

logarithmic method<sup>12</sup> fail to give the composition of the complex because the yellow colour is not developed even in the presence of 200-fold molar excess of INH. A 925-fold molar excess of INH is necessary for the complete complex formation. The cationic nature of the complex is indicated by the retention of the yellow colour on Dowex 50W-X8 cation exchange resin.

The following amounts ( $\mu\text{g/ml}$ ) of foreign ions are found to give less than 2% error in the determination of  $3\mu\text{g/ml}$  osmium:  $\text{Pd}^{2+}$  (20),  $\text{Pt}^{4+}$  (1.0),  $\text{Ru}^{3+}$  (1.0),  $\text{Rh}^{3+}$  (8.0),  $\text{Ir}^{3+}$  (8.0),  $\text{Cu}^{2+}$  (16.0),  $\text{Ni}^{2+}$  (400),  $\text{Co}^{2+}$  (44),  $\text{Au}^{3+}$  (0.2),  $\text{Fe}^{3+}$  (100),  $\text{Ag}^{+}$  (0.4),  $\text{Mn}^{2+}$  (80),  $\text{F}^{-}$  (1400),  $\text{Cl}^{-}$  (1600),  $\text{Br}^{-}$  (600),  $\text{I}^{-}$  (600),  $\text{SO}_4^{2-}$  (1000),  $\text{NO}_3^{-}$  (1600),  $\text{PO}_4^{3-}$  (400),  $\text{S}_2\text{O}_3^{2-}$  (20), EDTA (80), acetate (800), oxalate (12) and citrate (8).  $\text{Pt}^{4+}$  and  $\text{Ru}^{3+}$  interfere because of their colour.

**Determination of osmium in ores.**—Synthetic mixtures corresponding to syserkite were prepared and the osmium content was determined following

the standard procedure. The results are given in Table I.

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## PROTON-LIGAND FORMATION CONSTANTS AND FORMATION CONSTANTS OF Tl(I)-3-NITRO SALICYLATES

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### ABSTRACT

Proton-ligand formation constants and formation constants of Tl(I)-complexes with 3-nitro salicylic acid have been determined at  $30^\circ\text{C}$  (50% aqueous ethanol, 0.1 M  $\text{NaClO}_4$ ) by various computational methods. The average values of proton-ligand formation constants are found to be  $\log pK_1^H = 10.34$  and  $\log pK_2^H = 2.30$ , the corresponding values for formation constants are 7.87 and 5.05 respectively.

**ALTHOUGH** the co-ordination chemistry of salicylic acid is well documented, the study of its derivative, 3-nitro salicylic acid (3-NSA), remained neglected until quite recently. Khadikar *et al.*<sup>5-7</sup> have reported the complex forming tendency of 3-NSA with number of di- and tri-valent metal ions. The literature does not reveal the complex formation of Tl(I) with 3-NSA. The present study deals with the same. The proton-ligand formation constants of 3-NSA and the formation constants of its complexes with Tl(I) have been determined in the present investigation employing half-integral, point-wise calculation, and linear plot method. Refined values of formation constants are obtained by the method of least-squares.

### EXPERIMENTAL

All the chemicals used were of Analar B.D.H. grade.

Polymetron model CL-41 was used for pH titrations conducted at  $30^\circ$ . Measurements were made with an accuracy of  $\pm 0.05$  pH units and the reproducibility of the readings was of the same order. The pH-meter was calibrated using Cambridge buffer tablets of pH 4.1 and 9.1.

pH-metric titrations of solutions of (i) free  $\text{HClO}_4$ , (ii) free  $\text{HClO}_4 + 3\text{-NSA}$  and (iii) free  $\text{HClO}_4 + 3\text{-NSA} + \text{Tl(I)}$ , were performed in 50% (v/v) aqueous ethanol medium against standard NaOH solution while maintaining the ionic strength at 0.1 M  $\text{NaClO}_4$ .

