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pH Metric and thermal study of the gallacetophenoneoximate complexes of some bivalent metal ions

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Gallacetophenoneoxime reacts with various metal ions[1] giving either a precipitate or a soluble complex. Duval[2] discussed the thermodynamics of the metal complexes. The relationship between the thermal and the solution stability of the metal complexes of a number of oximes was investigated by Liptay *et al.*[3] and Seshagiri *et al.*[4].

Liptay *et al.* (*loc. cit.*) showed that the thermal decomposition of the complex occurs through the scission of a bond other than the metal–ligand bond. In order to arrive at the relationship between solution stability and the thermal stability and the structure of the metal chelate, the authors have studied the oximate complexes of Pd(II), Cu(II), Co(II), Ni(II) and Mn(II).

EXPERIMENTAL

All chemicals employed in the investigations were of analytical reagent grade. An ELICO pH meter model LI-10 was used for pH measurements. The thermogravimetric studies were made using a locally made unit.

The dissociation constant of the gallacetophenoneoxime was interpolated from the formation curve of the protonated oxime. The curve is constructed from $\bar{n}_a$ values calculated from the pH-titration data by Irving's method[5].

The pH metric method suggested by Calvin and Melchoir[6] was employed for the determination of the step-wise formation constants and overall stability constants of the metal complexes. The data are presented in Table 1.

A thermogravimetric study of the oxime and its complexes with Cu(II) and Pd(II) was made. The quantities used were:

Gallacetophenoneoxime:	64.2 mg
Copper complex:	126.2 mg
Palladium complex:	53.7 mg

The results are shown in Table 2.

DISCUSSION

Effect of solvent. The gallacetophenoneoxime behaved as a monobasic acid under our conditions. The dissociation of the ligand changed in the order:

Aqueous 2-ethoxy ethanol < Aqueous acetone < Aqueous dioxane

In acetone–water the dissociation is less than expected from the bulk dielectric constant.

The order of stability of the metal complexes in the three mixed solvents studied is Pd > Cu > Co > Ni > Mn, with the exception of the position of the cobalt, this corresponds to the Irving–William series. The order of stability with respect to the solvent is dioxane > acetone > 2-ethoxy ethanol. The dielectric constants of the mixed solvents, as well as the pure solvents are in the order:

Acetone > 2-Ethoxy ethanol > Dioxane

An abnormal behaviour is observed in the case of acetone–water mixture. Similar abnormalities have been reported by Grigorepopa *et al.*[7] and Brahmaji Rao *et al.*[8] The stability order therefore cannot be correlated with the dielectric constant of the medium alone. Other specific properties of the solvents may play a significant role. The increased stability of the metal complexes in acetone–water mixture may also be due to increased coordination of the complexes with the solvent molecules.

The thermodynamic stabilization energy (δH) is calculated by the method reported by George and McClure[9]. The values are similar to those found for other reagents coordinating through one nitroen and one oxygen atom.

Thermogravimetric study

The weight change suggests the Pd complex pyrolyses to give metallic Pd. This confirms the results of Duval *et al.* (*loc. cit.*) and Seshagiri *et al.* (*loc. cit.*). However, gravimetric studies carried out on the palladium chelate[10] indicate the presence of one water molecule in the dried state. The thermogram showed no change in the weight of the sample below 240°. This suggests that the water molecule is firmly bound.

The copper complex lost 52.3% of its weight at 400°C. This is less than the value corresponding to pyrolysis to the metallic or oxide states.

A comparison of the thermograms of copper resacetophenoneoxime and copper–gallacetophenoneoxime complex showed that the introduction of additional phenol hydroxyl group in the benzene ring of the oxime enhanced the thermal stability of the copper complex.

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Regional Engineering College K. ADINARAYANA REDDY
Warangal
India

Sri Venkateswara University Y. KRISHNA REDDY
Tirupati
India

SVU Autonomous Post-Graduate Centre S. BRAHMAJI RAO*
Anantapur
India

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*Author to whom correspondence should be addressed.