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Contents

Supply Chain Decisiveness in Indian Auto Sector

Dr Dharamvir Mangal*
*Mechanical Engineering Department, The Technological Institute of Textile and Sciences, Bhiwani, Haryana, India

ABSTRACT

Supply chain management has increasingly become an inevitable challenge to most companies to be continuously survived and prospered in the global chain-based competitive environment. The current challenges of the Indian automotive world, their implications on supply chain are summarized and analyzed in this paper. In this competitive era of 'LPG' i.e. Liberalization, Privatization and Globalization, modern marketing systems, introduction of products with short life cycles, and the discriminating expectations of customers have enforced business enterprises to invest in and focus attention on their Supply Chains (SCs) in order to meet out the level of customer's satisfaction and to survive in the competitive market. In fact, many of trends in the auto industry are reinforcing the need to redefine supply chain strategies layouts, and operations etc. Many manufacturing operations are designed to maximize throughput and lower costs with modest considerations for the crash on inventory levels and distribution capabilities. To improve profitability and efficiency, automotive players are seeking ways to achieve operational excellence, reduce operating cost and enhance customer service through efficient supply chain management.

Keywords: Automotive Industry, Supply chain, Challenges, market potential

1.INTRODUCTION

The most important perspective of modern business management is that individual businesses no longer compete as only autonomous entities, but rather within supply chains [13]. In this emerging competitive environment of the twenty first century, the ultimate success of the business will depend on management's ability to integrate the company's intricate network of business relationships. The term supply chain management refers to cooperative management of materials and information flows between supply chain partners, to reach goals that cannot be achieved acting individually [10] . The purpose of supply chain management is to improve trust and collaboration among supply chain partners, thus improving inventory visibility and the velocity of inventory movement [5]. Emergence of new technologies and the ever- increasing intensity of competition are forcing organizations, firms and industries to reexamine how they do business, meet new customer-driven challenges, companies are re-thinking, restructuring and re-investing their supply chains in order to survive, succeed, excel and even in some specific cases targeting to spearheading competitiveness [9]. Facing more demanding consumers, every chain member has to figure out how to increase flexibility so as to sustain good customer service while controlling or even better decreasing relevant costs from an entire chain standpoint. Indian Automotive industry has been facing major challenges due to fierce competition, increasing operational complexity, technology changes, shortened product lifecycle and frequently changing customer needs. Despite high stocks, the performance of the supply chain has failed to meet customer expectations in terms of delivering the exact specification desired within an acceptable timescale. Today Indian automotive industry is completely capable of producing various kinds of vehicles and can be divided into three broad categories: two-wheelers, cars and heavy vehicles. Vast scope exists for Indian automobile and auto component manufacturers to reduce their logistics costs with the implementation of SCM solutions. As India is a developing country, and fascinatingly, there has

been an upward trend of realization of supply chain optimization. SCM solution market has been making inroads in India and it is being established widely by many automobile industries in the country, particularly manufacturing ones where inventory carrying cost is very high. Several automobile manufacturers in India have taken positive actions to manage their logistics cost and get better customer services and measures have been undertaken by Indian companies to develop their supply chain [12]. Total turnover of the Indian automobile industry is expected to grow from USD 34 Billion in 2006 to USD 122 Billion in 2016 [16]. The automotive industry is today a key sector of the Indian economyand a major foreign exchange earner for the country. Today, India is the 2nd largest tractor and 5th largest commercial vehicle manufacturer in the world. Hero Honda with 3.9 million motorcycles a year is now the largest motorcycle manufacturer in the world. With the growth of transportation system the automotive industry of India is also growing at rapid speed, occupying a vital place on the 'canvases of Indian economy. By exploring Indian automobile sector, it has been found that uncertainties like demand and lead-time have direct impact on managing inventories and managers are facing great difficulties while controlling these parameters [17]. Customer satisfaction and cost reduction are again the key issues to be handled effectively and efficiently. To improve profitability and efficiency, automotive players are seeking ways to achieve operational excellence, reduce operating cost and enhance customer service through efficient supply chain management. Efficient and effective supply chain management plays a very important role in the auto industry. The automotive industry is changing its business model with innovative supply chain to reduce cost, create customer buying experience and quality. Mahindra & Mahindra has implemented one of the most efficient supply chain systems in use by Dealers today, though it still stands room for improvement. The regulatory factors that can stimulate competitiveness of any firm if they are effectively taken care of during the due process of supply chain are: Decision phases, Performance, Drivers and obstacles, Network Designing, Managing & planning inventories, Managing uncertainties, Sourcing, transporting and pricing products, Coordination and technology. Nowadays, a considerable number of companies like Maruti Udyog Ltd., Mahindra and Mahindra, Dell and HP etc. are implementing supply chain management practices. Many of them are striving hard for spearheading competitiveness in their respective sphere through cross-functional collaboration, both within the enterprise and supply chain partners.