TABLE I

pH	$\bar{n}_A$	$\log \frac{\bar{n}_A}{1 - \bar{n}_A}$	$\log \frac{\bar{n}_A - 1}{2 - \bar{n}_A}$	Point-wise	
				$\log pK_1^H$	$\log pK_2^H$
2.2	1.614		+0.201		2.401
2.3	1.518		+0.031		2.331
2.4	1.449		-0.089		2.311
2.6	1.259		-0.456		2.144
2.8	1.156		-0.733		2.067
3.0	1.017				
4.0	0.992				
5.0	0.985				
6.0	0.980				
8.0	0.975				
9.0	0.945				
9.8	0.831	+0.691		10.491	
10.0	0.742	+0.459		10.459	
10.1	0.706	+0.381		10.481	
10.2	0.623	+0.219		10.419	
10.3	0.472	-0.048		10.252	
10.4	0.452	-0.082		10.318	
10.5	0.327	-0.311		10.189	
10.6	0.277	-0.416		10.184	

The experimental set-up and the method of calculation is the same as described earlier<sup>1-3</sup>.

#### RESULTS AND DISCUSSION

The Irving-Rossotti expression<sup>4</sup> was used for the calculation of  $\bar{n}_A$  (Degree of formation of proton-ligand complex),  $\bar{n}$  [Degree of formation of Tl(I)-complex], and  $p(L)$  (Free ligand exponent). The concentrations were corrected for the changes in volume as a result of addition of alkali during titration. A series of values of  $\bar{n}_p$ ,  $\bar{n}$  and  $p(L)$  corresponding to different B-values (pH-meter readings) were calculated (Tables I-II) and the formation curves for ligand and complex were obtained by plotting  $\bar{n}_A$  vs. pH and  $\bar{n}$  vs.  $p(L)$  respectively (Figs. 1-2). The values of  $\log pK_1^H$ ,  $\log pK_2^H$  (Practical proton-ligand formation constants) and also  $\log K_1$  and  $\log K_2$  were recorded directly from the respective formation curves from integral values

of  $\bar{n}_A$  and  $\bar{n}$  and are recorded in Table III. Values of these constants were also obtained by point-wise calculation as well as linear plot method<sup>1</sup> (Figs. 3-4). Refined values of  $\log K_1$  and  $\log K_2$  were obtained by the method of least-squares.

