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# AN OPTICAL MULTIPLEXER - DEMULTIPLEXER SCHEME IN THE VIEW OF TREE ARCHITECTURE.

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## Abstract

The tree architecture may take important roles in interconnection system of Optical parallel Computing. This is used, here, in optical multiplexing and de-multiplexing also.

Optical interconnecting networks generally function as the basis in optical logic, arithmetic and algebraic processors. Optical tree architecture, in this connection, has been seen to take the roles in arithmetic conversion and expression of Optical data (1-2). Here in this communication the above authors propose a method of using optical tree in multiplexing and demultiplexing systems.

The tree structure is explained in figure 1. Here a light path AB forms two branch paths BC and BD. The branch BC then breaks into two subbranches CE, CF and branch BD to DG, DH. The tree architecture has been successfully exploited in arithmetic conversion from binary to decimal and decimal to binary (1). Here the opto-electronic modulators like Surface Stimulated ferro-electric liquid Crystal (SSFLC), savat plates and polarised light as the basic light source are used with their necessary perfection. At the same time optical implementation of binary to decimal can also be performed by this type of network. In the first conversion the addressing are done by electrical/electronic/opto-electronic signals. These address signals work on carrying the optical beam from the main path of the tree (AB) to the respective subbranch path. This conversion circuit from binary to decimal can be seen in regard of a demultiplexer system.

Now we will exploit the tree architecture in the view of multiplexing and de-multiplexing scheme. This scheme will use spatial light modulators (SLMs), or optical switches (electrically controlled or optically controlled) extensively (3-7). Such switches have been used in various optical/opto-electronic processors (3-7). In our present work we use both positive and negative SLMs or optical switches. Positive SLM allows the light signal to pass through it (transparent) if the external triggering signal is present (1). In contrast the negative SLM becomes transparent at the withdrawal of the signal (0). In figure 2 these types of SLMs or optical switches are used for the function of a multiplexer. Here the input channels are marked by 0, 1, 2 and 3. These input channels are passed through either +ve or -ve spatial light modulators to form a tree. The output point (Op) where the branches and subbranches (input channels) meet to form the main streamline of the tree. Positive spatial light modulators or the optical switches, here, are marked by + and the negative SLMs or optical switches are done same by - signs in fig. 2. The dotted lines are electronic or optical signal carrying lines to trigger these modulators. Now by the application of proper triggering signals in these triggering channels optical signal of a particular input channel will appear in the output. For example if the triggering signals are both zero the negative SLM corresponding the input channel 0 in the subbranch line and the negative SLM in the 1st branch line will take part (being transparent)

to carry the light from the input 0 to the output. In the same way if the signals in the triggering channels are 0 and 1 (i.e. the triggering channel in the left ( $A_1 = 1$ ) takes the signal amount 1 and that of the right ( $A_2 = 0$ ) takes 0) the signal in the input 1 will be passed to the output. The optical signal in input 2 will come to the output for the triggering signal 10 and the beam of the input 3 will do so the same for triggering signals 11.

This architecture of figure 2 can be considered for implementing the function of a demultiplexer. For a demultiplexer the tree is to be followed by a main radiation which breaks into two branches and the branches are again breaking into four subbranches. The +ve and -ve SLMs are placed in the same position as in fig. 2. Now by the application of proper electronic/optical/opto-electronic triggering signals the light in the main channel can be carried to the respective subbranch channels. For example, the triggering signal 10 will make the +ve SLM in the branch channel and -ve SLMs in the 3rd subbranch channel (channel marked by 2 in fig. 2) transparent and optical signal from the main line will pass to the subbranch channel marked by 2.

These types of optical multiplexing and demultiplexing circuits are advantageous because of the tree organisation. In fig. 2 and fig.1 the tree architecture having four subbranch lines each from one main line to four subbranch lines or from four to one are shown. This architecture can be extended more by the breaking of each subbranch line again and again. Here the demultiplexing from one main line to eight subbranch lines and multiplexing from those subbranches to one can be possible. For this particular circuit the triggering channels will be three in number. Similarly demultiplexing from one main line to sixteen, thirty-two or  $2^n$  ( $n$  is an integer) lines and multiplexing from  $2^n$  lines to a single main line are possible where triggering channels are  $n$  in number.

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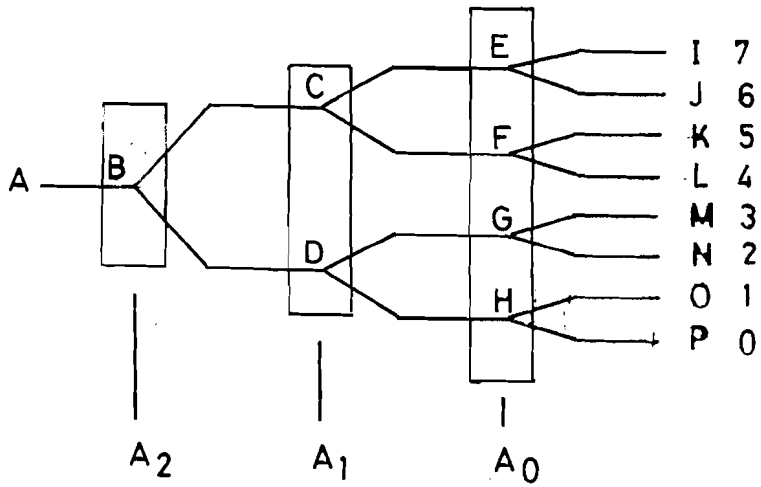


Figure Captions. Fig. 1. A tree structure.

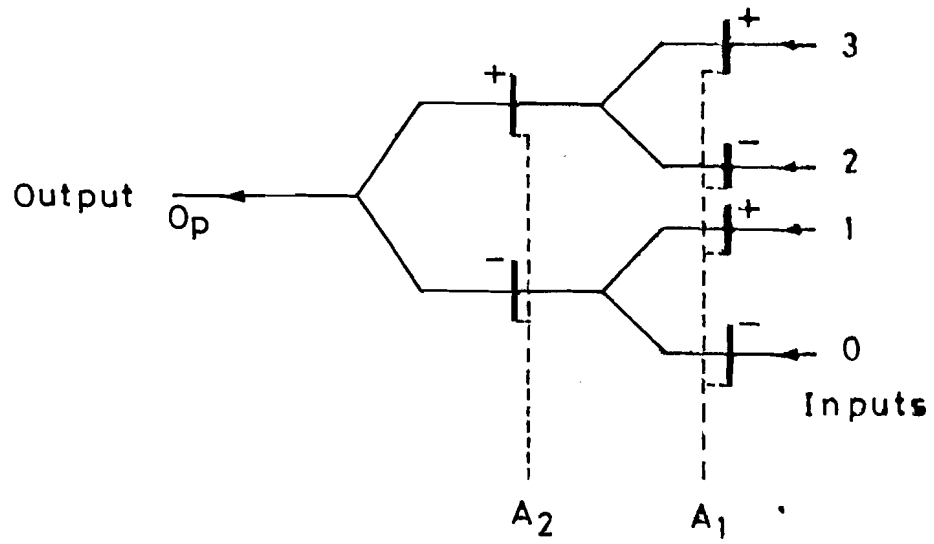


Fig. 2 A tree Structure used as a multiplexer.

# MULTIOBJECTIVE LINEAR PROGRAMMING PROBLEM AN ALTERNATIVE METHOD OF SOLUTION

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## Abstract

As suggested by Zimmermann (1978), the solution of a Multiobjective Linear Programming Problem (MOLPP) with  $p$  objectives,  $m$  constraints, and  $n$  variables is achieved by solving an equivalent single objective Linear Programming Problem (LPP) with  $m+p$  constraints and  $n+1$  variables. In the present paper, the authors have proposed an alternative method of solution to the MOLPP that involves solution of an equivalent single objective LPP with  $m+p-1$  constraints and  $n$  variables. Since the number of constraints and the number of variables are one less than those in Zimmermann's method, the computations involved in achieving the solution is less in the present method than that in Zimmermann's. The method has been illustrated using two numerical examples.

## 1. INTRODUCTION :

Most of the real world problems are multiobjective in nature. Multiobjective problems arise in the design, modelling and planning of many complex resource allocation systems in the areas such as industrial production, urban transportation, layout and landscaping of new cities, energy production and distribution, operation and control of the firm, local government, administration, etc.

The multiobjective problem was first proposed by Kuhn and Tucker [1]. The four major approaches to get optimal compromise solution of multiobjective linear programming problem (MOLPP) are :

- (i) The utility approaches [2,3,4]
- (ii) Goal programming [5,6]
- (iii) Interactive procedures [7]
- (iv) Fuzzy approach by Zimmermann [8]

The first two methods assume that the decision maker (DM) can specify his preference function with respect to the combination of the individual objective functions in advance. The third approach uses local information while the fourth approach uses fuzzy concept.

The advantage of the fourth approach as suggested by Zimmermann [8] is that in the process of obtaining solution DM will not be disturbed by the analyst, which is preferable from the point of view of DM. Also in the situation where DM is not closely accessible to the analyst this method appears to be appealing. In the fuzzy approach of Zimmermann [8], the optimal compromise solution of the MOLPP is obtained by solving a LPP formed by using fuzzy concept. The method proposed in this



paper leads to the same optimal compromise solution as obtained by fuzzy approach. Here also the MOLPP is converted to an equivalent LPP by introducing additional constraints in the form of hyperplanes but this LPP always contains one variable and one constraint less in comparison with the LPP obtained using fuzzy concept.

## 2. DEFINITIONS AND RESULTS

Definition 2.1 Multiobjective linear programming problem (MOLPP)

The general MOLPP is defined as

$$\text{Maximize } z = Cx$$

$$\text{subject to } Ax \leq = \geq b, x \geq 0$$

where  $z = [z_1, z_2, \dots, z_p]^t$ ,  $C = [c_1, c_2, \dots, c_p]^t$   
 $= [c_{kj}]_{p \times n}$   
 $A = [a_{ij}]_{m \times n}$ ,  $b = [b_1, b_2, \dots, b_m]^t$ , and  
 $x = [x_1, x_2, \dots, x_n]^t$ .

Definition 2.2 Lowest justifiable value of the objective functions

For each  $k$  ( $k = 1, 2, \dots, p$ ), the optimal solution of the LPP

$$\text{Max } z_k = c_k x$$

$$\text{subject to } Ax \leq = \geq b, x \geq 0$$

is denoted by  $x^k$  and the optimal value of the objective function  $z_k$  by  $M_k (= c_k x^k)$ .

The lowest justifiable value of the objective function  $z_k = c_k x$  is defined as

$$m_k = \min \{ c_k x^1, c_k x^2, \dots, c_k x^{k-1}, c_k x^{k+1}, \dots, c_k x^p \}.$$

Definition 2.3 Efficient solution, Optimal compromise solution

Let  $X = \{ x \mid Ax \leq = \geq b, x \geq 0 \}$ . Then  $\bar{x} \in X$  is said to be an efficient solution, if there is no  $x' \in X$  such that

$$z_k(x') \geq z_k(\bar{x}) \text{ for all } k = 1, 2, \dots, p$$

and  $z_k(x') > z_k(\bar{x})$  for at least one  $k \in \{ 1, 2, \dots, p \}$ .

Optimal compromise solution is an efficient solution singled out from the set of all efficient solutions by some suitable method.

Theorem 2.1 The optimal compromise solution of the MOLPP

$$\text{Max } z = Cx$$

$$\text{subject to } Ax \leq = \geq b, x \geq 0 (p \leq n)$$

is the optimal solution of the LPP

$$\text{Max } z_1 = c_1 x \text{ or } z_2 = c_2 x \text{ or } \dots \text{ or } z_p = c_p x$$

$$\text{subject to } Ax \leq = \geq b,$$

$$\frac{c_r x - m_r}{M_r - m_r} = \frac{c_{r+1} x - m_{r+1}}{M_{r+1} - m_{r+1}}, \quad r = 1, 2, \dots, p-1,$$

and  $x \geq 0$ .

Proof.

We define  $X_0 = \{x \mid c_r x = m_r, r = 1, 2, \dots, p\}$

and  $X^0 = \{x \mid c_r x = M_r, r = 1, 2, \dots, p\}$ .

Since  $p \leq n$  and  $z_r = c_r x, r = 1, 2, \dots, p$  are non-parallel objective functions,  $X_0$  and  $X^0$  are non-empty. For any  $x_0 \in X_0, x^0 \in X^0$  and  $\lambda \in [0, 1]$ ,  $(1-\lambda)x_0 + \lambda x^0$  is a point on the line joining  $x_0$  and  $x^0$  and the value of the  $r$ th objective function at this point is

$$\begin{aligned} z_r^\lambda &= c_r \{ (1-\lambda)x_0 + \lambda x^0 \} = (1-\lambda) c_r x_0 + \lambda c_r x^0 \\ &= (1-\lambda) m_r + \lambda M_r \end{aligned}$$

which is independent of  $x_0$  and  $x^0$  but dependant only on  $\lambda$ . Thus when  $\lambda$  increases from 0 to 1, a point moves from any point  $x_0$  on  $X_0$  (for  $\lambda = 0$ ) to any point  $x^0$  on  $X^0$  (for  $\lambda = 1$ ) and the value of each of the objective functions  $z_1, z_2, \dots, z_p$  increases from its lowest justifiable value to its highest value simultaneously. Hence, the optimal compromise solution of the MOLPP must be a point of the form  $(1-\lambda)x_0 + \lambda x^0$  in the feasible region  $X = \{x \mid Ax \leq b, x \geq 0\}$  for maximum possible value of  $\lambda$  in  $[0, 1]$ .

For any point  $(1-\lambda)x_0 + \lambda x^0, 0 \leq \lambda \leq 1, x_0 \in X_0, x^0 \in X^0$ , we have

$$\begin{aligned} c_r \{ (1-\lambda)x_0 + \lambda x^0 \} &= (1-\lambda) c_r x_0 + \lambda c_r x^0 \\ &= (1-\lambda) m_r + \lambda M_r \end{aligned}$$

or

$$\frac{c_r \{ (1-\lambda)x_0 + \lambda x^0 \} - m_r}{M_r - m_r} = \lambda \quad (2.1)$$

This is true for each  $r = 1, 2, \dots, p$ .

Thus the solution set of the system

$$\frac{c_r x - m_r}{M_r - m_r} = \lambda, \quad r = 1, 2, \dots, p, \text{ i.e. of the system}$$

$$\frac{c_r x - m_r}{M_r - m_r} = \frac{c_{r+1} x - m_{r+1}}{M_{r+1} - m_{r+1}}, \quad r = 1, 2, \dots, p-1, \quad (2.2)$$

always contains the points  $(1-\lambda)x_0 + \lambda x^0$ .

Hence, the additional criteria to be introduced to distinguish the optimal compromise solution are the  $(p-1)$  hyperplanes (2.2). Further, as  $\lambda$  increases from 0 to 1, all the  $p$  objective functions increases simultaneously. Thus, it follows that maximization of any one of the  $p$  objective functions will lead to the optimal compromise solution.

## ALGORITHM

The MOLPP is

$$\begin{aligned} & \text{Max } \{ c_1 x, c_2 x, \dots, c_p x \} \\ & \text{subject to } Ax \leq = \geq b, x \geq 0 \text{ (} p \leq n \text{)}. \end{aligned}$$

The major steps of the solution procedure are as follows :

Step 1. Solve the LPP

$$\begin{aligned} & \text{Max } z_k = c_k x \\ & \text{subject to } Ax \leq = \geq b, x \geq 0 \\ & \text{for each } k = 1, 2, \dots, p \end{aligned}$$

using simplex method. Let the optimal solution be  $x^k$  and  $M_k = c_k x^k$ .

Step 2.

$$\text{Find } m_k = \min \{ c_k x^1, c_k x^2, \dots, c_k x^{k-1}, c_k x^{k+1}, \dots, c_k x^p \}.$$

Step 3. Form the  $p-1$  constraints

$$(c_r x - m_r) (M_{r+1} - m_{r+1}) - (c_{r+1} x - m_{r+1}) (M_r - m_r) = 0 \text{ for } r = 1, 2, \dots, p-1.$$

Step 4. Maximise any one of the  $p$  objective functions

$$\begin{aligned} & z_1 = c_1 x, z_2 = c_2 x, \dots, z_p = c_p x \\ & \text{subject to } Ax \leq = \geq b, \end{aligned}$$

$$\frac{c_r x - m_r}{M_r - m_r} = \frac{c_{r+1} x - m_{r+1}}{M_{r+1} - m_{r+1}}, \quad r = 1, 2, \dots, p-1,$$

and  $x \geq 0$ .