1.1 Tribulations in a Supply Chain

The very concept of supply chain management has its own drawbacks to be addressed. The following problems are some of the burning issues [14]:

• **Unjustified networking distribution:** Though this is a unified system yet it lacks deciding parameters related to number, location and network missions of suppliers, production facilities, distribution centers, warehouses, cross-docks and customers [6].

• **Distribution strategy:** In some specific cases supply chain management may not offer any ultimate solution to the questions related to operational control (centralized, decentralized or shared); delivery scheme, e.g., direct shipment, pool point shipping,cross docking, DSD (direct store delivery), closed loop shipping; mode of transportation, e.g., motor carrier, including truckload, parcel; railroad; intermodal transport. Issues related to ocean freight; airfreight; replenishment strategy (e.g., pull, push or hybrid); and transportation control (e.g., owner-operated, private carrier, common carrier, or contract carrier) are also to be explored for ensuring a safer business environment [8].

• **Trade-offs impacts:** Ensuring well coordination in due process of all concerned activities to achieve the lowest total logistics cost is mandatory. Trade-offs may increase the total cost if only one of the

activities is optimized e.g. full truckload (FTL) rates are more economical on a cost per pallet basis than less than truckload (LTL) shipments. If, however, a full truckload of a product is ordered to reduce transportation costs, there will be an increase in inventory holding costs which may increase total logistics costs and therefore it is imperative to take a systems approach when planning logistical activities. These trades-offs are key to developing the most efficient and effective Logistics and SCM strategy [3].

• **Information:** Process integration through the supply chain to share valuable information, including demand signals, forecasts, inventory, transportation, potential collaboration, etc. is another major concern [1].

• **Managing inventory:** Issues related to quality, quantity and locations of inventory, including raw materials, work-in-progress (WIP) and finished goods and ensuring an effective working inventory in unforeseen circumstances are yet to be managed [7].

• **Cash-flow:** Managing the payment and its mode, terms and methodologies for exchanging funds across entities within the supply chain are other functional hurdles to be encountered. Supply chain execution means managing and coordinating the movement of materials, information and funds across the supply chain. The flow is bi- directional i.e. from supplier to customer and vice versa[4].

2.AUTOMOTIVE INDUSTRY SCENARIO

In order to raise profits and customer satisfaction, many international auto players (Ford, Honda, Suzuki and Toyota etc.) are implementing lateral transshipment approach for controlling uncertainties at different echelons in their supply chain which is a topic receiving a great deal of attention in the industry today. The augment in competitive pressure in the business environment has resulted in SCM becoming a serious component of most new competitive strategy models. The automotive industry includes multiple players in extensive,complicated, global supply chains. According to Treleven et al. (2000) [18] many auto companies are using SCM improvements as a constituent of a quick response implementation around the world. On the canvas of the Indian economy, auto industry occupies a prominent place. Due to its deep forward and backward linkages with several key segments of the economy, automotive industry has a strong multiplier effect and is capable of being the driver of economic growth. A sound transportation system plays an essential role in the country's speedy economic and industrial development. The well-developed Indian automotive industry skillfully fulfils this catalytic role by producing a broad variety of vehicles: passenger cars, light, medium and heavy commercial vehicles, multi-utility vehicles such as jeeps, scooters, motorcycles, mopeds, three wheelers, tractors etc. India's quest to become a worldwide auto- manufacturing hub has made the world's top automakers increasingly turn to India for their vehicle components. Riding this achievement and capitalizing on the strengthening demand from domestic auto companies, the Indian auto industry is intensifying the demand and is emerging as one of fastest growing manufacturing sectors, and a worldwide competitive one [12] . However, there is still a lack of noteworthy study of supply chain practices and its presentation in developing countries, in general and India, in particular [2]. Many dominant factors affect decisions made in the automotive world. Consumer preferences decide the current styles, consistency, and presentation standards of vehicles. Government trade, safety, and environmental regulations found incentives and requirements for upgrading and change in design or production. Competitive rivalries and corporate strategies provide equally important momentum for research, design innovations, and changes in the manufacturing process. Auto manufacturers in India and all tiers of the supply chain have immense opportunities to enhance their entire supply chain process

