

and 90 km with electron density change maximizing at 80 km, and a decrease again beyond 90 km.

It is not strictly valid to assume a uniform temperature enhancement in an ordinary heating experiment, since the region (altitude) of maximum absorption of radiation (and thereby temperature rise) depends on the frequency of the disturbing transmitter and also the mode of excitation. Nevertheless, the present result is significant in the sense that it brings out the variation in the effect of temperature enhancement on the various chemical processes. It may be of interest to note that the regions of crossover (figure 1) coincide, respectively, with the region of transition from negative ion to electron-dominant regime (at around 74 km) and the region where  $O^+$  ions dominate over  $NO^+$  ions. A detailed investigation using a realistic temperature distribution under disturbed conditions is being carried out and the results will be published elsewhere.

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## POLAROGRAPHIC STUDIES OF MIXED-LIGAND COMPLEXES OF THE In(III)-1-METHYLIMIDAZOLE-TARTRATE SYSTEM

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STUDIES on mixed-ligand complexes, particularly those of biological significance, have been of interest

during the past decade. Earlier work from this laboratory and elsewhere<sup>1-3</sup> has indicated that in the combination of metals with serum albumin the principal binding sites are the imidazole groups of the protein molecule. Norman *et al.*<sup>4</sup> have studied polarographically the overall formation constant of cadmium and copper complexes of imidazole and 1-methylimidazole. The results indicated that the site of binding on the imidazole molecule was the pyridine-nitrogen rather than pyrrole-nitrogen. A survey of data cited in the literature revealed that further studies are required. Also, there has been no report on mixed-ligand complexes of In(III)-1-methylimidazole-tartrate system. The present work is devoted to a polarographic investigation of the composition and stability constants of simple and mixed-ligand complexes of the above system.

All chemicals used were of BDH reagent grade. Solutions were prepared in conductivity water. The ionic strength was maintained constant at  $\mu=2.0$  using  $NaNO_3$  supporting electrolyte. The concentration of Cd(II) was kept at  $1 \times 10^{-3}$  M. All measurements were made at  $25 \pm 0.1^\circ C$  and pH 8. The pH measurements of the solutions were made using a Beckman extended scale digital pH meter model 4500 with accuracy  $\pm 0.002$  pH units. The pH meter was calibrated by means of saturated buffer solutions (Burroughs Wellcome, England).

Polarographic measurements were carried out using a PAR model 174A polarographic analyser in conjunction with a three-electrode cell system, with a saturated Ag/AgCl as reference, platinum as the counter electrode and a dropping mercury electrode as working electrode. The polarograms were recorded on Houston Omnigraphic model RE 0074 X-Y recorder. All the test solutions were degassed with pure nitrogen.

The stability constants of simple complexes of In(III) with 1-methylimidazole and tartrate were determined separately prior to a study of the mixed-ligand system. Identical conditions were maintained in both the simple and mixed-ligand systems.

The reduction of In(III) in 1-methylimidazole and tartrate media, separately, was found to be reversible and diffusion-controlled. The same was true with the mixed system. The slopes of linear plots of  $\log(i/i_d - i)$  vs  $E_{de}$  were of the order of 33 mV and the plots of  $i_d$  vs  $i_{corr}^{\frac{1}{2}}$  were linear and passed through the origin.

### In(III)-1-methylimidazole

A plot of  $E_{\frac{1}{2}}$  vs  $\log [1-MeIm]$  indicated that two

complexes were formed, with stability constants  $\log B_{10} = 3.60$  and  $\log B_{20} = 5.86$ . Deford and Hume's<sup>5</sup> method was applied to determine the stability constants of successive complexes.

#### *In(III)-tartrate system*

The  $E_{\frac{1}{2}}$  vs  $\log [\text{Tart}^{-2}]$  curve gave a straight line indicating the formation of one complex species and hence the method of Lingane<sup>6</sup> was adopted for the evaluation of stability constants and co-ordination number. The stability constant of the simple complex formed was found to be  $\log B = 3.4$ .