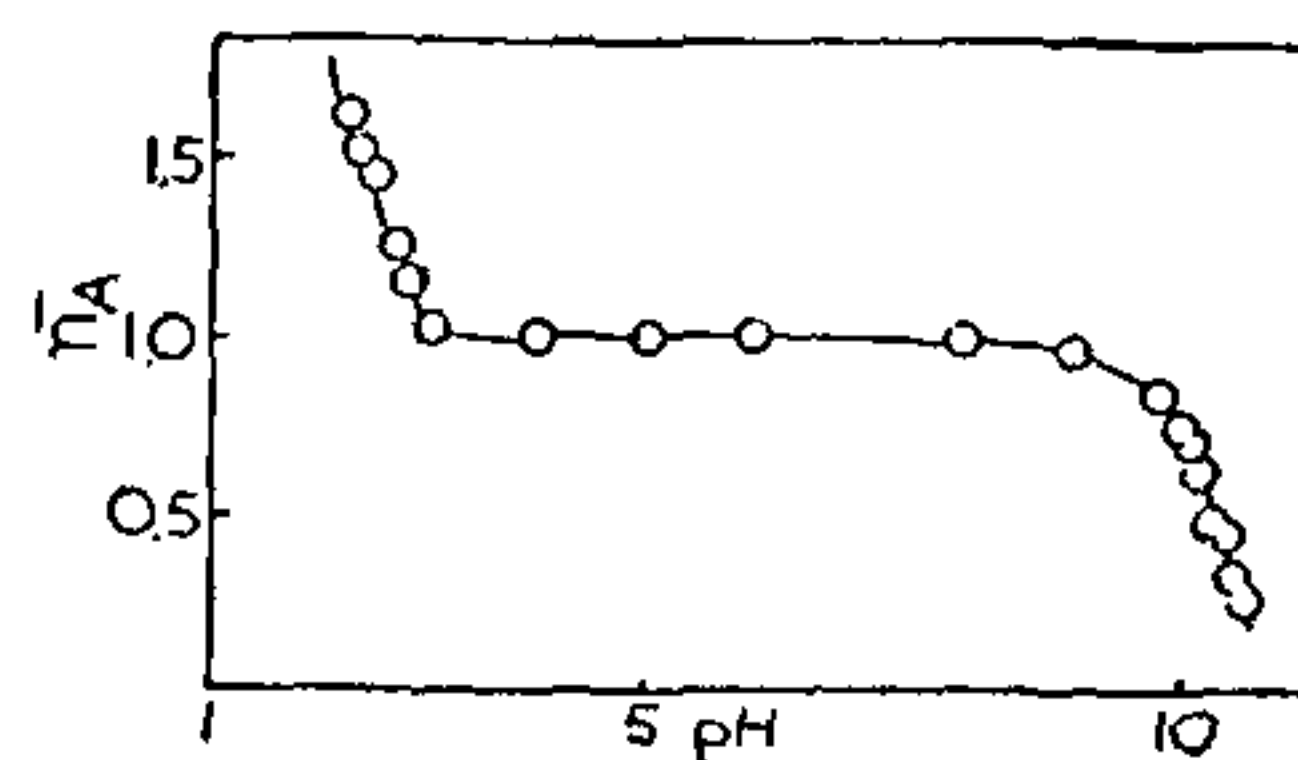


FIG. 1

Persual of Table II (Fig. 2) shows that  $\bar{n}$  value never exceeds 1.7 indicating thereby the formation

TABLE II

$\bar{n}_v$	$\bar{n}$	$\log \frac{\bar{n}}{1-\bar{n}}$	$\log \frac{\bar{n}-1}{2-\bar{n}}$	$p(L)$	Point-wise	
					$\log K_1$	$\log K_2$
0.985	0.158	-0.458		8.798	8.340	
0.983	0.310	-0.345		8.567	8.222	
0.984	0.453	-0.08		8.034	8.954	
0.985	0.670	+0.308		7.382	7.690	
0.983	0.723	+0.417		7.132	7.549	
0.981	0.778	+0.547		6.902	7.449	
0.982	1.086		-1.026	5.590		4.564
0.978	1.148		-0.760	5.480		4.720
0.975	1.365		-0.240	5.230		4.990
0.974	1.525		+0.043	5.112		4.155
0.972	1.637		+0.244	4.997		3.241
0.970	1.750		+0.477	4.877		4.354

TABLE III

Method	$\log pK_1^H$	$\log pK_2^H$	$\log K_1$	$\log pK_2$
Half-integral	10.35	2.30	7.91	5.12
Linear-plot	10.32	2.35	7.90	5.12
Point-wise calc.	10.35	2.25	7.86	5.00
Least-square	..	..	7.80	5.01
Average	10.34	2.30	7.87	5.05