Step 5. The solution of the LPP in Step 4 is the optimal compromise solution of the MOLPP.

### 3. DEDUCTION OF THE EQUIVALENT LPP IN FUZZY APPROACH

We have noted that the optimal compromise solution of the MOLPP is a point of the form  $(1-\lambda)x_0 + \lambda x^0$  in the feasible region  $X$  for maximum possible  $\lambda$  in  $[0,1]$ . Also from (2.1) it follows that the points  $(1-\lambda)x_0 + \lambda x^0$ ,  $0 \leq \lambda \leq 1$ ,  $x_0 \in X_0$ ,  $x^0 \in X^0$ , satisfy

$$\frac{c_1 x - m_1}{M_1 - m_1} = \frac{c_2 x - m_2}{M_2 - m_2} = \dots = \frac{c_p x - m_p}{M_p - m_p} = \lambda.$$

Hence the optimal compromise solution is the optimal solution of the LPP

$$\begin{aligned} & \text{Max } \lambda \\ & \text{subject to } \frac{c_r x - m_r}{M_r - m_r} = \lambda, \quad r = 1, 2, \dots, p \end{aligned} \quad (3.1)$$

$$Ax \leq = \geq b$$

$$\text{and } x \geq 0.$$

Since  $p \leq n$  and  $z_r = c_r x$ ,  $r = 1, 2, \dots, p$ , are non-parallel objectives, the system  $(c_r x - m_r)/(M_r - m_r) = \lambda$ ,  $r = 1, 2, \dots, p$ , always has solution lying at the boundary points of the convex region

$$\lambda \leq \frac{c_r x - m_r}{M_r - m_r}, \quad r=1,2,\dots, p.$$

Hence the LPP

$$\begin{aligned} & \text{Max } \lambda \\ & \text{subject to } \lambda \leq \frac{c_r x - m_r}{M_r - m_r}, \quad r=1, 2, \dots, p \\ & \quad \quad \quad Ax \leq = \geq b, \\ & \quad \quad \quad \text{and } x \geq 0 \end{aligned} \tag{3.2}$$

has the same optimal solution as (3.1) and so leads to the optimal compromise solution of MOLPP. It is very important to note that the LPP (3.2) always contains one variable and one constraint more than the LPP obtained in theorem (2.1)

#### 4. EXAMPLES

Two numerical examples are given one due to Zimmermann containing two objective functions with two decision variables and the other containing three objective functions with three variables.

Example 4.1

This example is due to Zimmermann [8]

$$\begin{aligned} & \text{Max } z_1 = -x_1 + 2x_2 \\ & \quad \quad z_2 = 2x_1 + x_2 \\ & \text{subject to } -x_1 + 3x_2 \leq 21 \\ & \quad \quad x_1 + 3x_2 \leq 27 \\ & \quad \quad 4x_1 + 3x_2 \leq 45 \\ & \quad \quad 3x_1 + x_2 \leq 30 \\ & \quad \quad \text{and } x_1, x_2 \geq 0. \end{aligned}$$

Here  $M_1 = 14$ ,  $M_2 = 21$ ,  $m_1 = -3$ ,  $m_2 = 7$ .

The LPP obtained using fuzzy concept is

$$\text{Max } z = x_3$$

$$\begin{aligned}
\text{subject to } & 2x_1 + x_2 - 14x_3 \geq 7 \\
& x_1 - 2x_2 + 17x_3 \leq 3 \\
& -x_1 + 3x_2 \leq 21 \\
& x_1 + 3x_2 \leq 27 \\
& 4x_1 + 3x_2 \leq 45 \\
& 3x_1 + x_2 \leq 30 \\
\text{and } & x_1, x_2, x_3 \geq 0.
\end{aligned}$$

The optimal solution  $x_1 = 5.0323$ ,  $x_2 = 7.3226$ ,  $x_3 = 0.7419$  is obtained in the fourth iteration by simplex method.

Using the method presented here the equivalent LPP is

$$\begin{aligned}
\text{Max } & z = 2x_1 + x_2 \\
\text{subject to } & -x_1 + 3x_2 \leq 21 \\
& x_1 + 3x_2 \leq 27 \\
& 4x_1 + 3x_2 \leq 45 \\
& 3x_1 + x_2 \leq 30 \\
& 48x_1 - 11x_2 = 161 \\
\text{and } & x_1, x_2 \geq 0.
\end{aligned}$$

This LPP has one less constraint and one less variable and needs only three iterations to get the same solution by simplex method.

Example 4.2

$$\begin{aligned}
\text{Max } & z_1 = x_1 + 3x_2 + 2x_3 \\
& z_2 = 2x_1 - x_2 + x_3 \\
& z_3 = 6x_1 + x_2 - 2x_3 \\
\text{subject to } & x_1 + 2x_2 \leq 10 \\
& 2x_1 + x_3 \leq 8 \\
& 2x_2 + x_3 \leq 6 \\
\text{and } & x_1, x_2, x_3 \geq 0.
\end{aligned}$$

Here  $M_1 = 13$ ,  $M_2 = 8$ ,  $M_3 = 27$ ,  $m_1 = 4$ ,  $m_2 = 5$  and  $m_3 = -6$ .

The LPP obtained using fuzzy concept is

$$\begin{array}{ll}
\text{Max} & z = x_4 \\
\text{subject to} & x_1 + 3x_2 + 2x_3 - 9x_4 \geq 4 \\
& 2x_1 - x_2 + x_3 - 3x_4 \geq 5 \\
& -6x_1 - x_2 + 2x_3 + 33x_4 \leq 6 \\
& x_1 + 2x_2 \leq 10 \\
& 2x_1 + x_3 \leq 8 \\
& 2x_2 + x_3 \leq 6 \\
\text{and} & x_1, x_2, x_3, x_4 \geq 0.
\end{array}$$

and the LPP obtained using present concept is

$$\begin{array}{ll}
\text{Max} & z = x_1 + 3x_2 + 2x_3 \\
\text{subject to} & 5x_1 - 6x_2 + x_3 = 11 \\
& 16x_1 - 12x_2 + 13x_3 = 61 \\
& x_1 + 2x_2 \leq 10 \\
& 2x_1 + x_3 \leq 8 \\
& 2x_2 + x_3 \leq 6 \\
\text{and} & x_1, x_2, x_3 \geq 0.
\end{array}$$

The number of variables and constraints in the second LPP are one less in comparison to the first LPP. The second LPP needs four iterations whereas the first LPP needs five iterations to obtain the same optimal solution  $x_1 = 3.0625$ ,  $x_2 = 1.0313$ .

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# A new Modification of spherical harmonic method in solving transport problems

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## Abstract :

A new modification of the form of intensity in the double interval spherical harmonic method has been introduced. The equation of radiative transfer in isotropically scattering atmosphere has been solved with this modified spherical harmonic method.

## 1. Introduction

Kourganoff (1952) analyzed the method of single interval spherical harmonics for solving the equation of transfer and suggested a possible modification. Wilson and Sen (1963, 1964, 1964a, 1964b, 1965a, 1965b, 1965c) solved several radiative transfer problems in plane and spherical geometry and also a neutron transport problem using some approximations to the intensity with the spherical harmonic method.

Bishnu (1968) solved the equation of transfer for plane parallel isotropic scattering using a different approximate form of the intensity.

Karanjai and Talukdar (1992) solved the equation of transfer with general phase function using the form of intensity given by Bishnu (1964) and deduced the results with phase functions like (i) Planetary, (ii) Rayleigh, (iii) Henyey Greenstein from the general solution.

Wan et al (1977, 1986) used another form of intensity function to get the solution of the equation of transfer.

Karanjai and Biswas (1992, 1993) applied the same method with the form of intensity given by Wan et al (1986) to solve transfer equation with Rayleigh phase function and with

$$p(\mu, \mu') = 1 + \omega_1 P_1(\mu) P_1(\mu') + \omega_2 P_2(\mu) P_2(\mu').$$

Here in this paper we like to introduce a new form of the intensity viz,

$$I^+(\tau, \mu) = I(0, 0) \left[ \phi(\tau) + \psi(\mu) + \sum_{l=0}^{l_0} (2l+1) I_l(\mu) P_l(2\mu-1) \right] \quad 0 \leq \mu \leq 1 \quad (1.1)$$

$$I^-(\tau, \mu) = I(0, 0) \left[ \phi(\tau) + \psi(\mu) + \sum_{l=0}^{l_0} (2l+1) I_l(\mu) P_l(2\mu+1) \right] \quad -1 \leq \mu < 0 \quad (1.2)$$

where  $\phi(\tau)$  a function of  $\tau$  only and  $\psi(\mu)$  is given by,

$$\psi(\mu) = 1 \text{ if } 0 \leq \mu \leq 1 \quad (1.3a)$$

$$\psi(\mu) = 0 \text{ if } -1 \leq \mu < 0 \quad (1.3a)$$

## 2. The Equation of Transfer and boundary conditions

The equation of transfer for plane parallel isotropically scattering atmosphere is given by

$$\frac{\partial}{\partial \tau} I(\tau, \mu) = I(\tau, \mu) - \frac{1}{2} \int_{-1}^{+1} I(\tau, \mu') d\mu' \quad (2.1)$$

Where  $I(\tau, \mu)$  is the specific intensity of radiation at an optical depth  $\tau$  and in a direction  $\theta$  with the outward drawn normal and  $\mu = \cos(\theta)$ . The optical thickness is given by

$$\tau = \int_0^z k \rho dz \quad (2.2)$$

where  $k$  is the absorption coefficient.

The Equation of Transfer (2.1) is to be solved subject to the boundary conditions,

(a) Absence of incident radiation from outside at the free surface  $\tau = 0$ , i.e.,

$$I(\tau, \mu) \equiv 0 \text{ for } -1 \leq \mu \leq 0 \quad (2.3)$$

(b) The convergence of intensity as  $\tau$  tends to  $\alpha$  i.e.,

$$I(\tau, \mu) e^{-\tau} \rightarrow 0 \text{ as } \tau \rightarrow \alpha \quad (2.4)$$

We shall seek a solution to equation (2.1) so that  $I(\tau, \mu)$  can be represented by two different expressions  $I^+(\tau, \mu)$  and  $I^-(\tau, \mu)$  for  $\mu$  in the intervals  $(0, 1)$  and  $(-1, 0)$  respectively in the form given by equations (1.1) – (1.3).

With these two representations the equation of transfer (2.1) takes the following forms,

$$\frac{\mu \partial I^+(\tau, \mu)}{\partial \tau} = I^+(\tau, \mu) - \frac{1}{2} \left[ \int_0^{+1} I^+(\tau, \mu) d\mu + \int_{-1}^0 I^-(\tau, \mu) d\mu \right] \quad (2.5)$$

$$\frac{\mu \partial I^-(\tau, \mu)}{\partial \tau} = I^-(\tau, \mu) - \frac{1}{2} \left[ \int_0^{+1} I^+(\tau, \mu) d\mu + \int_{-1}^0 I^-(\tau, \mu) d\mu \right] \quad (2.6)$$

We shall use the recurrence formulae,

$$\mu P_1(2\mu \pm 1) = \frac{1}{2(2l+1)} \left[ (l+1) P_{2\mu \pm 1} + (2l+1) P_{2\mu \pm 1} + l P_{2\mu \pm 1} \right] \quad (2.7)$$

We shall take advantage of orthogonal properties of  $P_l(2\mu-1)$  and  $P_l(2\mu+1)$  in  $(0, 1)$  and  $(-1, 0)$  respectively.

Using these we find that

$$\int_0^{+1} I^+(\tau, \mu) d\mu = I(0, 0) \left[ \phi(\tau) + 1 + \frac{1}{2}(I_0^+ + I_1^+) \right] \quad (2.8a)$$

and

$$\int_{-1}^0 I^-(\tau, \mu) d\mu = I(0, 0) \left[ \phi(\tau) + \frac{1}{2}(-I_0^- + I_1^-) \right] \quad (2.8b)$$

using (2.8a) and (2.8b) in the equation of transfer (2.5) we find that,

$$\frac{\mu \partial I^+(\tau, \mu)}{\partial \tau} = I^+(\tau, \mu) - \frac{1}{2} I(0, 0) \left[ 2\phi(\tau) + 1 + \frac{1}{2}(I_0^+ - I_0^- + I_1^+ + I_1^-) \right] \quad (2.9)$$



Similarly using (2.8a) and (2.8b) in the equation of transfer (2.6) we find that

$$\frac{\mu \partial I^{\pm}}{\partial \tau}(\tau, \mu) = I^{\pm}(\tau, \mu) - \frac{1}{2} I(0,0) \left[ 2\phi(\tau) + 1 + \frac{1}{2}(I_0^+ - I_0^- + I_1^+ + I_1^-) \right] \quad (2.10)$$

Using (1.1) in (2.9) and then multiplying by  $P_l(2\mu-1)$ , we find after integrating over  $[0,1]$ ,

$$\begin{aligned} \phi'(\tau) \int_0^1 \mu P_l(2\mu-1) d\mu + \frac{1}{4(2l+1)} \left[ \frac{l^2-1}{2l-1} \frac{l+1}{l-2} \frac{l+1}{l-1} \frac{12l^3+18l^2-2l-4}{(2l+3)(2l-1)} \right. \\ \left. + 2(l+1) \frac{l+1}{l+1} \frac{l^2+3l+2}{2l+3} \frac{l+1}{l+2} \right] = \int_0^1 \psi(\mu) P_l(2\mu-1) d\mu + \frac{1}{2(2l+1)} \left[ \frac{l+1}{l-1} \right. \\ \left. + (2l+1) I_1^+ + (l+1) I_{l+1}^+ - \frac{1}{2} \delta_{0l} - \frac{1}{4} \delta_{0l} \right] [I_0^+ - I_0^- + I_1^+ + I_1^-] \end{aligned} \quad (2.11)$$

Similarly using (1.2) in (2.10) and then multiplying (2.10) by  $P_l(2\mu+1)$  and integrating over  $[-1,0]$  we find that,

$$\begin{aligned} \phi'(\tau) \int_{-1}^0 \mu P_l(2\mu+1) d\mu + \frac{1}{4(2l+1)} \left[ \frac{l^2-1}{2l-1} \frac{l-1}{l-2} \frac{l-1}{l-1} \frac{12l^3+18l^2-2l-4}{(2l+3)(2l-1)} \right. \\ \left. - 2(l+1) \frac{l-1}{l+1} \frac{l^2+3l+2}{2l+3} \frac{l-1}{l+2} \right] = \int_{-1}^0 \psi(\mu) P_l(2\mu+1) d\mu + \frac{1}{2(2l+1)} \left[ \frac{l-1}{l-1} \right. \\ \left. + (2l+1) I_1^- + (l+1) I_{l+1}^- \right] - \frac{1}{2} \delta_{0l} - \frac{1}{4} \delta_{0l} [I_0^+ - I_0^- + I_1^+ + I_1^-] \end{aligned} \quad (2.12)$$

where  $I_l^{\pm}$  are derivatives of  $I_l$  with respect to the optical thickness  $\tau$ .