#### *Mixed In(III)-1-methylimidazole-tartrate system*

The 1-methylimidazole concentration was varied from 0.02 to 0.20 M and that of tartrate was kept constant at 0.1 M. The  $E_{\frac{1}{2}}$  values were greater than those obtained in the absence of tartrate, thereby indicating the formation of mixed complexes. The system was studied at another concentration of tartrate (0.20 M). To determine the values of the stability constants of mixed-ligand complexes, the method of Schaap and McMasters<sup>7</sup> was applied. The polarographic characteristics and function  $F_{ij}(X)$  of the mixed complexes at fixed  $[\text{Tart}^{-2}]$  (0.1 and 0.2 M) are presented in tables 1 and 2.

**Table 1** *In(III)-1-methylimidazole-tartrate system,  $[\text{In(III)}] = 1 \times 10^{-3}$  M and  $[\text{Tart}^{-2}] = 0.1$  M (fixed)*

[1-Melm]	$-E_{\frac{1}{2}}$	$F_{00}(X) \cdot 10^{-1}$	$F_{10}(X) \cdot 10^{-3}$	$F_{20}(X) \cdot 10^{-5}$
0.00	0.510			
0.02	0.520	3.95		
0.04	0.530	21.53	3.98	
0.08	0.540	179.55	22.00	26.59
0.10	0.550	339.00	32.97	28.00
0.15	0.560	1504.98	99.87	41.98
0.20	0.570	2139.99	106.79	24.89

$\mu = 2.0$  NaNO<sub>3</sub>, pH 7.4, temp. 25°C.

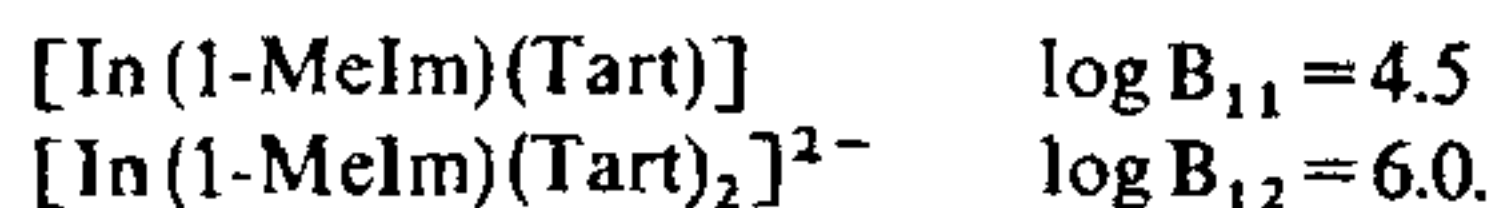
**Table 2** *In(III)-1-methylimidazole-tartrate system,  $[\text{In(III)}] = 1 \times 10^{-3}$  M and  $[\text{Tart}^{-2}] = 0.2$  M (fixed)*

[1-Melm]	$-E_{\frac{1}{2}}$	$F_{00}(X) \cdot 10^{-1}$	$F_{10}(X) \cdot 10^{-3}$	$F_{20}(X) \cdot 10^{-5}$
0.00	0.510			
0.02	0.530	2.09		
0.04	0.540	6.98	13.31	23.20
0.08	0.550	35.31	42.00	47.56
0.10	0.560	72.00	70.00	58.00
0.15	0.570	339.87	229.00	94.99
0.20	0.580	960.99	279.98	72.98

$\mu = 2.0$  NaNO<sub>3</sub>, pH 7.4, temp. 25°C.

The stability constants were calculated from the analysis of  $F_{ij}(X)$  functions.

The values are reproducible to  $\pm 4\%$ . Two mixed complexes as noted below are formed:



The value of the mixing constant  $K_M$  is +0.7 (ref. 8, 9). The positive value of the mixing constant shows that the mixed complex  $[\text{In(1-Melm)(Tart)}]$  is somewhat more stable than the simple biscomplexes of In(III) with 1-methylimidazole and tartrate.

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### REACTION OF SOME *p*-SUBSTITUTED PHENACYLDIMETHYLSULPHONIUM BROMIDES WITH AROMATIC ALDEHYDES: SYNTHESIS OF 2,4,6-TRIARYLPYRIMIDINES

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SULPHONIUM salts have gained considerable importance in the synthesis of a large variety of heterocyclic compounds, viz. substituted pyridines<sup>1,2</sup>, indoles<sup>3</sup>, tetrazines<sup>4</sup>, azaridines<sup>5</sup>, etc. But they have not been utilized in the synthesis of 2,4,6-triarylpyrimidines. Work described here involves aza ring closure with condensation of sulphonium salts