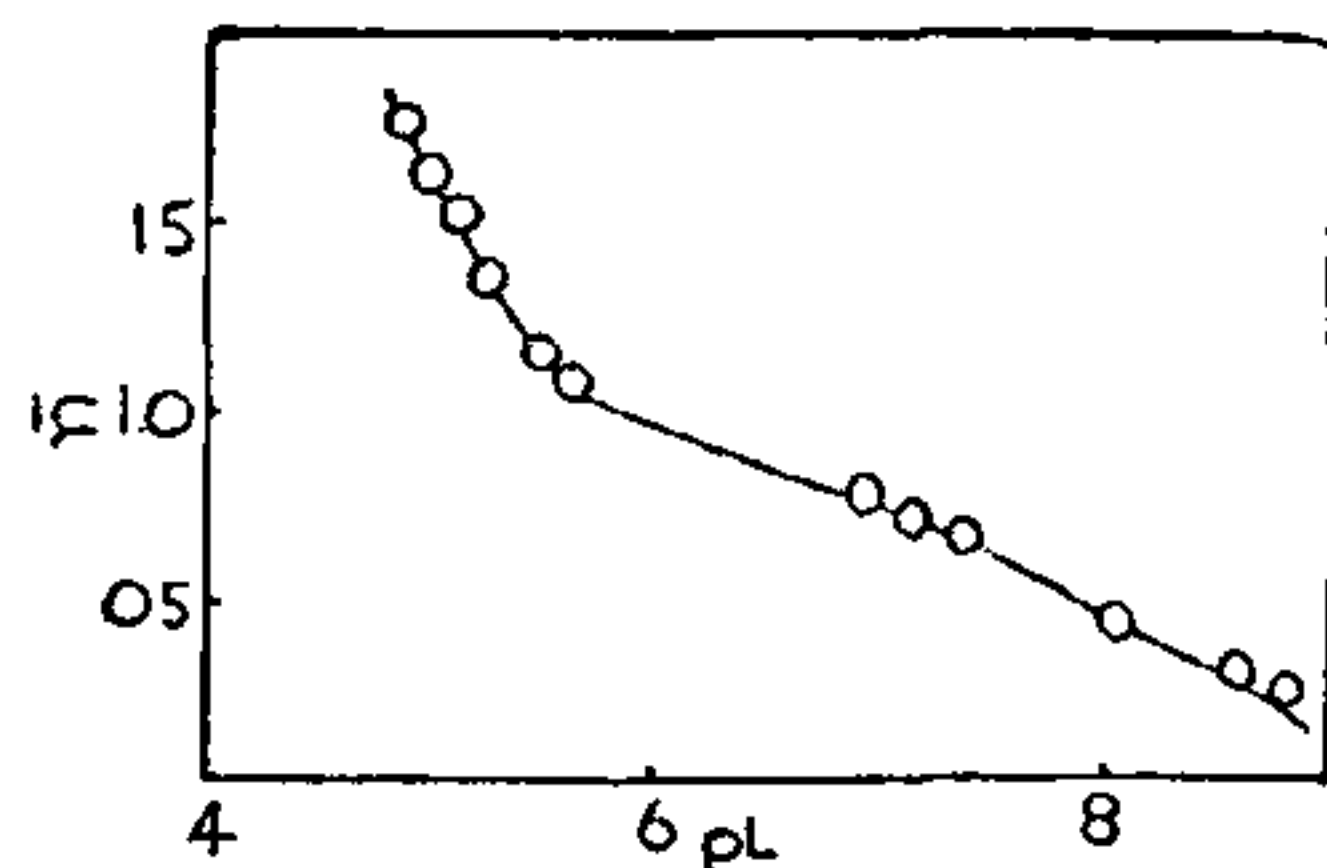


FIG. 2

of only 1:1 and 1:2 complexes of Tl(I) with 3-NSA. In view of the very low concentration of Tl(I) ( $1 \times 10^{-4}$ ) used in the titration, formation of polynuclear complexes may be ignored. Titrations performed with different ratios of metal to ligand

showed that the formation constants are independent of metal ion concentration.