Separating the equations for  $l=0$  and  $l=1$  from rest of the equations in (2.11) we have

$l=0$ :

$$\frac{1}{2} \phi'(\tau) + \frac{1}{4} \left[ \frac{4}{3} I_0^+ + 2 I_1^+ + \frac{2}{3} I_2^+ \right] = \frac{1}{2} + \frac{1}{2} (I_0^+ + I_1^+) - \frac{1}{4} (I_0^+ - I_0^- + I_0^+ + I_1^-) \quad (2.13)$$

$l=1$ :

$$(2 I_0^+ + \frac{24}{5} I_1^+ + 4 I_2^+ + \frac{6}{5} I_3^+) - 2 [ I_0^+ + 3 I_1^+ + 2 I_2^+ ] = -2 \phi'(\tau) \quad (2.14)$$

$l \neq 0, 1$ :

$$\begin{aligned} \phi'(\tau) \int_0^1 \mu P_l(2\mu-1) d\mu + \frac{1}{4(2l+1)} \left[ \frac{l^2-1}{2l-1} \frac{l+1}{l-2} \frac{l+1}{l-1} \frac{12l^3+18l^2-2l-4}{(2l+3)(2l-1)} \right. \\ \left. + 2(l+1) \frac{l+1}{l+1} \frac{l^2+3l+2}{2l+3} \frac{l+1}{l+2} \right] = \int_0^1 \psi(\mu) P_l(2\mu-1) d\mu + \frac{1}{2(2l+1)} \left[ \frac{l+1}{l-1} \right. \\ \left. + (2l+1) I_1^+ + (l+1) I_{l+1}^+ \right] \end{aligned} \quad (2.15)$$

Similarly separating the equations for  $l=0$  and  $l=1$  from rest of the Equations in (2.12) we have,

$l=0$ :

$$-\frac{1}{2}\phi'(\tau) + \frac{1}{4} \left[ \frac{4}{3}I_0^- - 2I_1^- + \frac{2}{3}I_2^- \right] = -\frac{1}{2} - \frac{1}{2}(-I_0^- + I_1^-) - \frac{1}{4}(I_0^+ - I_0^- + I_1^+ + I_1^-) \quad (2.16)$$

$l=1$ :

$$(-2I_0^- + \frac{24}{5}I_1^- - 4I_2^- + \frac{6}{5}I_3^-) - 2[I_0^- - 3I_1^- + 2I_2^-] = -2\phi'(\tau) \quad (2.17)$$

$l \neq 0, 1$ :

$$\begin{aligned} \phi'(\tau) \int_{-1}^0 \mu P_l(2\mu+1) d\mu + \frac{1}{4(2l+1)} \left[ \frac{l^2-1}{2l-1} \frac{-}{l-2} + 2l \frac{-}{l-1} + \frac{12l^3+18l^2-2l-4}{(2l+3)(2l-1)} \frac{-}{l} \right. \\ \left. - 2(l+1) \frac{-}{l+1} + \frac{l^2+3l+2}{2l+3} \frac{-}{l+2} \right] = \int_{-1}^0 \psi(\mu) P_l(2\mu+1) d\mu + \frac{1}{2(2l+1)} \left[ \frac{-}{l-1} \right. \\ \left. (2l+1) I_l^- + (l+1) I_{l+1}^- \right] \end{aligned} \quad (2.18)$$

Using the condition given in (1.3) we find that equations (2.15) and 2.18) reduce for  $l \neq 0, 1$ :

$$\begin{aligned} \phi'(\tau) \int_0^1 \mu P_l(2\mu-1) d\mu + \frac{1}{4(2l+1)} \left[ \frac{l^2-1}{2l-1} \frac{+}{l-2} + 2l \frac{+}{l-1} + \frac{12l^3+18l^2-2l-4}{(2l+3)(2l-1)} \frac{+}{l} \right. \\ \left. + 2(l+1) \frac{+}{l+1} + \frac{l^2+3l+2}{2l+3} \frac{+}{l+2} \right] = \int_0^1 \psi(\mu) P_l(2\mu-1) d\mu + \frac{1}{2(2l+1)} \left[ \frac{+}{l-1} \right. \\ \left. + (2l+1) I_l^+ + (l+1) I_{l+1}^+ \right] \end{aligned} \quad (2.19)$$

and

$$\begin{aligned} \phi'(\tau) \int_{-1}^0 \mu P_l(2\mu+1) d\mu + \frac{1}{4(2l+1)} \left[ \frac{l^2-1}{2l-1} \frac{-}{l-2} - 2l \frac{-}{l-1} + \frac{12l^3+18l^2-2l-4}{(2l+3)(2l-1)} \frac{-}{l} \right. \\ \left. - 2(l+1) \frac{-}{l+1} + \frac{l^2+3l+2}{2l+3} \frac{-}{l+2} \right] = \frac{1}{2(2l+1)} \left[ \frac{-}{l-1} - (2l+1) \frac{-}{l} + (l+1) \frac{-}{l} \right] \end{aligned} \quad (2.20)$$

We take the form of  $\phi(\tau)$  as

$\phi(\tau) = Ae^{-\tau} + Be^{\tau}$  where  $\tau$  is small and A and B are constants. Equations (2.13), (2.14), (2.16), (2.17) are to be solved subject to the boundary conditions (2.3) and (2.4).

It is assumed that when we are working in the  $l^{\text{th}}$  approximation,

$$I_{l+1}^+ = I_{l+1}^- = 0 \quad (2.21)$$

### 3. First Approximation

We try a solution of the form

$$I_1^+(\tau) = g_{1,\alpha} e^{-k\tau} + g_{1,\beta} e^{-\tau} + g_{1,\gamma} e^{\tau} \quad (3.1a)$$

$$I_1^-(\tau) = h_{1,\alpha} e^{-k\tau} + h_{1,\beta} e^{-\tau} + h_{1,\gamma} e^{\tau} \quad (3.1b)$$

For first approximation solution we have  $I_0 = 1$

Hence (1.1) and (1.2) give us

$$I^+(\tau, \mu) = I(0,0) [\phi(\tau) + \psi(\mu) + I_0^+(\tau)\mu + 3I_1^+(\tau)\mu P_1(2\mu-1)] \quad 0 \leq \mu \leq 1 \quad (3.2a)$$

$$I^-(\tau, \mu) = I(0,0) [\phi(\tau) + \psi(\mu) + I_0^-(\tau)\mu + 3I_1^-(\tau)\mu P_1(2\mu+1)] \quad -1 \leq \mu \leq 0 \quad (3.2b)$$

Taking  $I_2^+ = 0$  we get from (2.13)

$$\left(\frac{4}{3}I_0^+ + 2I_1^+\right) - (I_0^+ + I_0^- + I_1^+ - I_1^-) = 2 [1 - \phi'(\tau)] \quad (3.3)$$

Similarly from (2.16) we get

$$\left(\frac{4}{3}I_0^- - 2I_1^-\right) - (I_0^+ + I_0^- + I_1^+ - I_1^-) = 2 [\phi'(\tau) - 1] \quad (3.4)$$

Likewise (2.14) and (2.17) give us

$$(2I_0^+ + \frac{24}{5}I_1^+) - 2(I_0^+ + 3I_1^+) = -2\phi'(\tau) \quad (3.5)$$

$$(-2I_0^- + \frac{24}{5}I_1^-) - 2(I_0^- + 3I_1^-) = -2\phi'(\tau) \quad (3.6)$$

Substituting (3.1a) and (3.1b) in (3.3), (3.4), (3.5) and (3.6) and then equating the coefficients of  $e^{-k\tau}$  on each side we obtain the following equations,

$$\left. \begin{aligned} (1 + \frac{4K}{3})g_{0,\alpha} + (1 + 2K)g_{1,\alpha} + h_{0,\alpha} - h_{1,\alpha} &= 0 \\ (2 + 2K)g_{0,\alpha} + 6(1 + \frac{4K}{5})g_{1,\alpha} &= 0 \\ g_{0,\alpha} + g_{1,\alpha} + (1 - \frac{4K}{3})h_{0,\alpha} - (1 - 2K)h_{1,\alpha} &= 0 \\ -(2 - 2K)h_{0,\alpha} + 6(1 - \frac{4K}{5})h_{1,\alpha} &= 0 \end{aligned} \right\} \quad (3.7)$$

The determinant corresponding to (3.7) will be

$$D_1(K) = \begin{vmatrix} 1 + \frac{4K}{3} & 1+2K & 1 & -1 \\ 2+2K & 6(1 + \frac{4K}{5}) & 0 & 0 \\ 1 & 1 & 1 - \frac{4K}{3} & -1+2K \\ 0 & 0 & 2-2K & 6(1 - \frac{4K}{5}) \end{vmatrix}$$

where  $D_1(K) = 0$  gives us

$$(16K^2/225)(81K^2 - 270) = 0$$

$$\therefore K=0, 0, \pm 1.8257$$

Retaining the positive root we have  $K=1.8257$ .

We have a set of boundary conditions,

$$I_0^+(0) = I_0^+(1) = 0, I_0^-(\tau_0) = I_1^-(\tau_0) = 1 \quad (3.8)$$

Using the first equation in (3.7) on  $\phi(\tau) = Ae^{-\tau} + Be^\tau$  we obtain  $A=5.5166547, B=4.5166547$

Again equating the coefficients of  $e^\tau$  and  $e^{-\tau}$  on each side we obtain,

$$\frac{7}{3}g_{0,\beta} + 3g_{1,\beta} + h_{0,\beta} - h_{1,\beta} = -2A \quad (3.9a)$$

$$\frac{7}{3}g_{0,\gamma} + 3g_{1,\gamma} + h_{0,\gamma} - h_{1,\gamma} = -2B \quad (3.9b)$$

$$2g_{0,\beta} + \frac{27}{5}g_{1,\beta} = -A \quad (3.9c)$$

$$\frac{3}{5}g_{1,\gamma} = B \quad (3.9d)$$

$$g_{0,\beta} + g_{1,\beta} - \frac{1}{3}h_{0,\beta} + h_{1,\beta} = -2A \quad (3.9e)$$

$$g_{0,\gamma} + g_{1,\gamma} + \frac{7}{3}h_{0,\gamma} - h_{1,\gamma} = 2B \quad (3.9f)$$

$$\frac{4}{5}h_{1,\beta} = 2B \quad (3.9g)$$

$$-2h_{0,\gamma} + \frac{27}{5}h_{1,\gamma} = -B \quad (3.9h)$$

On solving the set of equations in (3.9) we obtain

$$\begin{aligned} g_{0,\beta} &= 21.1952 & h_{0,\beta} &= -46.6974 \\ g_{1,\beta} &= -8.8717 & h_{1,\beta} &= 13.7915 \\ g_{0,\gamma} &= 18.6307 & h_{0,\gamma} &= 48.0470 \\ g_{1,\gamma} &= -7.5276 & h_{1,\gamma} &= -5.6467 \end{aligned}$$

Now solving the set of equations in (3.7) and using the values of  $g_{1,\alpha}$ 's and  $h_{1,\alpha}$ 's obtained from (3.9) and using the boundary conditions (3.8) we find that,

$$\begin{aligned} g_{0,\alpha} &= -39.9259 & h_{0,\alpha} &= -13.0211 \\ g_{1,\alpha} &= 16.3993 & h_{1,\alpha} &= -7.4875 \end{aligned}$$

Finally from (3.1a) and (3.1b) we have

$$I_0^+ = 6.508, I_1^+ = -2.6912, I_0^- = 1.94549610^{-3}, I_1^- = -2.050410^{-5}$$

#### 4. Second Approximation

In this case we will take  $l_0 = 2$  and as before we will consider (2.11) and (2.12). We shall take  $\phi(\tau) = -Ae^{-\tau} + Be^\tau$ ,  $\tau$  is small. For  $l_0=2$ , the equations (1.1) and (1.2) respectively become

$$\begin{aligned} I^+(\tau, \mu) &= I(0,0) [\phi(\tau) + \psi(\mu) + I_0^+(\tau)\mu + 3I_1^+(\tau)\mu P_1(2\mu - 1) \\ &\quad + 5I_2^+(\tau)\mu P_2(2\mu - 1)] \quad 0 \leq \mu \leq 1 \end{aligned} \quad (4.1a)$$

$$\begin{aligned} I^-(\tau, \mu) &= I(0,0) [\phi(\tau) + \psi(\mu) + I_0^-(\tau)\mu + 3I_1^-(\tau)\mu P_1(2\mu + 1) \\ &\quad + 5I_2^-(\tau)\mu P_2(2\mu + 1)] \quad -0 \leq \mu \leq 0 \end{aligned} \quad (4.1b)$$

Therefore when  $l=0$  we have from (2.11)

$l=0$  :

$$\left(\frac{4}{3}l_0^+ + 2l_1^+ + \frac{2}{3}l_2^+\right) - [l_0^+ + l_0^- + l_1^+ - l_1^-] = 2 - 2\phi'(\mu) \quad (4.2)$$

and from (2.12)

$l=0$  :

$$\left(\frac{4}{3}l_0^- - 2l_1^- + \frac{2}{3}l_2^-\right) + [l_0^+ + l_0^- + l_1^+ - l_1^-] = -2 - 2\phi'(\tau) \quad (4.3)$$

For  $l=1$  Equation (2.11) gives

$l=1$  :

$$(2l_0^+ + \frac{24}{5}l_1^+ + 4l_2^+) - 2[l_0^+ + 3l_1^+ + 2l_2^+] = -2\phi'(\tau) \quad (4.4)$$

and from (2.14)

$l=1$  :

$$(-2l_0^- + \frac{24}{5}l_1^- + 4l_2^-) - 2[l_0^- + 3l_1^- + 2l_2^-] = -2\phi'(\tau) \quad (4.5)$$

Finally for  $l=2$  from (2.11) and (2.12)

$l=2$  :

$$\left(\frac{1}{3}l_0^+ + 2l_1^+ + \frac{80}{21}l_2^+\right) - [2l_1^+ + 5l_2^+] = -5\phi'(\tau) \quad (4.6)$$

and from (2.12)

$l=2$  :

$$\left(\frac{1}{3}l_0^- - 2l_1^- + \frac{80}{21}l_2^-\right) - [2l_1^- - 5l_2^-] = -5\phi'(\tau) \quad (4.7)$$

We will take a trial solution of the form

$$l_1^+(\tau) = g_{1,\alpha} e^{-k\tau} + g_{1,\beta} e^{-\tau} + g_{1,\gamma} e^{\tau} \quad (4.8a)$$

$$l_1^-(\tau) = h_{1,\alpha} e^{-k\tau} + h_{1,\beta} e^{-\tau} + h_{1,\gamma} e^{\tau} \quad (4.8b)$$

If we insert (4.8a) and (4.8b) in (4.2) to (4.7) and then compare the coefficients of  $e^{-k\tau}$  on each side we get.

$$\frac{4K}{3}g_{0,\alpha} + (2K + 1)g_{1,\alpha} + \frac{2K}{3}g_{2,\alpha} + h_{0,\alpha} - h_{1,\alpha} = 0 \quad (4.9a)$$

$$(2 + 2K)g_{0,\alpha} + 6\left(1 + \frac{4K}{5}\right)g_{1,\alpha} + (4 + 4K)g_{2,\alpha} = 0 \quad (4.9b)$$

$$\frac{K}{3}g_{0,\alpha} + (2K + 2)g_{1,\alpha} + 5\left(1 + \frac{16K}{21}\right)g_{2,\alpha} = 0 \quad (4.9c)$$

$$g_{0,\alpha} + g_{0,\alpha} + \left(1 - \frac{4K}{3}\right)h_{0,\alpha} + (2K - 1)h_{1,\alpha} - \frac{2K}{3}h_{2,\alpha} = 0 \quad (4.9d)$$

$$(2K - 2)h_{0,\alpha} + 6\left(1 - \frac{4K}{5}\right)h_{1,\alpha} + (4K - 4)h_{2,\alpha} = 0 \quad (4.9e)$$

$$\frac{K}{3}h_{0,\alpha} + (2K - 2)h_{1,\alpha} + 5\left(1 - \frac{16K}{5}\right)g_{2,\alpha} = 0 \quad (4.9f)$$

Similarly inserting (4.8a) and (4.8b) in (4.2) to (4.7) and then equating the coefficients of  $e^{-\zeta}$  and  $e^{\zeta}$  on each side we get respectively,

$$\frac{7}{3}g_{0,\beta} + 3g_{1,\beta} + \frac{2}{3}g_{2,\beta} + h_{0,\beta} - h_{1,\beta} = -2A \quad (4.10a)$$

$$4g_{0,\beta} + \frac{54}{5}g_{1,\beta} + 8g_{2,\beta} = -2A \quad (4.10b)$$

$$\frac{1}{3}g_{0,\beta} + 4g_{1,\beta} + \frac{185}{21}g_{2,\beta} = -5A \quad (4.10c)$$

$$g_{0,\beta} + g_{1,\beta} - \frac{1}{3}h_{0,\beta} + h_{1,\beta} - \frac{2}{3}h_{2,\beta} = 2A \quad (4.10d)$$

$$\frac{6}{5}h_{1,\beta} = 2A \quad (4.10e)$$

$$\frac{1}{3}h_{0,\beta} + \frac{25}{21}h_{2,\beta} = -5A \quad (4.10f)$$

and

$$\frac{1}{3}g_{0,\gamma} + g_{1,\gamma} + \frac{2}{3}g_{2,\gamma} + h_{0,\gamma} - h_{1,\gamma} = -2B \quad (4.11a)$$

$$\frac{6}{5}g_{1,\gamma} = -2B \quad (4.10b)$$

$$\frac{1}{3}g_{0,\gamma} - \frac{25}{21}g_{2,\gamma} = -5B \quad (4.11c)$$

$$g_{0,\gamma} + g_{1,\gamma} + \frac{7}{3}h_{0,\gamma} - 3h_{1,\gamma} + \frac{2}{3}h_{2,\gamma} = -2B \quad (4.11d)$$

$$-4h_{0,\gamma} - \frac{54}{45}h_{2,\gamma} - 8h_{2,\gamma} = -2B \quad (4.11e)$$

$$\frac{1}{3}h_{0,\gamma} - 4h_{1,\gamma} + \frac{185}{21}h_{2,\gamma} = 5B \quad (4.11f)$$

