Potentiometric Study of Vanadyl Complexes of o-Hydroxyaceto-phenone Oxime and its Substituted Derivatives

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The metal-ligand stability constants of 1 : 1 and 1 : 2 complexes of vanadyl ion have been deter-mined at $30 \pm 1°C$ by the Bjerrum-Calvin pH titration technique as adopted by Irving and Rossotti in 75% dioxane and 25% water by volume and ionic strength 0.1 m. The linear relations between metal-ligand stability constant and proton ligand stability constant were examined for 1 : 1 and 1 : 2 complexes of Vanadyl ion.

VANADYL complexes of acetylacetone[1], 8-hydroxy-quinoline[2], N,N'-dihydroxy-EDTA[3], 1,10-phenanthroline[3], tiron (4,2-dihydroxy-benzene 1,3-disulphonic acid)[3] etc. have been reported in the literature. The present work deals with a systematic study of stability constants of complexes of some substituted o-hydroxyacetophenone oximes with vanadyl ion in aqueous dioxane medium con-taining 75% dioxane by volume and $0.1M$ $NaClO_4$.

Experimental

The details regarding the ligands used and the experimental technique employed for the Bjerrum-Calvin titration curve have been described[4].

Metal salt solution : Vanadyl sulphate of AnalaR (BDH) quality was used and $VO(OH)_2$ was precipi-tated by the addition of sodium hydroxide solution. The vanadyl hydroxide was washed free from the sulphate ion and was then dissolved in perchloric acid to obtain a stable vanadyl perchlorate solution.

The Bjerrum-Calvin titrations : The experimental procedure involved potentiometric titrations of (i) free $HClO_4$ ($9.2 \times 10^{-3}M$), (ii) free $HClO_4$ ($9.2 \times 10^{-3}M$)+ reagent ($2 \times 10^{-3}M$), (iii) free $HClO_4$ ($9.2 \times 10^{-3}M$)+ reagent ($2 \times 10^{-3}M$)+vanadyl ion ($5 \times 10^{-4}M$) and (iv) free $HClO_4$+vanadyl ion ($5 \times 10^{-4}M$) against standard sodium hydroxide solution ($0.2M$) added from a burette. The ionic strength of the solution was maintained constant at $0.1M$ by addition of sodium perchlorate solution.

Results and Discussion

For the calculation of stability constants of vanadyl complexes it was assumed that factors like hydrolysis of vanadyl ion and presence of polynuclear hydrogen and hydroxyl bearing complexes may be ignored on the following grounds :

(i) The B (pH meter reading) of hydrolysis of vanadyl ion obtained from the deviation of the vanadyl ion curve from the acid curve was about 5.8. The departure of ($HClO_4$+reagent) curve was observed around B = 2.5. This indicated that the

hydrolysis of vanadyl ion did not take place at the pH of complex formation.

(ii) The solution employed being very dilute, the probability of existence of polynuclear species under experimental conditions is not expected to be high.

Values of n̄ (metal-ligand formation number) were calculated using the Irving and Rossotti expression[5]. The maximum value of n̄ was 2 which indicated the formation of 1 : 1 and 1 : 2 complexes in solution.

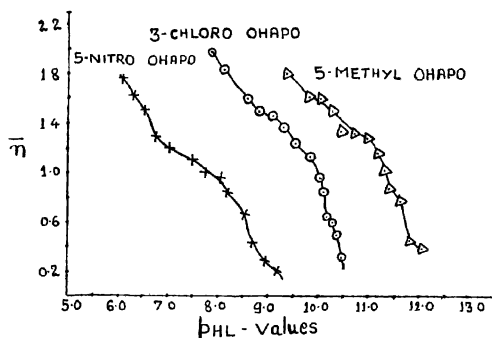The formation curve was not symmetrical and it had a wave like character (Fig. 1). The methods of

Fig. 1

point-wise calculations and half integrals were used to determine the stability constants. The stability constant values of log K_1 and log K_2 for 1 : 1 and 1 : 2 vanadyl complexes of substituted o-hydroxyaceto-phenone oximes are given in Table 1.