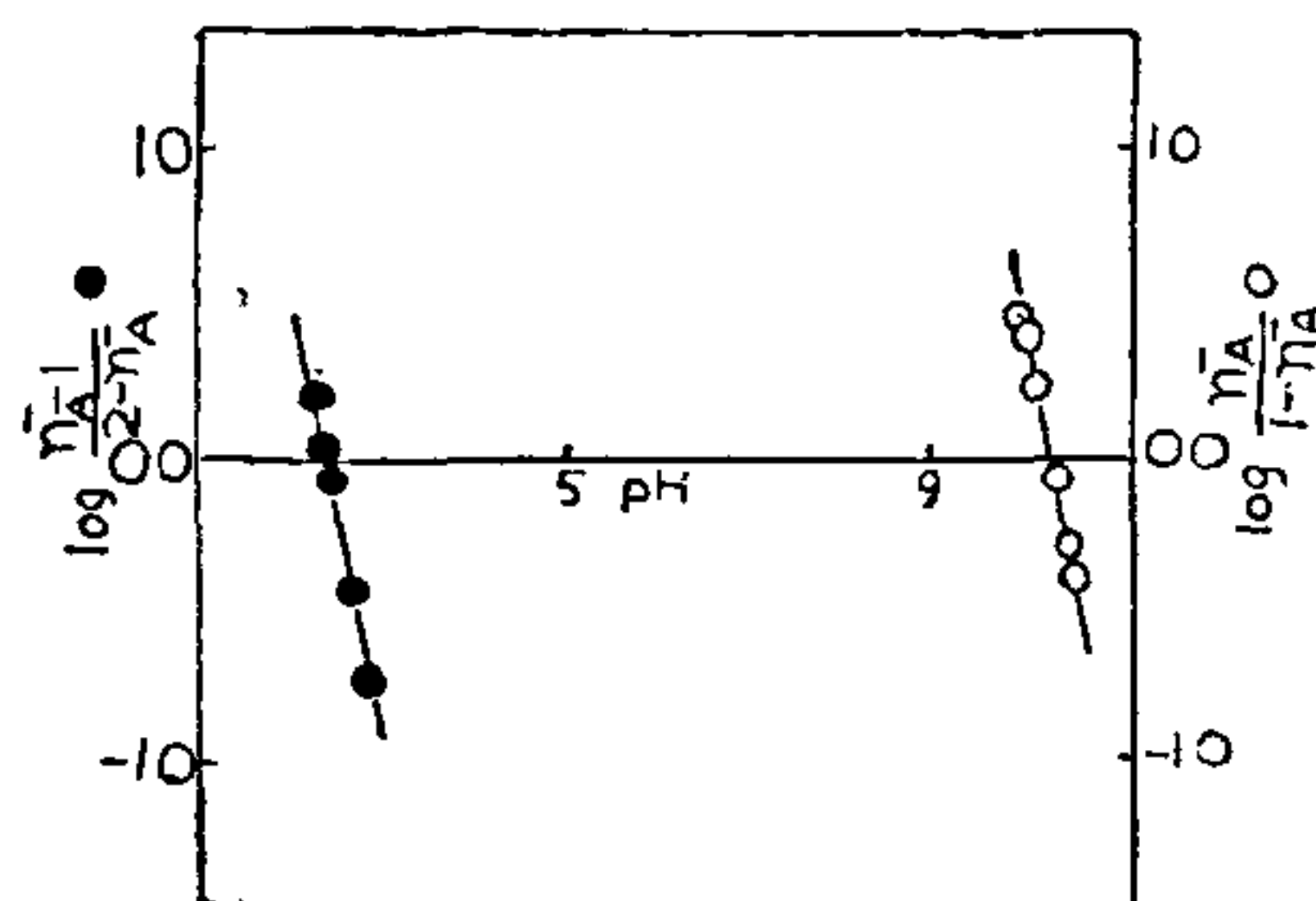


FIG. 3

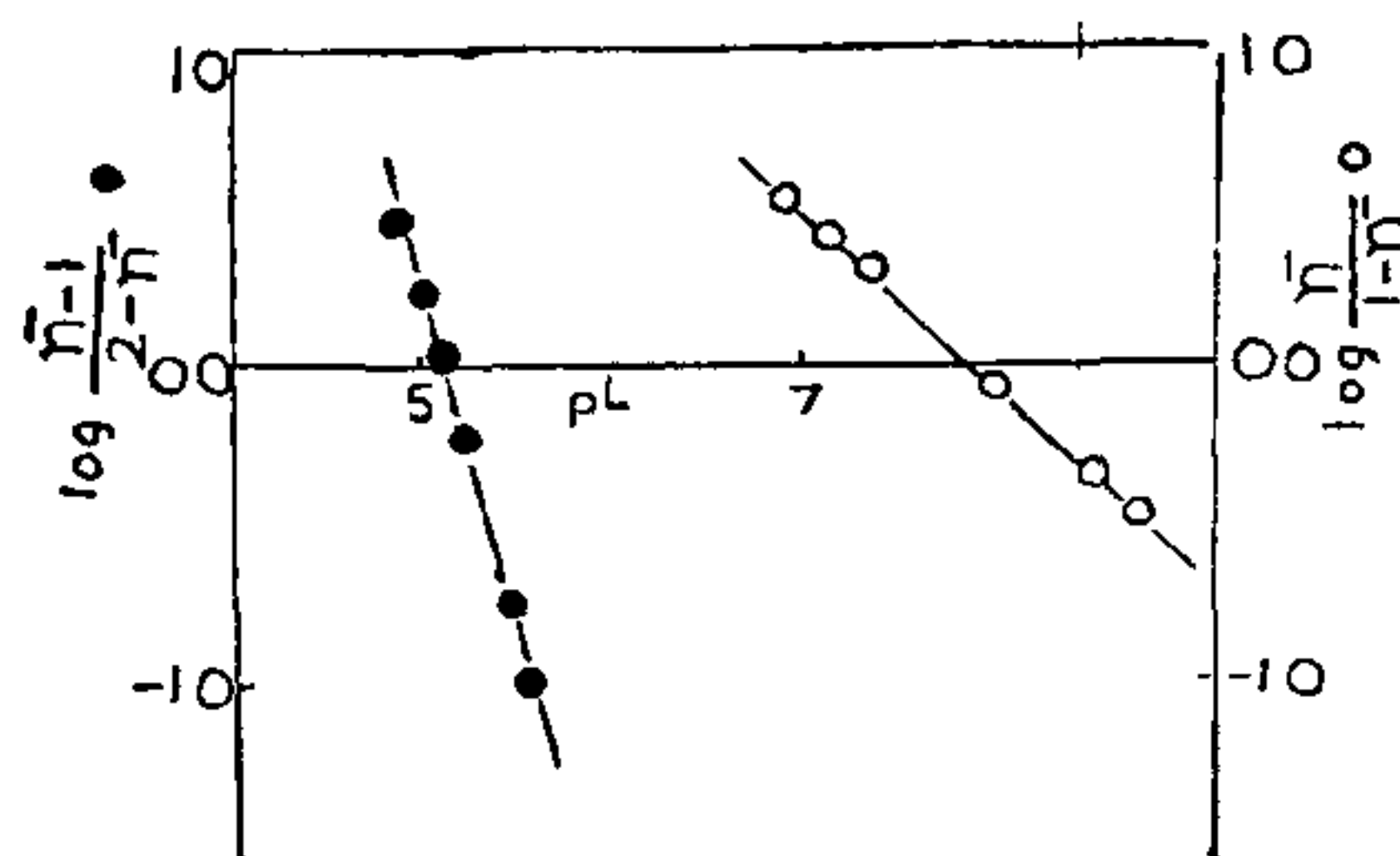


FIG. 4



The ratio of  $\log K_1/\log K_2$  is positive and that the separation factor between the first and the second formation constant is well within the range. A bigger difference between  $\log K_1$  and  $\log K_2$  is due to the possible steric hindrance on the linking of the second ligand molecule expected for  $Tl(I)$  ion.

#### ACKNOWLEDGEMENT

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### SPECTROPHOTOMETRIC INVESTIGATION OF Ti(IV) COMPLEXES OF N-SALICYL PHENYL HYDROXYLAMINE

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#### ABSTRACT

Yellow coloured complexes of Ti(IV) and N-salicyl phenyl hydroxylamine are extractable into isoamyl alcohol. The spectrophotometric studies following Job's and molar ratio methods have shown that 1:2 and 1:3 (metal:ligand) complexes predominate in the acidity ranges of 2-5 N and 7.5-9 N HCl respectively. The values of the stability constants, stepwise and overall, have been calculated following extended Yatsimirskii's, Leden's and Harvey-Manning's methods. An electronic computer, IBM 1130, using FORTRAN Programming was utilized for evaluating stability constants of 1:3 system. The analytical suitability of the reagent for microdetermination of titanium has also been investigated.

#### INTRODUCTION

THE application of the aryl hydroxamic acids and their N-phenyl analogues are well documented<sup>1-5</sup>. But in many cases<sup>6,7</sup>, investigations were carried out to study the complexes with the variation of acidity. The present paper deals with the spectrophotometric investigation of Ti(IV) complexes of N-salicyl phenyl hydroxylamine (NSPHA) at varied acidities. The study has established the existence of 1:2 