The determinant corresponding to (4.9) is

$$D_2(K) = \begin{vmatrix} \frac{4k}{3} & 2K+1 & \frac{2k}{3} & 1 & -1 & 0 \\ 2+2K & 6(1+\frac{4k}{5}) & 4+4K & 0 & 0 & 0 \\ \frac{k}{3} & 2+2K & 5(1+\frac{16k}{3}) & 0 & 0 & 0 \\ 1 & 1 & 0 & 1-\frac{4k}{3} & 2K-1 & \frac{2k}{3} \\ 0 & 0 & 0 & 2K-2 & 6(1-\frac{4k}{5}) & 4K-4 \\ 0 & 0 & 0 & -\frac{k}{3} & 2K-2 & 5(1-\frac{16k}{5}) \end{vmatrix}$$

when  $D_2(K) = 0$ , we have

$$8K^2 [.9404K^4 - 14.1061K^2 + 24] = 0 \text{ so that}$$

$$K = 0, 0, \pm 3.6116, \pm 1.3988$$

Let us take  $K_1 = 3.6116$ ,  $K_2 = 1.3988$  (4.12)

The boundary conditions may be restated as

$$I_1^-(\tau) \equiv 0 \quad (4.13a)$$

$$I_1^+(\tau) e^{-\tau} \rightarrow 0 \text{ as } \tau \rightarrow \alpha \text{ and } I_1^-(\tau) e^{-\tau} \rightarrow 0 \text{ as } \tau \rightarrow \alpha \quad (4.13b)$$

Using the (4.19a) and (4.19b) we can write (See Wilson and Sen 1963)

$$\sum_{l=1}^n h_{l,\alpha}^{(l)} + h_{l\beta} = 0 \text{ (for all } l) \quad (4.14)$$

Solving (4.9), (4.10), (4.11), (4.12) and using (4.14) we obtain

$g_{0,\alpha}^{(1)} = -180.8898$	$h_{0,\alpha}^{(1)} = -9.3888$
$g_{1,\alpha}^{(1)} = 101.9557$	$h_{1,\alpha}^{(1)} = -12.2123$
$g_{2,\alpha}^{(1)} = 38.5290$	$h_{2,\alpha}^{(1)} = 13.6550$
$g_{0,\alpha}^{(2)} = -11.5438$	$h_{0,\alpha}^{(2)} = -2.9256$
$g_{1,\alpha}^{(2)} = -6.1007$	$h_{1,\alpha}^{(2)} = 3.0180$
$g_{2,\alpha}^{(2)} = 13.8553$	$h_{2,\alpha}^{(2)} = 6.0737$
$g_{0,\beta} = -18.944322$	$h_{1,\beta} = -12.290109$
$g_{1,\beta} = 11.727565$	$h_{1,\beta} = 9.1943$
$g_{2,\beta} = -7.7392102$	$h_{2,\beta} = -19.728719$
$g_{0,\gamma} = -36.22498$	$h_{0,\gamma} = -155.71057$
$g_{1,\gamma} = -7.5277$	$h_{1,\gamma} = -8.869875$
$g_{2,\gamma} = -29.112963$	$h_{2,\gamma} = -33.825808$

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# ANALYSIS OF FUZZY EOQ MODEL USING FUZZY GOAL PROGRAMING

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## Abstract

A multi-item EOQ model has been formulated in fuzzy environment introducing fuzziness in the objective goal and one of the constraints. This model has been further modified making inventory costs fuzzy. These problems are reduced to fuzzy goal programming problems and solved using fuzzy nonlinear programming method. Models are illustrated with numerical examples and results are compared with those of the crisp model.

## 1. INTRODUCTION :

Multi-item inventory systems are widely studied in the literature of production and inventory control. In general, an organisation operates under resource constraints such as working capital, storage space, number of orders, etc. in multi-item situations. Many researchers have modelled these situations for minimization of total average cost using Lagrange multiplier technique. Naddor (1), Silver and Peterson (2), Love (2), Starr and Miller (4) have presented multi-item inventory models with one of the above mentioned constraints. Ben-Daya and Raouf (5) discussed a multi-item inventory model with stochastic demand under two constraints. Worrall and hall (6) discussed a multi-item inventory model with several constraints by geometric programming. Above mentioned models are formulated in either crisp or probabilistic environment. But, in a real life situation, generally the costs—unit cost, set-up cost and other parameters like total storage area, number of orders, total set-up time, total capital investment, etc. are uncertain, non-commensurable and imprecise in nature. This type of parameters escaped the determinism considered traditionally by conventional mathematics and also escaped the probability and statistical theory because they depend on subjective feeling and tastes. However, the models with above imprecised parameters can be realistically represented only in fuzzy environment.

In a standard goal programming formulation, goals and constraints are defined precisely (Charnes and Cooper (7), Lee (8), Ignigio (9) ). But, in many situations, it is difficult to assign precise aspiration levels to objectives. Also, in some cases, it is not possible to articulate precise boundaries of the constraints. In such situations, a fuzzy goal programming is more appropriate than crisp one.

Since Narasimhan (10) applied fuzzy set theory into goal programming in 1980, many achievements have been recorded in the literature (Hannan (11, 12), Ignigio (13), Rubin and Narasimhan (14) and Tiwari et al. (15) ). Padmanabhan and Prem-Vrat (16) solved several multi-item crisp inventory models by goal programming technique.

In the present paper, some investigations are made in fuzzy goal programming approaches for the multi-item EOQ fuzzy and crisp models. The non-linear goal programming problem is solved by partitioning gradient based algorithm [16]. The model is illustrated numerically and the results in crisp and fuzzy environment are comared with each other.

## 2. MATHEMATICAL MODEL :

A multi-item EOQ crisp model with capital investment and space constraints is :

$$\text{Type -0 : } \quad \text{Min } g_0(Q_i) = \sum_{i=1}^N \left( \frac{C_{3i} D_i}{Q_i} + \frac{OC_{1i} Q_i}{2} \right)$$

subject to :

$$g_1(Q_i) = \frac{1}{2} \sum_{i=1}^N C_{1i} Q_i \leq C, \quad \dots(2.0)$$

$$g_2(Q_i) = \sum_{i=1}^N A_i Q_i \leq A,$$

$$Q_i > 0,$$

where  $i = 1, 2, 3, \dots, N$ .

Now introducing fuzziness in the objective goal and available capital for investment of total average inventory, the model (2.0) reduces to :

$$\text{Type -1 : } \quad \text{Min } \tilde{g}_0(Q_i) = \sum_{i=1}^N \left( \frac{C_{3i} D_i}{Q_i} + \frac{OC_{1i} Q_i}{2} \right)$$

subject to :

$$g_1(Q_i) = \frac{1}{2} \sum_{i=1}^N C_{1i} Q_i \leq \tilde{C}, \quad \dots(2.1)$$

$$g_2(Q_i) = \sum_{i=1}^N A_i Q_i \leq A,$$

$$Q_i > 0,$$

where  $i = 1, 2, \dots, N$ .

Again, if set-up costs  $C_{3i}$  and unit costs  $C_{1i}$  of the above model are fuzzy in nature, we have :

$$\text{Type -2 : } \quad \text{Min } \tilde{g}_0(Q_i) = \sum_{i=1}^N \left( \frac{\tilde{C}_{3i} D_i}{Q_i} + \frac{OC_{1i} Q_i}{2} \right)$$

subject to :

$$g_1(Q_i) = \frac{1}{2} \sum_{i=1}^N \tilde{C}_i Q_i \leq \tilde{C}, \quad \dots(2.2)$$

$$g_2(Q_i) = \sum_{i=1}^N A_i Q_i \leq A,$$

$$Q_i > 0,$$

where  $i = 1, 2, 3, \dots, N$ .

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Here, for the  $i$ th item :

$Q_i$  = Production lot-size,

$D_i$  = Demand rate,

$C_{3i}$  = Set-up cost,

$C_{1i}$  = Unit cost,

$A_i$  = Space area per unit product,

$C$  = Total Capital investment,

$A$  = Total space area,

$O$  = Inventory carrying charge

and wavy bar ( $\sim$ ) represents fuzzification of the parameters.

### 3 (a) GOAL PROGRAMMING :

If the decision maker assign fairly aspiration levels  $p_i$  to the objectives and try to achieve those to the extent possible, then goal programming formulation of (3.1) can be stated as :

Determine  $x \in s$

subject to :

$$g_i(x) \leq p_i,$$

$$f_j(x) \leq b_j,$$

$$f_h(x) \geq b_h,$$

$$x \geq 0.$$

...(3.a.1)

where  $i = 1, 2, 3, \dots, k,$

$j = 1, 2, 3, \dots, m_1$

and  $h = m_1 + 1, m_1 + 2, \dots, m.$

( $s$  being the compact set of feasible region.)



Using achievement function, the above model (3.a.1) is reformulated as :

Determine  $x$

so as to :

$$\text{minimize } (U_1(dg_1^-, dg_1^+), U_2(dg_2^-, dg_2^+), \dots, U_k(dg_k^-, dg_k^+), \\ V_1(df_1^-, df_1^+), V_2(df_2^-, df_2^+), \dots, V_{m_1}(df_{m_1}^-, df_{m_1}^+))$$

$$\text{such that } g_i(x) + dg_i^- - dg_i^+ = p_i,$$

$$f_j(x) + df_j^- - df_j^+ = b_j,$$

$$f_h(x) \geq b_h, \quad \dots(3.a.2)$$

$$dg_i^- dg_i^+ = 0,$$

$$df_j^- df_j^+ = 0,$$

$$dg_i^-, dg_i^+, df_j^-, df_j^+, x \geq 0,$$

$$\text{where } i = 1, 2, 3, \dots, k;$$

$$j = 1, 2, 3, \dots, m_1$$

$$\text{and } h = m_1 + 1, m_1 + 2, \dots, m.$$

( $U_i(dg_i^-, dg_i^+)$ ,  $V_j(df_j^-, df_j^+)$ ) are linear functions of  $dg_i^-$ ,  $dg_i^+$  and  $df_j^-$ ,  $df_j^+$  respectively.)

### 3 (b) FUZZY GOAL PROGRAMMING :

Introducing fuzziness in the objective goals and constraints, the said goal programming (3.a.1) in fuzzy environment is :

Determine  $x \in S$

subject to :

$$g_i(x) \leq \tilde{p}_i,$$

$$f_j(x) \leq \tilde{b}_j, \quad \dots(3.b.1)$$

$$f_h(x) \geq \tilde{b}_h,$$

$$x \geq 0,$$

$$\text{where } i = 1, 2, 3, \dots, k,$$

$$j = 1, 2, 3, \dots, m_1$$

$$\text{and } h = m_1 + 1, m_1 + 2, \dots, m.$$

Some rigid constraints may also exist alongwith the fuzzy constraints in some models and for such a model, we have :

Determine  $x \in S$

subject to :

$$g_i(x) \leq \tilde{p}_i,$$

$$f_j(x) \leq \tilde{b}_j, \quad \dots(3.b.2)$$

$$f_h(x) \geq b_h,$$

$$x \geq 0,$$

where  $i = 1, 2, 3, \dots, k,$

$$j = 1, 2, 3, \dots, m_1$$

and  $h = m_1 + 1, m_1 + 2, \dots, m.$

Using Bellman and Zadeh (18) and Zimmermann (19) concept, fuzzy goal programming (3.b.2) is expressed as :

Maximize  $\alpha$

subject to :

$$\mu_{g_i}(x) \geq \alpha,$$

$$\mu_{f_i}(x) \geq \alpha,$$

$$f_h(x) \geq b_h,$$

$$x \geq 0, \alpha \in (0, 1)$$

...(3.b.3)

where  $i = 1, 2, 3, \dots, k; j = 1, 2, 3, \dots, m_1$

and  $h = m_1 + 1, m_1 + 2, \dots, m.$

Membership functions  $\mu_{g_i}(x)$ ,  $\mu_{f_i}(x)$  may be linear or non-linear. For simplicity, only linear membership functions are considered in this analysis.

$$\begin{aligned} \text{Let, } \mu_{g_i}(x) &= 1 && \text{for } g_i < C_i \\ &= 1 - \frac{g_i - C_i}{RC_i} && \text{for } C_i \leq g_i \leq C_i + RC_i \\ &= 0 && \text{for } g_i > C_i + RC_i \end{aligned}$$

$$\begin{aligned} \text{and } \mu_{f_i}(x) &= 1 && \text{for } f_i < b_i \\ &= 1 - \frac{f_i - b_i}{Rb_i} && \text{for } b_i \leq f_i \leq b_i + Rb_i \\ &= 0 && \text{for } f_i > b_i + Rb_i \end{aligned}$$

where  $RC_i$ ,  $Rb_i$  are maximum tolerances from  $C_i$  and  $b_i$  respectively.

(3.b.3) is based on treating the goals of equal importance which may not be always possible. Such situations may demand for choosing intuitive weights to the goals.

If  $w_{g_i}$ ,  $w_{f_i}$  are intuitive weights to the goals,  $g_i$  and constraints,  $f_i$  respectively, then fuzzy goal

programming model (3.b.2) can be written as :

Maximize  $\alpha$

subject to :

$$\begin{aligned} w_{g_i} \mu_{g_i}(x) &\geq \alpha, & \dots(3.b.4) \\ w_{f_j} \mu_{f_j}(x) &\geq \alpha, \\ f_h(x) &\geq b_h, \\ x &\geq 0, \quad \alpha \in (0,1) \end{aligned}$$

where  $i = 1, 2, 3, \dots, k,$

$j = 1, 2, 3, \dots, m_1$

and  $h = m_1 + 1, m_1 + 2, \dots, m.$

In the above model (3.b.2), when coefficients in the objectives and some constraints are also fuzzy, the problem is reduced to :

Determine  $x \in S$

subject to :

$$\begin{aligned} g_i(\tilde{a}, x) &\leq \tilde{p}_i, & \dots(3.b.5) \\ f_j(\tilde{b}, x) &\leq \tilde{b}_j, \\ f_h(x) &\leq b_h, \\ x &\geq 0 \end{aligned}$$

where  $i = 1, 2, 3, \dots, k,$

$j = 1, 2, 3, \dots, m$

and  $h = m_1 + 1, m_1 + 2, \dots, m.$

Here  $g_i(\tilde{a}, x), f_j(\tilde{b}, x)$  are polynomials with fuzzy coefficient vectors  $\tilde{a}, \tilde{b}$  respectively.

So, as before, using Bellman and Zadeh (18), Zimmermann (19) and Carlsson and Korhonen (20) concept, above fuzzy goal programming model (3.b.5) can be expressed as :

Maximize  $\alpha$

subject to :

$$\begin{aligned} \mu_{g_i}(g_i(\mu_a^{-1}(\alpha), x)) &\geq \alpha, \\ \mu_{f_j}(f_j(\mu_a^{-1}(\alpha), x)) &\geq \alpha, & \dots(3.b.6) \\ f_h(x) &\geq b_h, \\ x &\geq 0, \quad \alpha \in (0,1), \end{aligned}$$

for  $i = 1, 2, 3, \dots, k,$   $j = 1, 2, 3, \dots, m_1$

and  $h = m_1 + 1, m_1 + 2, \dots, m.$

where  $\mu_a^{-1}(\alpha) = \{ \mu_{a_{i1}}^{-1}(\alpha), \mu_{a_{i2}}^{-1}(\alpha), \dots, \mu_{a_{i\ell_i}}^{-1}(\alpha) \}$ ,

$\mu_b^{-1}(\alpha) = \{ \mu_{b_{j1}}^{-1}(\alpha), \mu_{b_{j2}}^{-1}(\alpha), \dots, \mu_{b_{j\ell_j}}^{-1}(\alpha) \}$ .

