *Egypt. J. Chem.*, **18**, 215 (1975).
6. ———, *Egypt. J. Chem.*, **18**, 221 (1975).
7. ———, *Egypt. J. Chem.*, **18**, 801 (1975).
8. R. M. Awadallah, *Asw. Sci. Tech. Bull.*, **2**, 1 (1980).
9. R. M. Awadallah, A. E. Mohamed and A. H. Amrallah, *Asw. Sci. Tech. Bull.*, **9**, 44 (1988).
10. I. M. Issa, M. K. Sherif, R. M. Issa and R. M. Awadallah, *Bull. Fac. Sci., Assiut Univ.*, Assiut, Egypt, **3**, 125 (1974).
11. ———, *Bull. Fac. Sci.*, Assiut Univ., Assiut, Egypt, **3**, 113 (1974).
12. R. M. Awadallah, *J. Indian Chem. Soc.*, **57**, 66 (1980).

13. N. H. Ferman, *Standard Methods of Chemical Analysis*, D. Van Nostrand, Princeton-New Jersey-London, Vol. 1, The Elements, 6th Ed. (1966).
14. L. Meites, *Hand Book of Analytical Chemistry*, McGraw-Hill, New York (1963).
15. H. T. S. Britton, *Hydrogen Ions*, D. Van Nostrand, Vol. 1, 4th Ed. (1956).
16. R. M. Issa, M. S. Massoud and S. E. Zayan, *Egypt. J. Chem.* **12**, 309 (1969).
17. E. M. Khairy, A. E. Mahgoub and I. M. Kenawi, *Egypt. J. Chem.*, **17**, 811 (1974).
18. Yoe and Jones, *Ind. Eng. Chem. Anal. Ed.*, **16**, 111 (1944).
19. E. I. Asmus, *Z. Anal. Chem.*, **178**, 104 (1960).
20. Korkuc, A. Sommer and T. Lipiec, in Trzebiatowaka (ed.), *Theory and Structure of Complex Compounds*, Pergamon Press (1962).
21. P. Job, *Compt. Rend. (Paris)*, **180**, 928 (1925); *Idem. Ann. Chim. (Paris)*, **9**, 133 (1928); *Idem. Ann. Chim.*, **6**, 97 (1936).
22. W. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, **63**, 437 (1941).
23. F. G. Scherief and A. A. Awad, *J. Inorg. Nucl. Chem.*, **24**, 149 (1962).
24. A. E. Harvey and D. L. Manning, *J. Amer. Chem. Soc.*, **72**, 4488 (1950).
25. H. E. Bent and C. L. French, *J. Amer. Chem. Soc.*, **63**, 568 (1941).
26. R. M. Awadallah, M. Sc. Thesis, Assiut University, Egypt (1971).
27. P. P. Kish and E. E. Monich, *Anal. Khim. Ekstr. Protsesty*, **7**, 60 (1970).

[Received: 8 June 1989; Accepted: 15 September 1989]

AJC-91

**SUCCESS AND CREATIVITY IN PHARMACEUTICAL  
RESEARCH AND DEVELOPMENT**

Place: **Royal College of Physicians, London**

Date: **30 April to 1 May 1990**

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