with the successful implementation of SCM solution. At present there are 15 manufacturers of passenger cars & multi utility vehicles, 9 manufacturers of commercial vehicles, 16 of 2/3 wheelers and 14 of tractors besides 5 manufacturers of engines. The automotive industry is today a key sector of the Indian economy and a major foreign exchange earner for the country. Today, India is the 2nd largest tractor and 5th largest commercial vehicle manufacturer in the world. Hero Honda with 3.9 million motorcycles a year is now the largest motorcycle manufacturer in the world. With the growth of transportation system the automotive industry of India is also growing at rapid speed, occupying a vital place on the 'canvases of Indian economy.

All automakers are continually under pressure to recognize consumer preferences, national biases, and new market segments where they can sell vehicles and gain market share. Their capability to be stretchy enough to quickly react to all these pressures is determining theirprospect in the industry. The implications of these factors are enormous and propagate along the supply chain of the automakers in India. The Indian Automotive industry is growing with pace domestically as well as internationally with remarkable milestones. Below figure shows the growth of an Indian Automotive Sector.

2.1 Domestic Market growth

Commercial vehicles segment registered growth of 49.77 percent in April-July 2010 as compared to the same period last year similarly during this period the Medium & Heavy Commercial Vehicles (M&HCVs) registered growth at 74.19 percent and Light Commercial Vehicles grew at 32.87 percent. During April-July 2010, three wheelers sales recorded a growth rate of 18.08 percent, while passenger carriers grew by 20.87 percent and goods carriers grew at 7.24 percent in this period. Two wheelers registered a growth rate of 28.31 percent in April-July 2010.

2.2 Exports

In April-July 2010, overall automobile exports registered a growth rate of 54.46 percent. Passenger vehicles, two wheelers, commercial vehicles and three wheelers segments grew by 9.01 percent, 61.52 percent, 95.31 percent and 141.97 respectively in April-July 2010 over April-July 2009.

3.UNCERTAINTIES EXPLORED BY SUPPLY CHAIN

One of the major issues in a supply chain is ensuring hassle free and smooth functioning of inventory and so the role of inventory as a cushion against uncertainties and unforeseen oddities has been established for a long time [11]. Figure 1 represents the uncertainties that are explored and solved by successful implementation of supply chain.

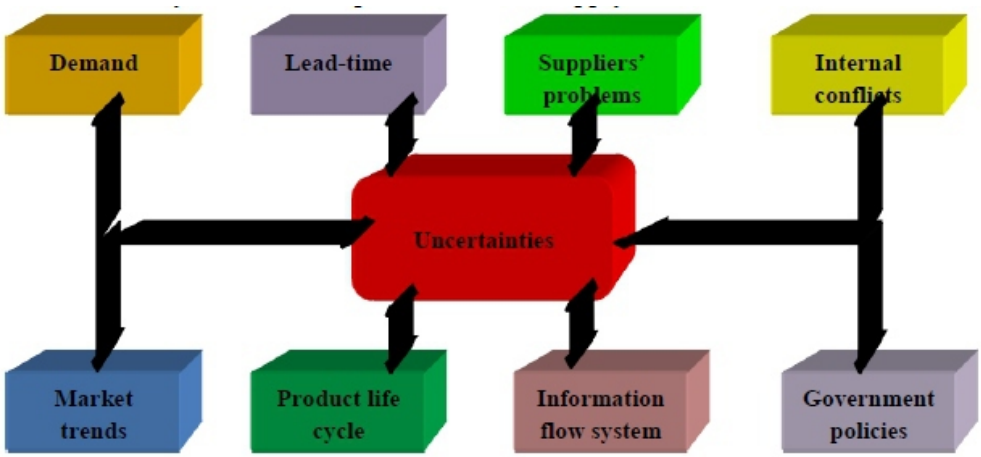

Figure 1. Uncertainties solved by supply chain.

To reduce the impact of these inventory uncertainties, supply chain managers must first understand their sources, the targeted market size, researched feasibility outcomes and the magnitude of their impact. Surprisingly many supply chains do not document and track these variables which may result into over-stock or under-stock, miscalculation of the lead-time and invest in the wrong resources for performance improvement. Besides these factors SCM covers inventory planning, replenishment planning, production scheduling, warehouse management, transportation and logistics management in auto sector [15].