Here,  $\mu_{a_{i1}}^{(t)}$ ,  $\mu_{a_{i2}}^{(t)}$ , ...,  $\mu_{a_{i\ell_i}}^{(t)}$  and  $\mu_{b_{j1}}^{(t)}$ ,  $\mu_{b_{j2}}^{(t)}$ , ...,  $\mu_{b_{j\ell_j}}^{(t)}$  are membership functions of the fuzzy coefficient vectors of objective functions  $g_i(\bar{a}, \bar{x})$  and constraints  $f_j(b, x)$  respectively.

These are defined as :

$$\begin{aligned} \mu_{a_{ir}}^{(t)} &= 1 && \text{for } t > a_{ir} \\ &= \frac{t - (a_{ir} - Ra_{ir})}{Ra_{ir}} && \text{for } a_{ir} - Ra_{ir} \leq t \leq a_{ir} \\ &= 0 && \text{for } t < a_{ir} - Ra_{ir} \\ r &= 1, 2, 3, \dots, \ell_i \end{aligned}$$

$$\begin{aligned} \mu_{b_{js}}^{(t)} &= 1 && \text{for } t > b_{js} \\ &= \frac{t - (b_{js} - Rb_{js})}{Rb_{js}} && \text{for } b_{js} - Rb_{js} \leq t \leq b_{js} \\ &= 0 && \text{for } t < b_{js} - Rb_{js} \\ s &= 1, 2, 3, \dots, \ell_j \end{aligned}$$

If  $w_i, w_{g_i}, w_j$  are respectively intuitive weights to each coefficient, objective goals  $g_i$  and constraints  $f_j$ , then fuzzy goal programming model (3.b.5) can be formulated as :

Maximize  $\alpha$

subject to :

$$\begin{aligned} w_{g_i} \mu_{g_i} (g_i (\mu_a^{-1}(\alpha/w), x)) &\geq \alpha, \\ w_j \mu_{f_j} (f_j (\mu_b^{-1}(\alpha/w), x)) &\geq \alpha, \\ f_h(x) &\geq b_h, \\ x &\geq 0, \alpha \in (0,1), \end{aligned} \quad \dots(3.b.7)$$

where  $\mu_a^{-1}(\alpha/w) = \{ \mu_{a_{i1}}^{-1}(\alpha/w), \mu_{a_{i2}}^{-1}(\alpha/w), \dots, \mu_{a_{i\ell_i}}^{-1}(\alpha/w) \}$ ,

$\mu_b^{-1}(\alpha/w) = \{ \mu_{b_{j1}}^{-1}(\alpha/w), \mu_{b_{j2}}^{-1}(\alpha/w), \dots, \mu_{b_{j\ell_j}}^{-1}(\alpha/w) \}$ ,

$i = 1, 2, 3, \dots, k$ ,  $j = 1, 2, 3, \dots, m$ , and  $h = m_1 + 1, m_1 + 2, \dots, m$ .

#### 4. GOAL PROGRAMMING FORMULATION OF THE PROPOSED FUZZY AND CRISP EOQ MODEL :

Here, according to (3.a.3), crisp EOQ model (2.0) can be written as :

Min ( $dc^+$  ,  $dc^+_0$ )

subject to :

$$\sum_{i=1}^N \left( \frac{C_{3i} D_i}{Q_i} + \frac{OC_{1i} Q_i}{2} \right) + dc^-_0 - dc^+_0 = C_0 ,$$

$$\frac{1}{2} \sum_{i=1}^N C_{1i} Q_i + dc^- - dc^+ = C , \quad \dots (4.0)$$

$$\sum_{i=1}^N A_i Q_i \leq A , \quad Q_i > 0 , \quad \dots (4.0)$$

$i = 1, 2, 3, \dots, N$ .

Following (3.b.3), the fuzzy EOQ model (2.1) can be written as :

Maximize  $\alpha$

subject to :

$$\sum_{i=1}^N \left( \frac{C_{3i} D_i}{Q_i} + \frac{OC_{1i} Q_i}{2} \right) \leq C_0 + (1 - \alpha) P_0 ,$$

$$\frac{1}{2} \sum_{i=1}^N C_{1i} Q_i \leq C + (1 - \alpha) P , \quad \dots (4.1)$$

$$\sum_{i=1}^N A_i Q_i \leq A ,$$

$Q_i > 0 , \quad \alpha \in (0, 1) , \quad \text{where } i = 1, 2, 3, \dots, N$ .

If  $w_0$  and  $w$  are intuitive weights to the objective goal and capital investment constraint respectively, following (3.b.4), the model (2.1) can be written as :

Maximize  $\alpha$

Subject to :

$$\sum_{i=1}^N \left( \frac{C_{3i} D_i}{Q_i} + \frac{OC_{1i} Q_i}{2} \right) \leq C_0 + (1 - \alpha/w_0) P_0 ,$$

$$\frac{1}{2} \sum_{i=1}^N C_{1i} Q_i \leq C + (1 - \alpha/w) P , \quad \dots (4.2)$$

$$\sum_{i=1}^N A_i Q_i \leq A , \quad Q_i > 0 , \quad \alpha \in (0, 1) , \quad \text{for } i = 1, 2, 3, \dots, N$$



If the costs (– set-up costs and unit costs ) are fuzzy in nature, following (3.b.6) the model (2.2) reduces to :

Maximize  $\alpha$

subject to :

$$\sum_{i=1}^N \left( \frac{(C_{3i} - P_{3i} + \alpha P_{3i}) D_i}{Q_i} + \frac{O(C_{1i} - P_{1i} + \alpha P_{1i}) Q_i}{2} \right) \leq C_0 + (1 - \alpha) P_0,$$

$$\frac{1}{2} \sum_{i=1}^N (C_{1i} - P_{1i} + \alpha P_{1i}) Q_i \leq C + (1 - \alpha) P, \quad \dots(4.3)$$

$$\sum_{i=1}^N A_i Q_i \leq A,$$

$Q_i > 0, \alpha \in (0, 1), i = 1, 2, 3, \dots, N,$

where  $P_{3i}, P_{1i}$  are maximum tolerances from costs  $C_{3i}, C_{1i}$  respectively.

If  $w_c, w_0$  and  $w$  be intuitive weights of the costs, objective goal and investment constraints, model (2.2) reduces to (following (3.b.7)) :

Maximize  $\alpha$

Subject to :

$$\sum_{i=1}^N \left( \frac{(C_{3i} - P_{3i} + \alpha P_{3i}/w_c) D_i}{Q_i} + \frac{O(C_{1i} - P_{1i} + \alpha P_{1i}/w_c) Q_i}{2} \right) \leq C_0 + (1 - \alpha/w_0) P_0,$$

$$\frac{1}{2} \sum_{i=1}^N (C_{1i} - P_{1i} + \alpha P_{1i}/w_c) Q_i \leq C + (1 - \alpha/w) P, \quad \dots(4.4)$$

$$\sum_{i=1}^N A_i Q_i \leq A,$$

$Q_i > 0, \alpha \in (0, 1), i = 1, 2, 3, \dots, N.$

## 5. NUMERICAL EXAMPLE :

We consider the following data for crisp model of (2.0) and fuzzy models of (4.1), (4.2) :

TABLE—1 : Data for crisp model (2.0).

ITEM	DEMAND $D_i$ (Rs.)	UNIT COST $C_{1i}$ (Rs.)	SET-UP COST $C_{3i}$ (Rs.)	SPACE $A_i$ (sq. ft.)
1	10000	30	60	2
2	6000	26	60	2.5
3	3000	49	60	3
4	2000	23	60	4

and Inventory carrying charge  $O = .2$   
 total capital investment  $C = \text{Rs. } 13500$   
 total space required  $A = 2370 \text{ sq. ft.}$

and objective goal  $C_0 = \text{Rs. } 7000$ . For the fuzzy models, we take  $P = \text{Rs. } 3000$ ,  $P_0 = \text{Rs. } 2000$  alongwith the crisp data in Table-1.

Solving with above parameters, results of fuzzy models (4.1), (4.2) and crisp model (4.0) are :

TABLE – 2 : Results of models (4.0), (4.1) and (4.2).

Model	Aspiration Level ( $\alpha$ )	Total average costs (Rs.)	Total capital investment (Rs.)
Crisp goal programming model (4.0)		7974.14	13500
Fuzzy goal programming model (4.1)	.57	7942.54	13712.68
Fuzzy goal programming model with direct weights (4.2) (taking $w_0 = .3$ , $w = .7$ )	.21	7931.34	13852.92

In goal programming model (4.0), objective goal is over achieved where as, in fuzzy goal programming model (4.1) the over achievement of the objective goal is within reasonable limit. Also, for fuzzy weighted goal programming model (4.2), the objective goal is within reasonable limit and less than that of (4.1). Here, constraint goals of (4.1) and (4.2) are within their reasonable limit.

We consider the following data for fuzzy models ((4.3) and (4.4)) with fuzzy coefficients.

TABLE—3 : Data for fuzzy models (4.3), (4.4).

ITEM	DEMANED $D_i$ (Rs.)	UNIT COST $C_{1i}$ (Rs.)	$P_{1i}$ (Rs.)	SETUP COST $C_{3i}$ (Rs.)	$P_{3i}$ (Rs.)	SPACE $A_i$ (sq.ft.)
1	10000	30	5	60	10	2
2	6000	26	6	60	10	2.5
3	8000	49	9	60	10	3
4	2000	23	8	60	10	4

and

TABLE-4 : Data for fuzzy models (4.3) and (4.4) .

INVENTORY CARRYING CHARGE $O$	TOTAL CAPITAL INVESTMENT $C$ (Rs.)	$P$ (Rs.)	TOTAL AVERAGE COST $C_0$ (Rs.)	$P_0$ (Rs.)	TOTAL SPACE $A$ (Sq. ft.)
.2	13500	3000	7000	2000	2600

With above parameters, results of fuzzy model (4.3) and fuzzy weighted model (4.4) are :

TABLE-5 : Results of the model (4.3) and (4.4) .

MODEL	ASPIRATION LEVEL ( $\alpha$ )	TOTAL AVERAGE COST (RS.)	TOTAL CAPITAL INVESTMENT (RS.)
FUZZY GOAL PROGRAMMING MODEL (4.3)	.78	7445.05	14167.57
FUZZY GOAL PROGRAMMING MODEL (4.4) WITH WEIGHTS ( $w_c = .3, w_o = .2, w = .5$ )	.18	7215.95	13882.32

Here, fuzzy models (4.3) and (4.4) are with fuzzy costs. From table-5, we see that (4.4) gives better result than (4.3) as before.

#### Conclusion :

In this paper, an inventory problem has been formulated as a nonlinear fuzzy programming problem. We have introduced a fuzzy non-linear goal programming method with or without intuitive weights. Fuzzy additive goal programming method may be used to solve the present problem. Weights which has been chosen here deterministically can also be taken as fuzzy. But to choose appropriate weights is an area of future research.

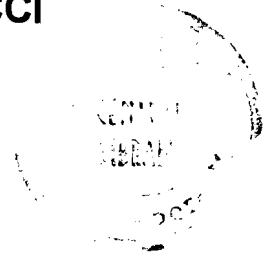
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# ON PSEUDO SYMMETRIC AND PSEUDO RICCI SYMMETRIC KÄHLER MANIFOLDS

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## INTRODUCTION.

The notions of Pseudo symmetric and pseudo Ricci symmetric manifolds were introduced by M.C. Chaki in 1987 [a] and 1988 [b] respectively.

A non-flat Riemannian manifold  $(M^n, g)$  ( $n \geq 2$ ) is called pseudo symmetric if its curvature tensor  $R$  satisfies the relation

$$(1) (\nabla_X R)(Y, Z)W = 2A(X)R(Y, Z)W + A(Y)R(X, Z)W + A(Z)R(Y, X)W + A(W)R(Y, Z)X + g(R(Y, Z)W, X)P$$

where  $A$  is a non-zero 1-form,

$$(2) g(X, P) = A(X)$$

for every vector field  $X$  and  $\nabla$  denotes the operator of covariant differentiation with respect to the metric tensor  $g$ . Such an  $n$ -dimensional manifold was denoted by  $(PS)_n$ .

A non-flat Riemannian manifold  $(M^n, g)$  ( $n > 2$ ) is called Pseudo Ricci symmetric if its Ricci tensor  $S$  of type  $(0, 2)$  is not identically zero and satisfies the condition

$$(3) (\nabla_X S)(Y, Z) = 2A(X)S(Y, Z) + A(Y)S(X, Z) + A(Z)S(Y, X)$$

where  $A$  is a non-zero 1-form and  $\nabla$  has the meaning already mentioned. Such an  $n$ -dimensional manifold was denoted by  $(PRS)_n$ .

On the other hand the notion of a Kähler manifold is as follows :

Let  $M^n$  be a Kähler manifold with Kähler metric  $g$ , almost complex structure  $F$ ,  $\dim M = n (= 2m)$  and Riemannian connection  $\nabla$  satisfies

$$\bar{X} + X = 0, \quad g(\bar{X}, \bar{Y}) = g(X, Y) \quad \text{and} \quad (\nabla_X F)(Y) = 0,$$

where  $F(X) = \bar{X}$  and  $X, Y$  are arbitrary vectors.

The present paper deals with a Pseudo symmetric and Pseudo Ricci symmetric manifolds which are Kähler manifolds. At first it is shown that in a Kähler  $(PS)_n$  ( $n > 2$ ),  $1/2$  is an eigen value of the Ricci tensor  $S$  corresponding to eigen vector  $P$  defined by  $g(X, P) = A(X)$ . In the last section, it is shown that a Kähler  $(PRS)_n$  ( $n > 2$ ) is of zero scalar curvature.

1. Preliminaries. Let  $R(X, Y)Z$  be the curvature tensor of type  $(1, 3)$  of  $M^n$ . Then we have [c]

$$\begin{aligned} R(\bar{X}, Y)Z &= -R(X, \bar{Y})Z, & R(X, Y)\bar{Z} &= \overline{R(X, Y)Z}, \\ R(X, Y)Z &= -R(Y, X)Z. \end{aligned}$$

Key words and phrases : Pseudo symmetric manifold, Pseudo Ricci symmetric manifold, Kähler manifold.

Let  $'R(X, Y, Z, T) = g(R(X, Y)Z, T)$  be the curvature tensor of type (0,4) of  $M^n$  which satisfied

$$(1.1) \quad 'R(X, Y, Z, T) = 'R(X, Y, \bar{Z}, \bar{T})$$

$$(1.2) \quad 'R(X, Y, Z, \bar{T}) + 'R(X, Y, \bar{Z}, T) = 0.$$

Let  $S(X, Y)$  be the Ricci tensor of  $M^n$ , then

$$(1.3) \quad S(\bar{X}, \bar{Y}) = S(X, Y)$$

$$(1.4) \quad S(\bar{X}, Y) + S(X, \bar{Y}) = 0$$

$$(1.5) \quad L(X) + \overline{L(\bar{X})} = 0$$

$$(1.6) \quad L(\bar{X}) = \overline{L(\bar{X})}$$

where  $L$  is the symmetric endomorphism of the tangent space at each point corresponding to the Ricci tensor  $S$  i. e.

$$g(LX, Y) = S(X, Y).$$

2. Pseudo symmetric Kahler manifold  $(PS)_n$  ( $n > 2$ ).

In this section we suppose that a  $(PS)_n$  ( $n > 2$ ) is a Kähler manifold.