Validity of log $K = apk+b$ relation : This has been examined by plotting the values of log K_1 and log K_2 against log $^PK_2{}^H$ (Fig. 2). The points corres-ponding to 5-methyl, 3-methyl, 3-chloro and 5-nitro OHAPOs showed larger deviation from the linear relation. However, these points fall on another straight line.

The linear relation suggested by May and Jones[5] was also examined for 1 : 1 complexes by plotting

TABLE 1. METAL-LIGAND STABILITY CONSTANTS

Ligand No.	Name of the ligand	*Proton ligand stability constant $\log {}^{P}K^{H}_{2}$	$\log K_1$	$\log K_2$
1.	o-Hydroxyacetophenone oxime (OHAPO)	11.86	12.47	11.89
2.	Resacetophenone oxime (RAPO)	11.14	10.86	9.69
3.	5-methyl OHAPO	12.11	11.72	10.19
4.	3-methyl OHAPO	12.05	11.80	10.15
5.	5-chloro OHAPO	11.28	11.22	9.77
6.	5-bromo OHAPO	11.27	11.23	9.65
7.	3-chloro OHAPO	10.77	10.46	8.86
8.	3-bromo-OHAPO	11.04	10.62	8.65
9.	5-iodo OHAPO	11.16	11.01	8.62
10.	5-nitro OHAPO	8.97	8.67	6.49

* The log ${}^{P}K_2{}^{H}$ values have been taken from Ph.D. thesis submitted to the Marathwada University by D. B. Ingle.
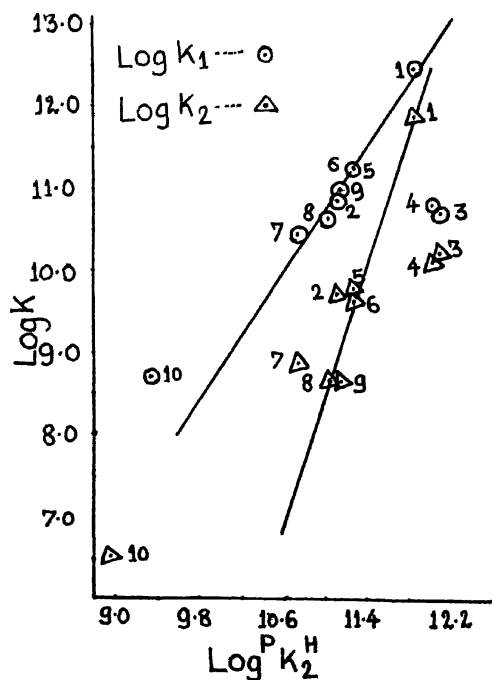

Fig. 2

$\log \dfrac{K}{K_0}$ values against $\log \dfrac{K'}{K'_0}$ (Fig. 3), where K is the metal-ligand stability constant of substituted
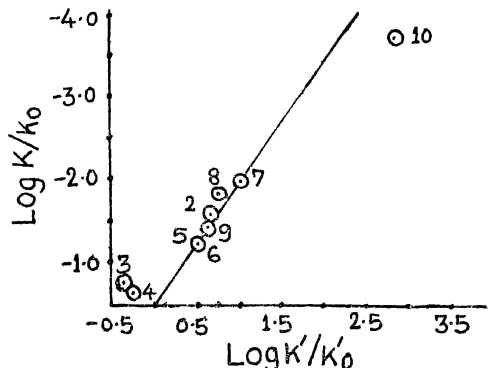

Fig. 3

derivatives of OHAPOs, K_0 is that of OHAPO, K' is the proton-ligand stability constant of substituted OHAPOs and K'_0 is that of OHAPO. Again the points corresponding to 5-methyl, 3-methyl, 3-chloro and 5-nitro OHAPOs did not fall on the straight line passing through the remaining points. The deviation in the case of 3-methyl and 3-chloro oximes may be attributed to the ortho effect. The nitro substituted compound gave anomalous results probably because of the possibility of direct conjugation of the nitro group with the phenoxide ion.

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