and 1:3 (metal:ligand) complexes depending on the pH. The stepwise and overall formation constants are evaluated by extended Yatsimirskii's<sup>8</sup>, Leden's<sup>9</sup> and Harvey-Manning's<sup>10</sup> method. The analytical suitability of the reagent for microdetermination of titanium is explored in the light of above observations.

#### MATERIALS

A stock solution of titanium (2.18 mg/ml) was prepared from potassium titanyl oxalate (A.R.) and was standardised<sup>11</sup>. The reagent, NSPHA (m.p. 106-107°C), was prepared following the method of Shome<sup>12</sup>. Chemicals used in all spectrophotometric

measurements were of A.R. or spectrograde quality. A Hilger Uvispek spectrophotometer was used for spectrophotometric measurements. For evaluation of the formation constants, a IBM 1130 scientific and electronic computer based on FORTRAN Programming was employed.

#### EXPERIMENTAL

An aliquot of titanium solution ( $8.352 \times 10^{-5}$  M) was taken in a 100 ml separatory funnel and its pH adjusted to the desired value. The reagent solution (0.087 M) in isoamyl alcohol was then added and the mixture shaken thoroughly for 10 minutes. The yellow coloured nonaqueous layer was collected in a small beaker. The extraction was repeated with a 5 ml portions of isoamyl alcohol. The combined extract, after drying over sodium sulphate, was diluted to 25 ml with isoamyl alcohol and its absorption was measured at 390 and 400 nm.

#### RESULTS AND DISCUSSION

The absorbance measurements of the complex solution at 8 N HCl show maximum absorbance at 370 nm. Due to low reagent absorption around 390-400 nm, all the absorption measurements were taken against the reagent blank at

\* A portion of this work was included in the Ph.D. Thesis submitted to Jadavpur University in 1974.