4. CONCLUSION

In today's ever changing markets, maintaining a well-organized and flexible supply chain is critical for every enterprise, particularly given the prevailing volatilities in the business situation with continually shifting and increasing customer expectations. The upstream and downstream coordination engendered by supply chain management with the goal of minimizing uncertainty and variations along the supply chain shows that businesses can no longer wait for that the objective of business can be met just by becoming efficient in itself. Indian automobile and auto components industry is on a roll and there is a massive scope for improvement and augmentation of supply chain in this sector. India has become a most sought after destination for foreign companies to establish their facilities and form alliances with domestic companies. The Indian economy is now gaining momentum in the world of free trade and liberal movements of goods and services between countries. Low cost of manufacturing and conducive government support have been the major drivers for foreign companies investing in India. Therefore efficiency in supply chain will be decisive for India's automobile success.

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Comparative Study of Structural and Magnetic Properties of Cobalt, Lithium and Tin Ferrite

Nishit Kumar Pandey*, Himanshu Kumar Pandey, Amarendra Narayan***, #Amresh Chandra Pandey******

*PGT, ADS +2 High School, Madhupur, Jharkhand,

**Principal, Shlokaa International School, Bhore, Gopalganj,

***Senior Lecturer, PG Deptt of Physics, Patna University, Patna,

****Scientist (Agril. Engg.), Birsa Agricultural University, Ranchi, Jharkhand, India

#Corresponding author : acpandey10@hotmail.com; acpandey2@rediffmail.com

ABSTRACT

We have prepared nano particles of Cobalt Ferrite $CoFe_2O_4$, Lithium Ferrite $LiFeO_8$ and Tin Ferrite $SnFe_2O_4$ with the help of citrate precursor method. Selection of lithium ferrite was done in order to detect any difference in properties due to different size. Their structural and magnetic properties were studied with the help of X- Ray diffractometer and vibrating sample magnetometer. All the samples were annealed at high temperature (450C – 650C), to reduce the chances of obtaining superparamagnetism. On increasing the temperature sharp rise in particle size of Tin ferrite was seen but in lithium ferrite and Tin ferrite, this was not significant. In the context of magnetic properties, the saturation magnetization was observed to be nearly constant with temperature in case of tin and lithium ferrite. The coercivity of Tin and Lithium ferrite was nearly independent of temperature but in cobalt ferrite there was sharp decrease in coercivity with temperature. We expect that present work will help in synthesis of ferrites by a low cost route making analysis of properties easier.

Keywords: Structure Magnetic properties Cobalt Lithium Tin Ferrite

1.INTRODUCTION

For many years, it has been known that magnetic nanoparticles with small size can be considered having single domain and they display properties markedly different from the bulk.1 One of their interesting properties is the presence of magnetic relaxation process that is due to the thermal effect and existence of energy barriers separating the local minima for different equilibrium states of system. So, the magnetic behaviour of a small particles depends on its relaxation time $\tau = \tau_0 \exp[\frac{KV}{K_B T}]$, where is τ_0 about 10^{-10} s and weakly depending on temperature, K_B Boltzmann constant, T is temperature, K and V are anisotropy and average volume2. At very small particle size the anisotropy factor is not sufficient to stop the magnetization vector from switching to a lower energy state.

Another interesting feature of nanoparticles is the due to surface spin disorder which is induced by broken exchange bonds at the surface. As a result, the system should be considered as a core shell structure with ferromagnetically aligned core spins and a spin glass like surface layer, whose thickness can vary1.

2.RESEARCH METHOD

For synthesizing Cobalt ferrite, Cobalt nitrate Co (NO) and Ferric Nitrate Fe (NO) were taken separately in stoichiometric proportion and dissolved in minimal amount of distilled water. In case of Lithium ferrite, we took lithium Nitrate and in case of Tin ferrite, SnCl2 was taken in place of Cobalt nitrate. This solution was mixed with citric acid solution and was heated for two hours with constant

stirring at 68^{0}C. The resulting brown jelly like substance was placed in oven for 24 hours at temperature 80^{0}C and became fluffy like bricks. This was sintered at two temperatures 450^{0}C and 650^{0}C.XRD and VSM measurements for these samples were carried out.

