ANALYTICAL APPLICATIONS OF ACYL PYRAZOLONES

by

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C E R T I F I C A T E

This is to certify that the thesis entitled "Analytical Applications of Acyl Pyrazolones" being submitted by Mr.H.C.Arora to the Indian Institute of Technology, Delhi for the award of Degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr.H.C.Arora has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

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S U M M A R Y

In the introductory chapter an exhaustive review of the solvent extraction of metals with acyl pyrazolones reported in literature so far has been presented. Scope of the present work has been indicated at the end of this chapter. Detailed investigation of solvent extraction of some metals with 4-benzoyl-2, 4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (BMPP), 4-p-nitrobenzoyl-2, 4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (NMPP) and 4-dinitro-benzoyl-2, 4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (DMPP) has been reported in the second chapter. Preparation of the ligands and experimental techniques employed for the extraction studies are described briefly at the beginning of the chapter. From the plots of log Kd vs pH and log Kd vs log (L) (Kd = distribution coefficient, (L) = ligand concentration), formulae of extracted species and extraction constants have been determined. Systems investigated are (a) copper (II), cadmium (II), cobalt (II), iron (III), lead (II), cerium (IV) and uranium (VI) with BMPP (b) copper (II), cobalt (II), nickel (II), uranium (VI), iron (III) and thorium (IV) with NMPP and DMPP.

Stoichiometry of the extracted species in general corresponded to 1:2 (metal:ligand) with copper (II), cobalt (II), nickel (II) and uranium (VI), 1:3 with iron (III) and 1:4 with

cerium (IV) and thorium (IV) respectively. In general the efficiency of the ligands for extraction varies in the order DMPP > NMPP > BMPP > HTTA (TTA = thenoyl trifluoroacetone). As the advantages of acyl pyrazolones compared to the commonly employed fluorinated β-diketones have been already pointed out the present study confirms the earlier findings. Introduction of nitrogroups is expected to decrease the pK value of the acyl pyrazolone and the present study shows that extraction of metals occurs at lower pH values with DMPP and NMPP as compared to BMPP. Thus DMPP and NMPP would be more useful than BMPP for the extraction of easily hydrolysable metal ions.

Synergistic extraction of copper (II), cadmium (II), lead (II), cobalt (II) and uranium (~~IV~~ VI) with BMPP and auxiliary ligands like pyridine (Py), tri-n-butyl phosphate (TBP) and tri-n-octyl phosphine oxide (TOPO) has been also described in this chapter. Formation of ternany complexes with the stoichiometry 1:2:1 or 1:2:2 (metal:BMPP:auxiliary ligand) in the organic phase has been established in these systems. Destruction of synergism in some systems has also been observed. Probable mechanism for the extraction of metals with BMPP, NMPP and DMPP has been suggested in all systems based on the experimental findings. Reasons for the variation of stoichiometry in uranium (VI)-BMPP (acetate medium), lead (II)-BMPP and iron (III)-BMPP have been pointed out. Most of the work has been performed using benzene as solvent. Solubility of NMPP and DMPP is not high in benzene but by employing mixtures of chloroform and isoamyl alcohol more concentrated solutions can be easily prepared. The equilibration time for the extraction of nickel (II) with NMPP and DMPP is found to be much less than that observed with BMPP, TTA or other β-diketones which is a considerable improvement since shaking for 24 hours or more is required with the latter ligands. Analytical applications of BMPP and NMPP in the separation of copper (II) and cadmium (II) at pH 3.0 and thorium (IV) and uranium (VI) (1M HCl) have been reported at the end of the second chapter.

Detailed experimental study of the spectrophotometric determination of iron (III) and cerium (IV) after extraction with BMPP, NMPP and DMPP is presented in the third chapter. Effect of various parameters like pH, presence of foreign ions, extraction time etc. have been investigated. Since iron (III) is extracted with BMPP in highly acidic media interference due to other ions commonly associated with iron (III) in alloys, ores and industrial materials like nickel (II), cobalt (II) etc. is negligible and a rapid, highly selective method is thus available for the determination of iron (III). Similarly the application of BMPP for the spectrophotometric determination of cerium (IV) in monazite sands have been tested and the advantages of the method developed are discussed.

BMPP, NMPP and DMPP proved to be efficient ligands in the gravimetric determination of uranium (VI) and thorium (IV). Uranium (VI) is almost quantitatively precipitated with BMPP, NMPP and DMPP at pH 2.20, 1.85 and 1.70 respectively. The pH values for the complete precipitation of thorium (IV) with BMPP, NMPP and DMPP was 2.90, 2.75 and 2.50 respectively. In addition to the method by weighing after ignition, BMPP proved to be an efficient ligand for the gravimetric determination of uranium (VI) by direct weighing method after drying at $100 \pm 10^{0}C$. The percentage relative error varies from 0.4 to 1.6 in the determination of uranium (VI) by this method. The effect of a number of interfering ions on the precipitation of uranium (VI) and removal of some of them (Ca^{2+}, Fe^{3+}, Cu^{2+}) by using masking agent ($EDTANa_2$) has been reported.

In order to understand the mechanism of the extraction process, physicochemical studies on the solid complexes isolated from solutions employed in solvent extraction have been carried out. Several complexes of BMPP, NMPP and DMPP with various metals and ternary complexes of acylpyrazolonates of metals with phosphorous esters and heterocyclic N-bases have been prepared and characterised by elemental analysis, visible spectra, infrared spectra, proton magnetic resonance spectra and thermal analysis techniques.

The infrared spectra of BMPP in CCl_4 and $CHCl_3$ shows the presence of a sharp intense band at 1600cm^{-1} and the absence of a band in the 1700cm^{-1} region thus indicating that enolic forms is predominant, a situation similar to that obtained with β-diketones like TTA or BTFA. Tentative assignments for the various bands obtained for BMPP, NMPP, DMPP and some selected metals complexes have been made.

Proton magnetic resonance spectra of BMPP indicate that BMPP exists predominantly in the enolic forms in CCl_4 and $CDCl_3$. Enolic peak disappears in the spectra of metal complexes e.g. uranium (VI), thorium (IV) and their adducts with TOPO.

Thermogravimetric studies have indicated that metal complexes containing water, pyridine or phosphorous esters decompose in steps on heating e.g.

$$Co(BMPP')_2 \cdot 2H_2O \xrightarrow{110-150^{\circ}C} Co(BMPP')_2$$

$$Co(BMPP')_2 \xrightarrow{300-500^{\circ}C} Co_2O_3 + \text{Products}$$

$$Co(BMPP')_2Py \xrightarrow{300-380^{\circ}C} Co(BMPP')_2 + Py$$

$$Co(BMPP')_2 \xrightarrow{380-600^{\circ}C} Co_2O_3 + \text{Products}$$

Since pyridine is removed in the first stage of decomposition it is assumed that pyridine may be directly bonded to the metal. The purity of certain metal complexes was also checked from these studies. Some metal complexes of BMPP decompose in one step yielding the oxide as the final product.

C O N T E N T S