From (1) we get

$$(2.1) \quad (\nabla_U 'R)(X, Y, Z, W) = 2A(U) 'R(X, Y, Z, W) + A(X) 'R(U, Y, Z, W) \\ + A(Y) 'R(X, U, Z, W) + A(Z) 'R(X, Y, U, W) + A(W) 'R(X, Y, Z, U).$$

Putting  $Z = \bar{Z}$  and  $W = \bar{W}$  in (2.1) we get

$$(2.2) \quad (\nabla_U 'R)(X, Y, \bar{Z}, \bar{W}) = 2A(U) 'R(X, Y, \bar{Z}, \bar{W}) + A(X) 'R(U, Y, \bar{Z}, \bar{W}) + A(Y) 'R(X, U, \bar{Z}, \bar{W}) \\ + A(\bar{Z}) 'R(X, Y, U, \bar{W}) + A(\bar{W}) 'R(X, Y, \bar{Z}, U).$$

Using (1.1) in (2.2) we have

$$(2.3) \quad (\nabla_U 'R)(X, Y, \bar{Z}, \bar{W}) = 2A(U) 'R(X, Y, Z, W) + A(X) 'R(U, Y, Z, W) \\ + A(Y) 'R(X, U, Z, W) + A(\bar{Z}) 'R(X, Y, U, \bar{W}) + A(\bar{W}) 'R(X, Y, \bar{Z}, U).$$

Now

$$(\nabla_U 'R)(X, Y, \bar{Z}, \bar{W}) = \nabla_U 'R(X, Y, \bar{Z}, \bar{W}) - 'R(\nabla_U X, Y, \bar{Z}, \bar{W}) - 'R(X, \nabla_U Y, \bar{Z}, \bar{W}) \\ - 'R(X, Y, \nabla_U \bar{Z}, \bar{W}) - 'R(X, Y, \bar{Z}, \nabla_U \bar{W}).$$

Using (1.1) the above equation can be written as

$$(2.4) \quad (\nabla_U 'R)(X, Y, \bar{Z}, \bar{W}) = \nabla_U 'R(X, Y, Z, W) - 'R(\nabla_U X, Y, Z, W) - 'R(X, \nabla_U Y, Z, W) - \\ - 'R(X, Y, \nabla_U Z, W) - 'R(X, Y, Z, \nabla_U W). [\because \nabla_U \bar{Z} = \overline{\nabla_U Z}] \\ = (\nabla_U 'R)(X, Y, Z, W).$$

In virtue of (2.1) and (2.4) the equation (2.3) reduces to

$$(2.5) \quad A(\bar{Z})'R(X, Y, U, \bar{W}) + A(\bar{W})'R(X, Y, \bar{Z}, U) = A(\bar{Z})'R(X, Y, U, W) + A(\bar{W})'R(X, Y, Z, U).$$

Applying (1.2) in (2.5) we get

$$(2.6) \quad -A(\bar{Z})'R(X, Y, \bar{U}, W) - A(\bar{W})'R(X, Y, Z, \bar{U}) = A(\bar{Z})'R(X, Y, U, W) + A(\bar{W})'R(X, Y, Z, U).$$

Putting  $X = U = e_i$  in (2.6) and using (1.2) it follows that

$$(2.7) \quad A(\bar{Z})S(Y, \bar{W}) - A(\bar{W})S(Y, \bar{Z}) = A(\bar{Z})S(Y, W) - A(\bar{W})S(Y, Z),$$

where  $\{e_i\}$ ,  $i = 1, 2, \dots, n$  is an orthonormal basis of the tangent space at a point and  $i$  is summed for  $1 \leq i \leq n$ .

Again putting  $Y = W = e_i$  in (2.7) and using (1.4) we get

$$(2.8) \quad S(Z, P) = \frac{1}{2} A(\bar{Z}).$$

Thus we have the following theorem :

Theorem 1. In a kahler (PS) $_n$  ( $n > 2$ ),  $\frac{1}{2}$  is an eigen value of the Ricci tensor S corresponding to the eigen vector P defined by  $g(X, P) = A(X)$ .

3. Pseudo Ricci symmetric Kähler manifold (PRS) $_n$  ( $n > 2$ ).

In this section we suppose that a (PRS) $_n$  ( $n > 2$ ) is a Kähler manifold.

Putting  $Y = \bar{Y}$  and  $Z = \bar{Z}$  in (3) we get

$$(3.1) \quad (\nabla_X S)(\bar{Y}, \bar{Z}) = 2A(X)S(\bar{Y}, \bar{Z}) + A(\bar{Y})S(X, \bar{Z}) + A(\bar{Z})S(\bar{Y}, X).$$

Now

$$(3.2) \quad \begin{aligned} (\nabla_U S)(\bar{Y}, \bar{Z}) &= \nabla_U S(\bar{Y}, \bar{Z}) - S(\nabla_U \bar{Y}, \bar{Z}) - S(\bar{Y}, \nabla_U \bar{Z}) \\ &= \nabla_U S(Y, Z) - S(\nabla_U Y, Z) - S(Y, \nabla_U Z) \end{aligned}$$

$$\text{[by (1.3) and } \nabla_U \bar{Z} = \overline{\nabla_U Z}]$$

$$= (\nabla_U S)(Y, Z).$$

In virtue of (1.3) and (3.2) the equation (3.1) reduces to

$$(3.3) \quad (\nabla_X S)(Y, Z) = 2A(X)S(Y, Z) + A(\bar{Y})S(X, \bar{Z}) + A(\bar{Z})S(\bar{Y}, X).$$

From (3) and (3.3) we have

$$(3.4) \quad A(\bar{Y})S(X, \bar{Z}) + A(\bar{Z})S(\bar{Y}, X) = A(Y)S(X, Z) + A(Z)S(Y, X).$$

Putting  $X = Z = e_i$  in (3.4) and using (1.4) we get

$$(3.5) \quad S(Y, P) = -\frac{1}{2} A(\bar{Y}).$$

Hence we can state the following theorem :

Theorem 2. In a Kähler (PRS) $_n$  ( $n > 2$ ),  $-\frac{1}{2}$  is an eigen value of the Ricci tensor S corresponding to the eigen vector P defined by  $g(Y, P) = A(\bar{Y})$ .

In a (PRS) $_n$  ( $n > 2$ ) it is known [b] that  $S(Y, P) = 0$ . Therefore from (3.5) it follows that  $r = 0$ .

This leads to the following corollary of the above theorem :

Corollary : A Kähler (PRS)<sub>n</sub> ( $n > 2$ ), is of zero scalar curvature.

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# Effect of Dimethyl Formamide in the Photopolymerisation of Methyl Methacrylate using Pyridine-Sulfur Dioxide Complex and CarbontetraChloride as photoinitiator.

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## Abstract

A combination of pyridine-sulfur dioxide complex (Py-SO<sub>2</sub>) and carbon tetrachloride in presence of dimethyl formamide (DMF) was used as photoinitiator for the photopolymerisation of methyl methacrylate (MMA) at 40°C. Polymerisation is considered to proceed by a radical mechanism through equilibrium complexation between the Py-SO<sub>2</sub> complex and monomer molecules. It has been observed that DMF enhances the polymerisation rate at all levels of [Py-SO<sub>2</sub>] and [CCl<sub>4</sub>]. The radical generation step is believed to be solvent (DMF) dependent. The kinetic parameter,  $k_p^2/k_t$  at all level of DMF dilution is  $1.40 \times 10^{-2} \text{ l. mol}^{-1} \text{ sec}^{-1}$  and the initiator exponent is 0.5.

## 1. INTRODUCTION :

It was reported<sup>1</sup> that a solution consisting of liquid sulfur dioxide and carbon tetrachloride instantly initiate polymerisation of certain vinyl monomers such as styrene, methyl methacrylate, acrylonitrile etc. at or above room temperature. It was also observed<sup>2</sup> that small amount of carbon tetrachloride can enhance the rate of photopolymerisation of methylmethacrylate (MMA) when Py-SO<sub>2</sub> complex is used as the photoinitiator. In the present study we have examined the role of dimethylformamide (DMF) as an additive for the polymerisation of MMA using a combination of Py-SO<sub>2</sub> in CCl<sub>4</sub> as the photoinitiator.

## EXPERIMENTAL PROCEDURE :

Monomer MMA and solvents were purified following standard procedures<sup>3,4</sup>. Preparation of the pyridine-sulfur dioxide (Py-SO<sub>2</sub>) complex was done by a procedure similar to one described before<sup>5,6</sup>. Polymerisation of MMA was studied dilatometrically under N<sub>2</sub> at 40°C employing a high pressure 125W Hg-vapour lamp (Philips India). Polymers formed at low conversions (<10%) were precipitated with excess petroleum ether and then dried at 45° C in vacuum. The degree of polymerisation ( $\bar{P}_n$ ) and molecular weights ( $\bar{M}_n$ ) of selected polymers were determined following usual procedures<sup>7,8</sup>.

## RESULTS AND DISCUSSION

The Py-SO<sub>2</sub> complex is not quite miscible with MMA when used in concentrations > 0.2 mol.l<sup>-1</sup>. Some quantities of methanol is therefore used to make them soluble. In presence of 2—3% CCl<sub>4</sub> (0.2-0.3 mol.l<sup>-1</sup>) the rate of polymerisation,  $R_p$ , is greatly enhanced. Almost instantaneous polymerisation was observed even with low [CCl<sub>4</sub>] (~0.05%). While there was usually an inhibition period (30—60 minutes) in systems containing no CCl<sub>4</sub>, at low [CCl<sub>4</sub>],  $R_p$  is dependent on both [CCl<sub>4</sub>] and [Py-SO<sub>2</sub>]. At high [CCl<sub>4</sub>],  $R_p$  is practically independent of [CCl<sub>4</sub>]. Photopolymerisation rates were measured in DMF diluted system at different [M] using a fixed [Py-SO<sub>2</sub>] = 1.59 [M], and a fixed [CCl<sub>4</sub>] = 0.69 [M]. The monomer order obtained from the plot of log  $R_p$  vs log [M] is 0.70; whereas

in pyridine and in toluene solvents the monomer orders are both 1.50 (Table 1). This shows the rate enhancing role of DMF in the present system.

### Rate enhancing role of DMF :

The rate enhancing effect of DMF is better appreciated from (Table 2) giving  $R_p$  at a fixed  $[M]$ ,  $[Py-SO_2]$  and  $[CCl_4]$  and at varied  $[DMF]$ . Initial (steady) rates of polymerisation were significantly higher in DMF diluted system.

### Initiator Exponent :

The dependence of  $R_p$  on initiator ( $Py-SO_2$  Complex) concentration remains unchanged and independent of level of dilution with DMF, [Table 3, Fig. 1] and the initiator exponent at all level of dilution in the DMF is 0.5.

### $k_p^2/k_t$ value and activation energy :

The kinetic parameter  $k_p^2/k_t$  at 40°C was evaluated from  $\bar{P}_n$  and  $R_p$  data using Mayo Equation in the following form for the present system :

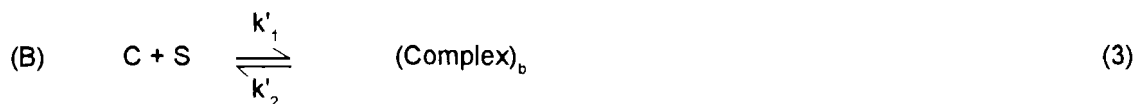
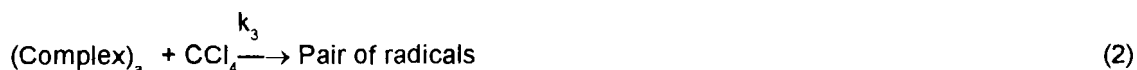
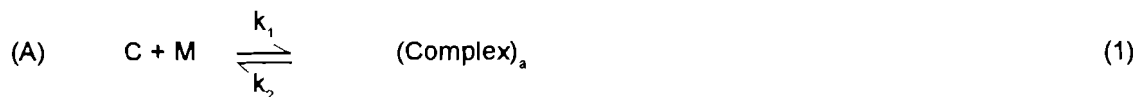
$$\frac{1}{\bar{P}_n} = 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} + C_M + C_I \frac{[I]}{[M]}$$

where  $C_I$  and  $C_M$  are initiator transfer constant and monomer transfer constant respectively,  $[I]$  and  $[M]$  are initiator and monomer concentrations. The value of the kinetic parameter,  $k_p^2/k_t$ , calculated from the plot of  $1/\bar{P}_n$  vs.  $R_p/[M]^2$  at all level of dilution with DMF remain constant. The value is  $1.40 \times 10^{-2} \text{ l. mol}^{-1} \text{ Sec}^{-1}$  (Table 3, Fig.2) which is in good agreement with some of the reported values in the literature <sup>5-10</sup>.

The activation energy for the present photopolymerisation system of MMA using the combination of  $Py-SO_2$  complex,  $CCl_4$  and DMF as photoinitiator was found to be 12.6  $\text{kJ mole}^{-1}$  which is close to some of the reported values for free radical photopolymerisation of MMA<sup>8-11</sup>.

### Mechanism

Kinetic data and the results of the end group analysis indicate a radical mechanism. The radical generation process may be considered according to the following reaction scheme. Both monomer and solvent molecules are considered to compete with each other in the initiator step to react with  $Py-SO_2$  complex (C) to form the respective association complexes,  $(Complex)_a$  and  $(Complex)_b$ .





Assuming that the termination takes place by bimolecular mechanisms, the rate of initiation  $R_i$  be expressed in the following form :

$$R_i = \frac{2R_p^2}{[M]^2} \cdot \frac{k_t}{k_p^2} = 2 \frac{k_1 k_3 [C] [M] [CCl_4]}{k_2 + k_3 [CCl_4]} + 2 \frac{k'_1 k'_3 [C] [S] [CCl_4]}{k'_2 + k'_3 [CCl_4]} \quad (5)$$

At constant  $[CCl_4]$ , the expressions

$$\frac{k_1 k_3 [CCl_4]}{k_2 + k_3 [CCl_4]} = K_a \quad (6)$$

$$\frac{k'_1 k'_3 [CCl_4]}{k'_2 + k'_3 [CCl_4]} = K_b \quad (7)$$

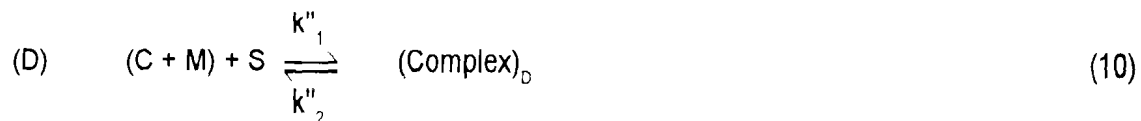
are constants.

The rate of initiation under this condition on may be written as

$$R_i = \frac{2R_p^2}{[M]^2} \cdot \frac{k_t}{k_p^2} = 2K_a [C] [M] + 2K_b [C] [S] \quad (8)$$

$$\text{or, } \frac{k_t R_p^2}{k_p^2 [M]^3 [C]} = K_a + K_b \frac{[S]}{[M]} \quad (9)$$

A plot of the left hand side of the equation (9) against  $[s]/[M]$  would give a straight line with zero slope if the solvent used plays the role of an inert diluent only without actively influencing the initiation reaction; while for active role for the solvent as envisaged in the reaction scheme, a positive slope for the linear plot would be indicated. Such plots for the data obtained in the present case for solvent like toluene, methanol, pyridine and DMF diluted systems are given in Figs. 3A & 3B (Table 4) which clearly indicate inert role for each of toluene and methanol, each giving monomer exponent of 1.50, quite expectedly. The slope of the respective plot as shown in Fig. 3A, is Zero in each case, while measurable positive slopes for such plots (Fig.3B) for pyridine and DMF diluted systems may be taken as evidences for their effective and active role in enhancing the rate of initiation, DMF appearing more effective than pyridine in this regard. The solvent dependent radical generation step i.e. step B in the above reaction scheme may be considered to occur as described in the reaction step D below :



Equation (9) deduced to analyse solvent dependency of the polymerisation rate in the diluted systems would then assume the following form :

$$\frac{k_t}{k_p^2} \cdot \frac{R_p^2}{[M]^3 [C]} = K_a + k' [S] \quad (12)$$

$$K_b = \frac{k_1'' k_3'' (\text{CCl}_4)}{k_1'' + k_3'' [\text{CCl}_4]} \quad (13)$$

Equation (13) permits a plot of the left hand side against [S], and such plots for the different diluted systems constant  $[\text{CCl}_4]$  and  $[\text{Py-SO}_2]$  in each case are shown in Fig.4 A&B (Table 4). Here again, methanol and toluene is clearly seen to play the role of inert solvent while DMF plays substantially active role through its participation in the initiation or radical generation reaction giving positive slope as shown in figure, 4B.

Table 1 : Variation of the rate of polymerisation with monomer concentration in Py-SO<sub>2</sub> complex induced photopolymerisation of MMA at 40° C activated by CCl<sub>4</sub>.

