Reprinted from the *Indian Journal of Chemistry*, Vol. 15A, No. 3, March 1977, pp. 255-256

208

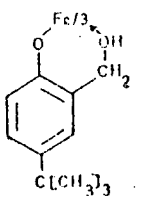
Spectrophotometric Studies of 2-Methylol-4-*tert*-butylphenol-Fe(III) Complex

P. Siva Rami Reddy*, S. Rajadurai & M. Santappa
Central Leather Research Institute, Madras 20

Received 27 *January* 1976; *accepted* 28 *August* 1976

2-Methylol-4-*tert*-butylphenol (2M4TBP) forms 1:3 (metal:ligand) complex with Fe(III) at *p*H4, showing maximum absorbance at 600 nm. The complex obeys Beer's law in the range $1{\cdot}0\times10^{-4}$-$1{\cdot}0\times10^{-3}M$.

WITH a view to developing a suitable analytical technique for the estimation of reactants in phenol-formaldehyde reaction, the complex formation of phenol/phenolmethylol with Fe(III) was investigated by Dakshinamurthy and Santappa[1] and Dejong *et al.*[2]. The present note deals with the spectrophotometric method of estimating 4-*tert*-butylphenol (4TBP)/2-methylol-4-*tert*-butylphenol (2M4TBP). A probable structure is proposed for the 2-methylol-4-*tert*-butylphenol-Fe(III) complex.



I

Stock solutions (0·2*M*) of 2-methylol-4-*tert*-butylphenol (2M4TBP)[3] and 2,6-dimethylol-4-*tert*-butylphenol (2, 6M4TBP) were prepared both in 50 and 80% dioxane-water. Suitable dilution of the stock solution with the same solvent system gave solution of lower concentration. Dioxane (AR, BDH) was purified using the procedure described by Baliah and Chandrasekharan[4].

Ferric chloride solution was prepared by dissolving hydrated ferric chloride (AR, BDH) in sufficient water and hydrochloric acid (AR, BDH) to make up exactly *N*/2 solution. The exact normality of the solution was determined by titrating ferric content by the usual iodometric method.

Preparation of 2-methylol-4-tert-butylphenol-Fe(III) complex — To 30 ml of 2-methylol-4-*tert*-butylphenol were added 10 ml of ferric chloride of equal concentration. The resultant solution was green in colour. It was then made up to 50 ml for optical density measurements employing 50 and 80% dioxane-water as blank.

The method of Vosburgh and Cooper[5] was employed to determine the nature of the complexes. Mixtures containing 1:1, 1:2 and 1:3 mole ratios of Fe(III) to 2M4TBP were prepared. Absorbance measurements were carried out between 400 and 700 nm. All the mixtures showed maximum absorbance at 600 nm, thus indicating the formation of a single complex. All the subsequent measurements were therefore carried out at 600 nm.

The complex was found to give constant maximum absorbance in the *p*H range 3·5-4·5. Therefore *p*H 4 was selected for all further studies and it was maintained using 41 ml of *M*/5 acetic acid and 9 ml of *M*/5 sodium acetate.

The composition of the complex was determined using mole ratio method[6], keeping $[Fe^{3+}] = 2{\cdot}0\times10^{-3}$ *M* and varying 4TBP/2M4TBP concentrations in the range $0{\cdot}5$-$8{\cdot}0\times10^{-3}M$. There was a rapid increase in the absorbance at 600 nm up to $[Fe^{3+}]/[2M4TBP]$ ratio 1:3 and thereafter it became constant thereby indicating a 1:3 stoichiometry of the complex. The above results were supported by the method of continuous variation[7,8].

A linear relationship was observed between concentration and optical density over the range $1{\cdot}0\times10^{-4}$ to $1{\cdot}0\times10^{-2}M$ at 600 nm.

The suppression of colour formation with increase in dioxane content (50 to 80% dioxane-water) indicated that the complex might be a non-electrolyte. The formation of coloured complexes were noticed only in the case of 2M4TBP where formation of chelate rings are possible and 4-methylol-2,6-ditert-butylphenol did not form coloured complex with Fe(III). Evidence for the ionization of only one hydrogen of phenolic hydroxyl group obviously, was provided by the potentiometric titrations. All these observations can be explained by assigning structure (I) to 2-methylol-4-*tert*-butylphenol-Fe(III) complex.

We are thankful to Dr V. V. Ramanujam, Professor of Inorganic Chemistry, A.C. College of Technology, University of Madras, for his valuable suggestions.

References

1. Dakshinamurthy, H. & Santappa, M., *J. org. Chem.*, 27 (1962), 1842.
2. Dejong, R. I., Dejonge, R. I. & Dejkstra, R., *Recl. Trav. Chim.*, 75 (1956), 1289.
3. Siva Rami Reddy, B., Rajadurai, S. & Santappa, M., *Leather Sci. India*, 22 (1975), 180.
4. Baliah, V. & Chandrasekharan, V., *Indian J. Chem.*, 10 (1972), 159.
5. Vosburgh, W. C. & Cooper, G. R., *J. Am. chem. Soc.*, 63 (1941), 437.
6. Yoe, J. H. & Jones, A. L., *Ind. Engng Chem., Anal. Ed.*, 16 (1944), 111.
7. Job, P., *Ann. Chim.*, 9 (1928), 113.
8. Job, P., *Ann. Chim.*, 16 (1936), 97.