[M] mol.l <sup>-1</sup>	R <sub>p</sub> x 10 <sup>4</sup> mol.l <sup>-1</sup> sec <sup>-1</sup>	Monomer exponent
Solvent – Methanol, [Py-SO <sub>2</sub> ] = 1.59 mol.l <sup>-1</sup> ; [CCl <sub>4</sub> ] = 0.69 mol.l <sup>-1</sup>		
2.45	1.35	1.50
3.07	1.87	
3.68	2.30	
4.29	3.24	
4.91	3.84	
5.52	4.70	
Solvent-Toluene, [Py-SO <sub>2</sub> ] = 1.59 mol.l <sup>-1</sup> , [CCl <sub>4</sub> ] = 0.69 mol.l <sup>-1</sup>		
2.45	1.09	1.50
3.07	1.54	
3.68	2.01	
4.29	2.52	
4.91	3.092	
Solvent — Pyridine, [Py-SO <sub>2</sub> ] = 1.34 mol.l <sup>-1</sup> , [CCl <sub>4</sub> ] = 0.43 mol.l <sup>-1</sup>		
3.07	1.45	1.00
3.83	1.81	
4.22	2.00	
4.60	2.34	
4.98	2.53	
5.37	2.70	
5.75	2.90	
Solvent-DMF, [Py-SO <sub>2</sub> ] = 1.59 mol.l <sup>-1</sup> , [CCl <sub>4</sub> ] = 0.69 mol.l <sup>-1</sup>		
3.35	4.56	0.70
3.69	4.93	
4.00	5.18	
4.30	5.52	
4.60	5.81	
4.91	6.07	

**Table 2 :** Rate accelerating effect of DMF at fixed monomer concentration in the Py-SO<sub>2</sub> induced photopolymerisation of MMA activated by CCl<sub>4</sub> (variable amount of methanol was used to achieve DMF variation).

[M] = 3.68 mol.l<sup>-1</sup> ; [Py-SO<sub>2</sub>] = 1.59 mol.l<sup>-1</sup> ;  
 [CCl<sub>4</sub>] = 0.69 mol.l<sup>-1</sup>

[DMF] x10 mol.l <sup>-1</sup>	R <sub>p</sub> x10 <sup>4</sup> mol.l <sup>-1</sup> sec <sup>-1</sup>
0	2.31
1.70	2.60
4.25	2.90
8.49	3.18
10.20	3.30
12.70	3.87
17.00	4.33
21.20	4.59
25.50	4.93

Table 3 : Variation of rates of polymerisation and average degree of polymerisation ( $\bar{P}_n$ ) with initiator concentration in DMF diluted polymerisation of MMA using Py-SO<sub>2</sub> complex as the photoinitiator and CCl<sub>4</sub> as activator ; Temp. 40°C.

$$[\text{CCl}_4] = 0.69 \text{ mole.l}^{-1}$$

[Py-SO <sub>2</sub> ) mole.l <sup>-1</sup>	R <sub>p</sub> x10 <sup>4</sup> mole.l <sup>-1</sup> sec <sup>-1</sup>	$\frac{R_p}{[M]^2} \times 10^5$	[η] μ/g	(1/P <sub>n</sub> )x10 <sup>3</sup>	Initiator exponent	$\frac{k_p^2}{k_t} \times 10^2$
[M] = 3.35 mole.l <sup>-1</sup> ; [DMF] = 3.01 mole.l <sup>-1</sup> ; [CCl <sub>4</sub> ] = 0.69 mole.l <sup>-1</sup>						
1.82	4.91	4.37	0.13	6.68	0.5	1.40
1.59	4.56	4.06	0.14	6.24		
1.16	3.85	3.43	0.15	5.41		
0.80	3.49	3.11	0.16	4.97		
0.51	2.79	2.48	0.19	4.11		
[M] = 4.00 mole.l <sup>-1</sup> ; [DMF] = 2.12 mole.l <sup>-1</sup> ; [CCl <sub>4</sub> ] = 0.69 mole.l <sup>-1</sup>						
1.82	5.38	3.36	0.16	5.18	0.5	1.40
1.59	5.18	3.24	0.17	4.71		
1.16	4.34	2.72	0.19	4.08		
0.80	3.83	2.39	0.20	3.84		
0.51	3.04	1.90	0.23	3.10		
[M] = 4.30 mole.l <sup>-1</sup> ; [DMF] = 1.70 mole.l <sup>-1</sup> ; [CCl <sub>4</sub> ] = 0.69 mole.l <sup>-1</sup>						
1.82	5.71	3.15	0.164	4.89	0.5	1.40
1.59	5.52	2.98	0.175	4.48		
1.16	4.64	2.51	0.197	3.84		
0.80	4.02	2.17	0.21	3.48		
0.51	3.19	1.72	0.250	2.82		
[M] = 4.91 mole.l <sup>-1</sup> ; [DMF] = 0.845 mole.l <sup>-1</sup> ; [CCl <sub>4</sub> ] = 0.69 mole.l <sup>-1</sup>						
1.82	6.40	2.65	0.18	4.22	0.50	1.40
1.59	6.07	2.51	0.20	3.18		
1.16	4.98	2.06	0.22	3.26		
0.80	4.44	1.84	0.25	2.86		
0.51	3.59	1.48	0.27	2.54		

Table 4 : Kinetic data for analysis of role of solvents in modifying the initiation reaction in the Py-SO<sub>2</sub> Complex initiated photopolymerisation of MMA activated by CCl<sub>4</sub>.

[S]	[S] / [M]	$\frac{2K_t R_p^2}{k_p^2 [M]^3 [Py-SO_2]} \times 10^{10}$
Solvent = Methanol ;	[Py-SO <sub>2</sub> ] = 1.59 mol.l <sup>-1</sup> ;	[CCl <sub>4</sub> ] = 0.69 mol.l <sup>-1</sup>
11.50	4.69	7.80
9.86	3.22	7.66
8.21	2.23	7.65
6.57	1.78	8.34
4.93	1.00	7.90
3.29	0.60	8.26
Solvent = Toluene ;	[Py-SO <sub>2</sub> ] = 1.59 mol.l <sup>-1</sup> ;	[CCl <sub>4</sub> ] = 0.69 mol.l <sup>-1</sup>
4.26	1.73	5.05
3.65	1.19	5.17
3.04	0.82	5.10
2.43	0.56	5.05
1.82	0.37	5.02
Solvent = Pyridine ;	[Py-SO <sub>2</sub> ] = 1.34 mol.l <sup>-1</sup> ;	[CCl <sub>4</sub> ] = 0.43 mol.l <sup>-1</sup>
4.65	1.52	5.48
3.62	0.94	3.37
3.10	0.74	4.19
2.58	0.56	3.86
2.07	0.42	3.51
1.55	0.29	3.30
1.03	0.18	2.60
Solvent = DMF ;	[Py-SO <sub>2</sub> ] = 1.59 mol.l <sup>-1</sup> ;	[CCl <sub>4</sub> ] = 0.69 mol.l <sup>-1</sup>
2.98	0.89	35.24
2.55	0.69	30.77
2.12	0.53	26.51
1.70	0.39	24.18
1.26	0.28	21.18
0.84	0.17	19.15



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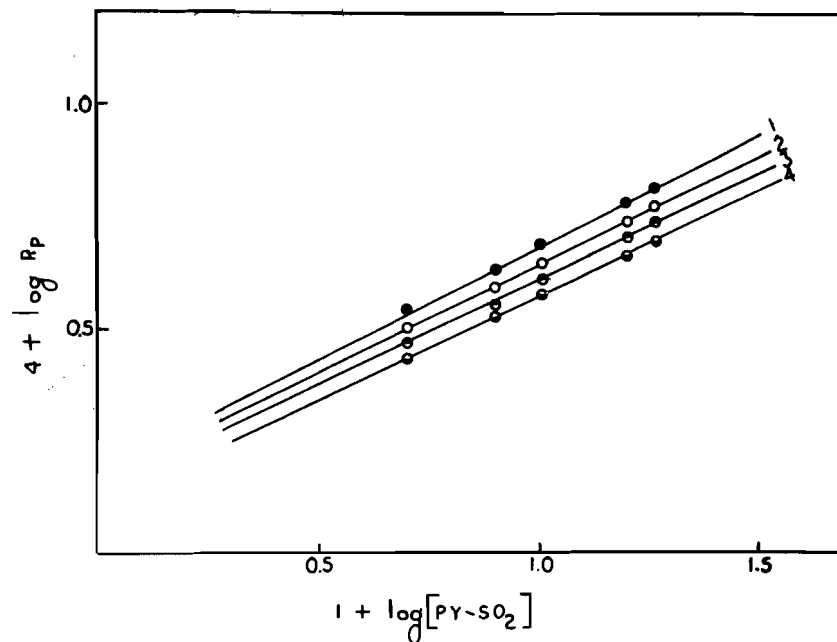


Fig. 1 Photopolymerisation of MMA using (Py-SO<sub>2</sub>) complex as initiator in presence of CCl<sub>4</sub> at 40°C. Plot of log R<sub>p</sub> vs log [Py-SO<sub>2</sub>]; [CCl<sub>4</sub>] = 0.69 mol.l<sup>-1</sup> (fixed). For each curve data given are [M] and [DMF] in mol.l<sup>-1</sup>.  
 ● - 4.91, 0.845; ○ - 4.30, 1.70; ◐ - 4.00, 2.12; ◑ - 3.35, 3.01.

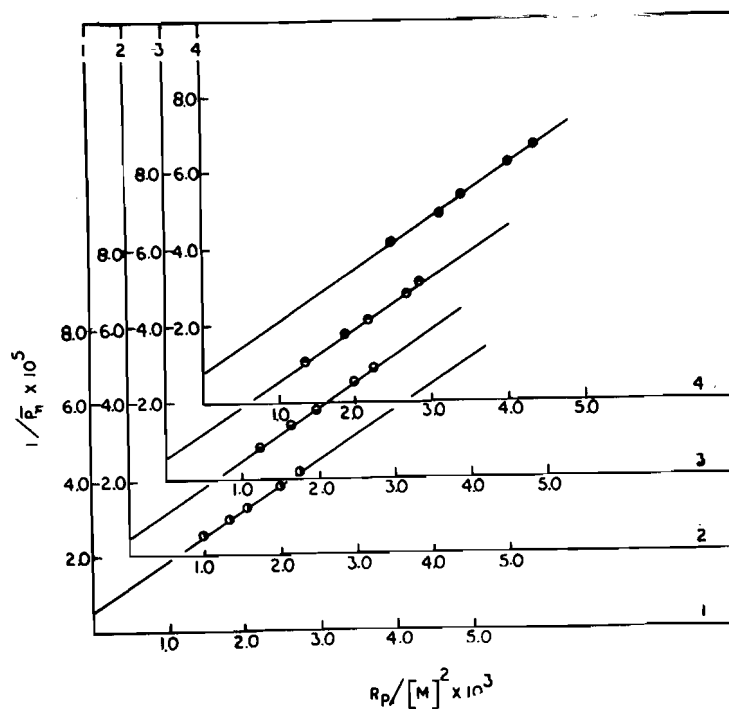


Fig. 2 Photopolymerisation of MMA using (Py-SO<sub>2</sub>) complex as initiator in presence of CCl<sub>4</sub> at 40°C. Plot of 1/P<sub>n</sub> vs. R<sub>p</sub>/[M]<sup>2</sup>; [CCl<sub>4</sub>] = 0.69 mol.l<sup>-1</sup> (fixed). For each curve data given are [DMF] in mol.l<sup>-1</sup>.  
 ○ - 0.845; ◐ - 1.70; ◑ - 2.12; ● - 3.01

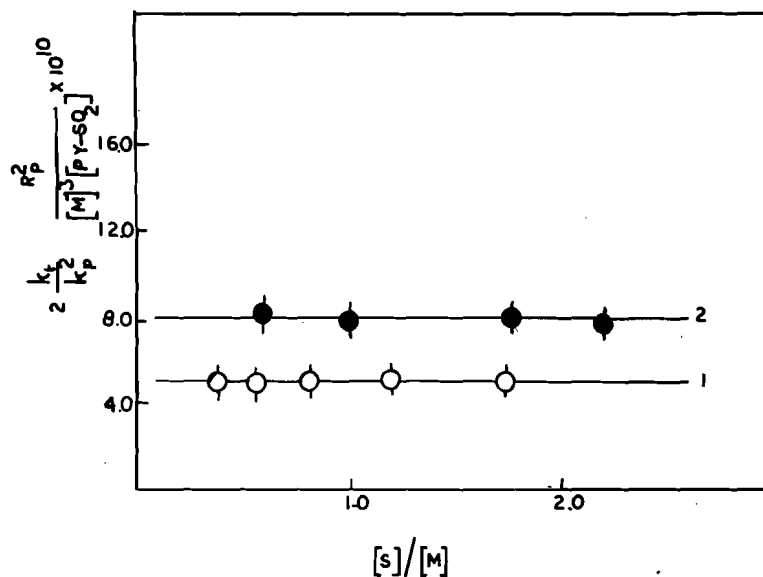


Fig. 3A. Photopolymerisation of MMA using (Py-SO<sub>2</sub>) complex as initiator in presence of CCl<sub>4</sub> at 40°C. Plot of  $2k_t/k_p^2 \cdot R_p^2/[M]^3 [Py-SO_2]$  vs.  $[S]/[M]$ .

[Py-SO<sub>2</sub>] = 1.59 mol.l<sup>-1</sup> (fixed) ; [CCl<sub>4</sub>] = 0.69 mol.l<sup>-1</sup> ;  
Solvent - ○ Toluene ; ● - Methanol.

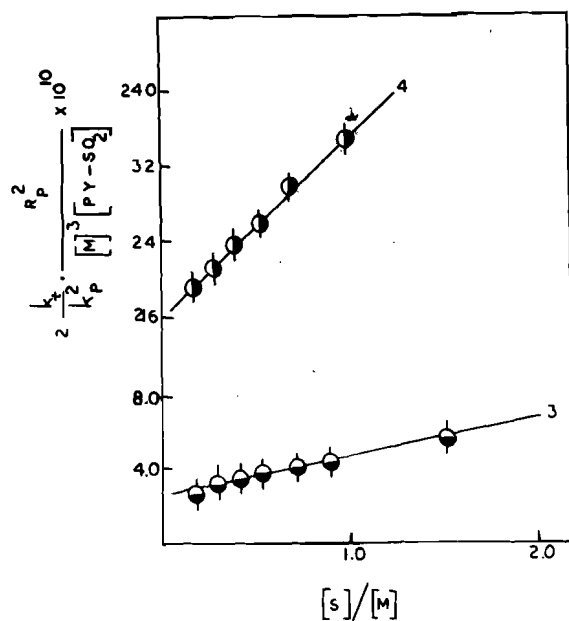


Fig. 3B Photopolymerisation of MMA using (Py-SO<sub>2</sub>) complex as initiator in presence of CCl<sub>4</sub> at 40°C. Plot of  $2k_t/k_p^2 \cdot R_p^2/[M]^3 [Py-SO_2]$  vs.  $[S]/[M]$ . Solvent ○ -Pyridine.

[Py-SO<sub>2</sub>] = 1.34 mol.l<sup>-1</sup> (fixed); [CCl<sub>4</sub>] = 0.43 mol.l<sup>-1</sup> (fixed); ● -DMF, [Py-SO<sub>2</sub>] = 1.59 mol.l<sup>-1</sup> (fixed) ; [CCl<sub>4</sub>] = 0.69 (fixed).

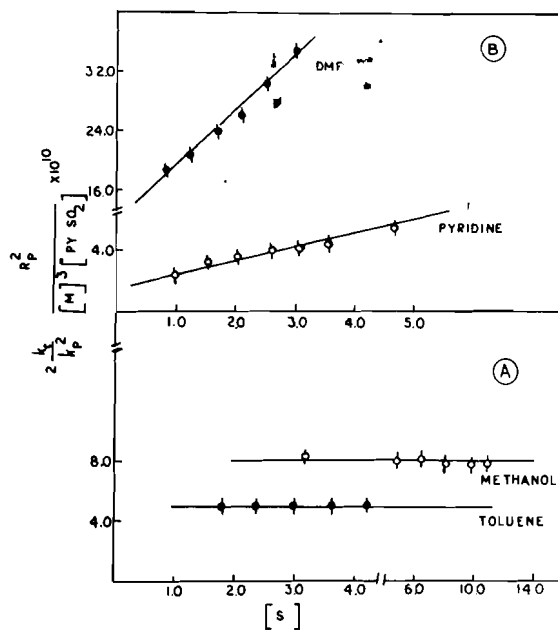


Fig. 4A & 4B. Photopolymerisation of MMA using (Py-SO<sub>2</sub>) complex as initiator in presence of CCl<sub>4</sub> as initiator at 40°C.

Plot of  $2k_t/k_p^2 \cdot R_p^2 / [M]^3 [Py-SO_2]$  vs.  $[S]$ .

Fig. 4A. Solvent ● - Toluene ;  $[Py-SO_2] = 1.59 \text{ mol.l}^{-1}$  (fixed);  $[CCl_4] = 0.69 \text{ mol.l}^{-1}$  (fixed) ; O -Methanol  $[Py-SO_2] = 1.59 \text{ mol.l}^{-1}$  (fixed);  $[CCl_4] = 0.69 \text{ mol.l}^{-1}$  (fixed).

Fig. 4B. Solvent O - Pyridine  $[Py-SO_2] = 1.34 \text{ mol.l}^{-1}$ ;  $[CCl_4] = 0.43 \text{ mol.l}^{-1}$ .

● - DMF,  $[Py-SO_2] = 1.59 \text{ mol.l}^{-1}$  (fixed);  $[CCl_4] = 0.69 \text{ mol.l}^{-1}$  (fixed).

# SYNTHESIS AND CHARACTERISATION OF COBALT (III) COMPLEXES OF -ARYLAZOPHENOL CARBOXYLIC ACIDS

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## Abstract :

Cobalt (III) complexes of type  $[\text{Co}(\text{ONO})_2](\text{H}_2\text{ONO}=\text{RC}_6\text{H}_3(12\text{-OH})\text{N}=\text{NC}_6\text{H}_4(2\text{-COOH}))$ . O-arylazophenolcarboxylic acids. R=9-Me, 9-Cl, 9- $\text{NO}_2$ , 9-Bu and 8,9-Benzo) have been synthesized. The complexes (2) have been characterised by elemental analyses, molar conductances, IR and UV-Vis spectral data. The meridional binding of tridentate (O,N,O) chelate has been confirmed by  $^1\text{H}$  NMR spectroscopy.

**Key words :** Arylazophenol carboxylates, cobalt (III) complexes, meridional binding, spectroscopy,  $^1\text{H}$  NMR.

## Introduction

The study of reactions and structures of transition metal complexes may be due to their involvement in some important chemical, biochemical and industrial processes.<sup>1-3</sup> The azo compounds are widely used as ligands for their considerable use in analytical and biological chemistry and in textile industry as dyeing agents. Mostly used azo compounds are azophenols. They are N,O chelators, suitable substitution changes their nature and activity,<sup>5,6</sup> Azophenolcarboxylates are excellent agents to increase the nuclearity of the complexes<sup>7</sup>. On this background we have undertaken a programme on the synthesis and structural characterisation metal complexes of o-arylazophenolcarboxylates (1). Herein we report synthesis and spectroscopic

Structures 1,2, see page 12

characterisation of o-arylazophenolatocarboxylato-cobalt(III) complexes (2).

## Experimental

The solvents used in the reactions were of reagent grade and were dried whenever necessary by reported procedure<sup>8</sup>. o-Arylazophenolatocarboxylic acids were synthesised following reported procedure<sup>4</sup> by coupling diazotised anthranilic acid and para substituted phenols. All other chemicals and solvents were reagent grade and were used as received.

Infrared spectra were recorded on a Perkin Elmer 783 spectrometer in KBr disk. The UV-vis spectral data were obtained from Shimadzu UV-160 spectrophotometer. There elemental analyses were carried out on Perkin Elmer model 240C elemental analyser. The magnetic susceptibility was measured on a PAR 155 vibrating sample magnetometer.  $^1\text{H}$  NMR data were collected in  $\text{DMSO}-d_6$  using Varian XL 200 MHZ FTNMR spectrometer. Thermogravimetric data were collected from Shimadzu DT-40 thermal analyser under nitrogen, cobalt analysis was performed by complexometric titrations<sup>9</sup>.

## Synthesis of Sodium bis (2- (2- phenolato-5-methyl) -phenylazo) phenyl carboxylato Cobaltate (III), (2a).

The synthesis was carried out by slight modification of two different procedures <sup>10</sup>.

### A. Cobalt (III) hydroxide method

Hydrous Co (OH)<sub>3</sub> was prepared by adding an excess of hydrogen peroxide cautiously to an aqueous alkaline solution of Co (NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (0.35 g, 1 mmol + 20% excess), centrifuging and washing the gelatinous precipitate until the wash water was neutral. This product was slurried under nitrogen with methanolic solution of (1a) (0.52 g, 2.03 mmol), NaOH (0.09 g, 2.25 mmol) and refluxed over steam bath for 2 h. Undissolved Co. (OH)<sub>3</sub> was filtered from the deep green solution and the solution was evaporated in air slowly. The precipitated dark coloured compound was filtered and washed with 1:1 (v/v) H<sub>2</sub>O : MeOH (5x5 cm<sup>3</sup>) and dried over P<sub>4</sub>O<sub>10</sub>. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) and the solution was chromatographed on silica gel column (45 x 1 cm) prepared in benzene. The desired green compound was eluted by MeCN : C<sub>6</sub>H<sub>6</sub> (1:3, v/v). Evaporation of the solvent in air afforded the pure crystalline product in 70% yield.

### B. Hexaammine cobalt (III) chloride method

Aqueous solution (10 cm<sup>3</sup>) of Co (NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> (0.27 g, 1.01 mmol) was added to methanolic solution (10 cm<sup>3</sup>) of (1a) (0.52 g 2.03 mmol) and NaOH (0.09 g, 2.25 mmol). The mixture was warmed on steam bath for 1 h. As the reaction proceeded, ammonia was evolved and the mixture became dark green. The solution was filtered and evaporated in air. The residue so left was purified as described in method A.

## RESULTS AND DISCUSSION

The ligands (1) are prepared following the procedure<sup>4</sup> of coupling of diazotised anthranilic acid with para-substituted phenols in alkaline medium. They are effective tridentate chelating ligands of (O,N,O) types. The cobaltate (III) complexes (2) are obtained by two different procedures<sup>10</sup>; cobalt (III) hydroxide method and hexaammine cobalt (III) chloride method.

The elemental analyses, molar conductances, IR and UV-vis spectral data are set out in Table 1. The molar conductances ( $\Lambda_m$ ) in MeCN show that the complexes are 1 : 1 electrolytes and magnetic

Table 1, see page 10

susceptibility measurements suggest they are diamagnetic. Thermal analyses of the complexes (2) under nitrogen lose weight at 110-130°C corresponding to one mole of lattice water per mole of the complex. The IR Spectra also confirm the presence of lattice water (vide infra).

The ligands (1) show broad IR bands in the region 3300-2800 cm<sup>-1</sup> due to  $\nu$ (O-H) modes of carboxylic acid and phenolic OH group 11a. The complexes (2) also exhibit broad IR bands in the region 3600-3200 cm<sup>-1</sup> due to  $\nu$ (O-H) modes of lattice water<sup>11b</sup> and are completely removed on thermal study to 110-130°C. The presence of moderate band around 1700 cm<sup>-1</sup> in ligand is the indication of -CO<sub>2</sub>H group <sup>12</sup> which is absent in the complexes suggesting coordination of the carboxylato group. The appearance of IR bands around 1540-1570 and 1350-1370 cm<sup>-1</sup> correspond to  $\nu_{\text{asym}}$  (COO) and  $\nu_{\text{sym}}$  (COO) respectively indicated monodentate coordination (= 200 cm<sup>-1</sup>) of carboxylato group <sup>13</sup>. The  $\nu$ (N=N) around 1410 cm<sup>-1</sup> in ligands (1) is red shifted by 30-50 cm<sup>-1</sup> indicating coordination of azo nitrogen<sup>14</sup>.

The green methanolic solution of complexes display characteristic absorption in the UV-vis region.

The characteristic visible spectra may be ascribed to transitions <sup>15</sup> from  $1A_{1g}$  to  $1T_{1g}$  and  $1T_{2g}$  states respectively, The second transition is vitiated by ligand transitions <sup>16</sup>. Other transitions can be assigned to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions centred primarily on the azo group<sup>17</sup>.

The sparing solubility of the complexes in chloroform leads to run <sup>1</sup>H NMR Spectra in DMSO - d<sub>6</sub>. All aromatic proton signals of the complexes have been completely assigned on the basis of spin-spin structure and changes therein on substitution. Representative spectra of (2a) is shown in Figure 1 and data are collected in Table 2.

Figure 1,

The signal movement is in accord with the inductive and resonance effect of the substituted group R<sup>18</sup>. A singlet signal in aromatic region is certainly due to 8-H and suffers a shift to higher field in (2a) and (2b) via electron releasing inductive effect. 3-H to 6-H protons suffer relatively little shifting with the substituent R. The signals those move appreciably with the substitution at 9th position are assigned to 10-H and 11-H. The signal movements shown schematically in Figure 2. The aromatic region in (2e) is complicated by signals from naphthyl group and hence is not assigned. Thus the meridional binding of the (O,N,O) tridentate chelate in the bis complex is confirmed.

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**Table 1.** Elemental analyses, infrared spectra, molar conductances and UV-Vis spectral data of complexes (2).

Compound	Elemental analyses <sup>a</sup>				IR Spectra <sup>b</sup>			max, ( ) <sup>d</sup>		
	C(%)	H(%)	N(%)	Co(%)	(N=N) (cm <sup>-1</sup> )	$\nu_{as}(C)$ (cm <sup>-1</sup> )	$\nu_s(C)$ (cm <sup>-1</sup> )	C (nm), M	(mol <sup>-1</sup> cm <sup>-1</sup> )	
Na[Co(C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>32</sub> )]·H <sub>2</sub> O (2.892);		55.12	3.71	9.09	9.56	1370	1540	1350	110.8	620
									375	(9.572);
									305	(19.795);
									290	(18.120)
Na	47.92	2.59	8.74	9.21	1370	1550	1370	124.5	625	(2.030);
	(48.07)	(2.47)	(8.63)	(9.09)					380	(8.630);
									310	(20.580);
									295	(17.650)
Na	59.09	4.80	8.18	8.34	1375	1545	1360	108.4	625	(3.045);
	(58.96)	(4.91)	(8.09)	(8.53)					385	(10.435);
									305	(22.830);
									285	(26.340)
Na	46.39	2.44	12.38	8.74	1360	1570	1375	135.4	620	(2.430);
	(46.57)	(2.39)	(12.54)	(8.81)					370	(11.640);
									300	(22.830);
									285	(25.550)
Na	59.89	3.16	8.11	8.80	1365	1550	1365	128.5	620	(55.93);
	(60.00)	(3.24)	(8.24)	(8.68)					410	(16.500);
									315	(20.265),
									285	(23.832)

<sup>a</sup>Calculated values are in parentheses

<sup>b</sup>In KBr disk.

<sup>c</sup>In acetonitrile.

<sup>d</sup>In methanol.



**Table 2. <sup>1</sup>H NMR Spectral data <sup>a,b</sup>**

δ(ppm), J(Hz)

Compound	3-H <sup>c</sup>	4-H <sup>d</sup>	5-H <sup>d</sup>	6-H <sup>c</sup>	8-H <sup>c</sup>	10-H <sup>c</sup>	11-H <sup>c</sup>
<u>2a</u> <sup>f</sup>	8.05 (8.4)	7.45 (9.0)	7.18 (9.0)	7.05 (8.4)	7.35	5.85 (8.0)	6.65 (8.0)
<u>2b</u>	8.08 (9.0)	7.48 (8.0)	7.28 (8.0)	7.15 (9.0)	7.65	6.81 (8.0)	6.00 (8.0)
<u>2c</u>	8.11 (8.4)	7.50 (8.0)	7.36 (8.0)	7.21 (8.4)	7.84	7.08 (8.0)	6.74 (8.0)
<u>2d</u> <sup>g</sup>	8.04 (9.0)	7.43 (8.0)	7.16 (8.0)	7.05 (9.0)	7.25	5.92 (8.0)	6.77 (8.0)

<sup>a</sup>Atom numbering scheme as shown in structure 1.

<sup>b</sup>Solvent : DMSO-d<sub>6</sub>

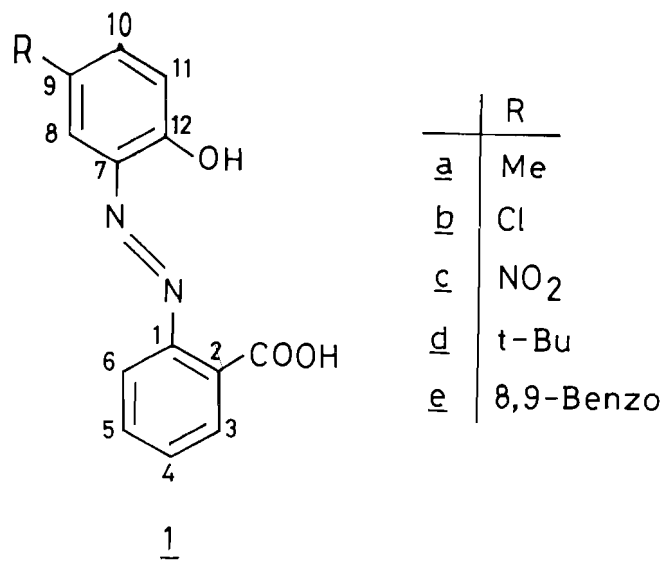
<sup>c</sup>Doublet

<sup>d</sup>Triplet

<sup>e</sup>Singlet

<sup>f</sup>9-Me resonates at 2.18 ppm.

<sup>g</sup>9-t-Bu resonates at 1.27 ppm.



Structures

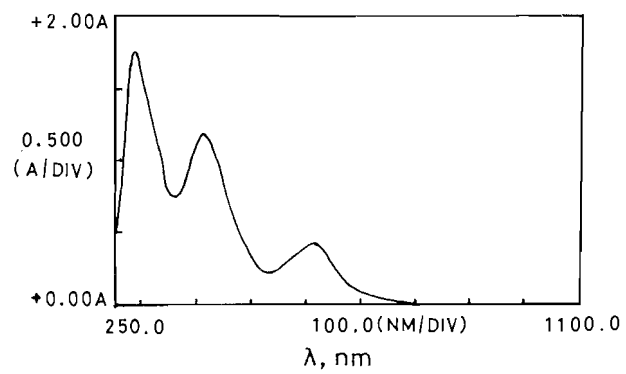


Fig.1. UV-Vis spectra of 2d in MeOH.  
Conc.  $7.4 \times 10^{-5}$ (M).

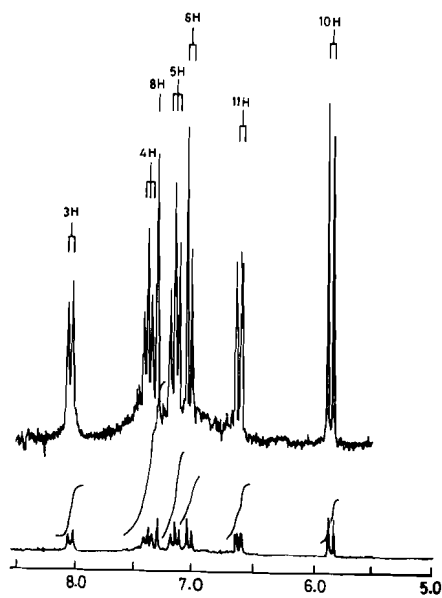


Fig.2.  $^1\text{H}$  NMR spectra of 2a at 200 MHz in  $\text{DMSO-d}_6$ .

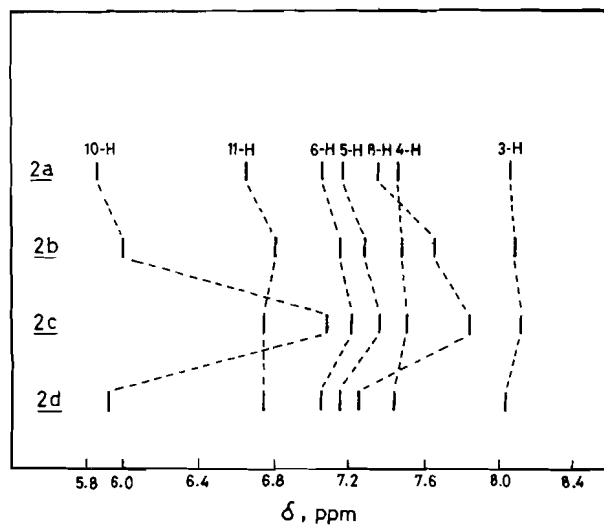


Fig.3. Schematic  $^1\text{H}$  NMR spectra of 2a-2d.