3.RESULTS AND ANALYSIS

The X-Ray diffraction analysis was done and crystallite size was calculated by Scherrer's formula[13,14]. At the same time, the measurements of saturation magnetization, coercivity etc. was done by vibrating sample magnetometer and overall, shown in table 1.

We can see that although the particle size has increased but the percentage rise is very small in lithium ferrite and it is very large in Tin ferrite with temperature. This trend is in agreement with LD Tung et. al.[1] It has also been found that the annealing temperature affects the particle size significantly[4]. The fig 1 is a comparative view of XRD plots, showing peaks approximately at same locations in all samples. We can say that molecular formula of Lithium ferrite is giving it somewhat other structure, but it is Tin ferrite, whose crystallite size changed much.

None of the samples were found to have superparamagnetism because the selected temperature range was high and particles size was large (40 to 90 nm). Tin ferrite is seen exhibiting large change in particle size with rise of temperature. (fig 2)

The following graphs (figure 3 and figure 4) show the VSM plots obtained by us at 450 and 650C ^{0} temperatures.

In very first sight, we can see that in all, the area of the graph has decreased when the temperature was raised. The Tin ferrite graph has very small area, indicating that it is better material for the applications where cyclic magnetization process is being done. On the other side its coercivity and retentivity seems very less as compared to others.

Saturation magnetization of Lithium Ferrite (29.5 to 27.3 emu/g) and Tin ferrite (2.3 to 1.76 emu/g) has very small change in comparison to cobalt ferrite (36.7 to 41.4 emu/g). (figure 5).

There is possibility that lithium ferrite and tin ferrite samples have canted spins at the surface. With increasing size, due to increasing temperature, the thickness of shell having canted spin might have increased in proportion, the result being reduced saturation magnetization[5,6]. This study can be extended further with the help of Mössbauer spectra in which shift in peaks may assure about existence of core shell model[3, 4].

The wohlfarth model assumes that there is a uniform magnetization throughout the particle and it remains so throughout the rotation process [10]. Generally the energies required to reverse the spin orientation within single domain are larger than those needed in bigger ones so coercivity is larger in small particles. In other word, when particle size decreases to single domain, the domain rotation is preferred, consuming more strength of external field making coercivity high. At the blocking temperature, when thermal energy is sufficient to break the anisotropy barrier, the coercivity gets zero. Below this temperature, the coercivity is the field which together with thermal energy can overcome the anisotropy. Therefore coercivity increases with size, below blocking temperature[10] (Figure 6)

In our samples, we easily conclude that in case of lithium ferrite (171.9 to 134.7 G) and Tin ferrite (186.8 to 171.6 G), there is no significant increase in coercivity with temperature and say particle size. It can be attributed to core shell structure of them already discussed above10. In all the samples, the coercivity is more at lower temperature which verified the established theories about dependence of coercivity with temperature[11].

Retentivity of cobalt ferrite was seen to decrease with temperature (19.5 to 16.8 G). The increasing temperature causes vigorous vibrations of magnetization vector and memory of earlier magnetization is erased. Sample of Tin ferrite also demonstrated fall in retentivity (0.54 to 0.3 G) but lithium ferrite shows rise in retentivity (7.69 to 8.3 G) with temperature. (Figure 7)

This anomaly can be attributed if we assume varying thickness of shell having canted spins surrounding the core. In Lithium ferrite the enhancement in thickness of canted spin surface layers may have screened the inner core from external changes. The increasing fraction of atoms having canted spin can also lead to this anomaly.

After plotting the graphs, it could be seen that in Tin ferrite the change in particle size with temperature is maximum, but saturation magnetization, coercivity and retentivity changed minimally with temperature. On the other hand, Cobalt and Lithium Ferrite show little change in particles sizes, but there magnetic properties change substantially, although in opposite manner. This trend may a coincidence but should be studied further.

The purity of samples was also analyzed with ICDD database available to us. The sample $CoFe_2O_4$ at 450^{0}C was found containing traces of FeO in some amount, but FeO_3 was not found. Low intensity peaks at 33.162, 35.630 and 49.465 degrees indicate presence of very small amount of Fe_3O_4 in this. At higher temperature these impurities are almost absent. Tin Ferrite sample was also free from SnO, FeO, Fe_3O_4 etc, but had some Fe_2O_3 at 450^{0}C as some lines indicating its presence are seen.

Table 1. The table of data obtained

Sample 450^{0}C	**Crystallite size (nm)**	**Saturation Magnetization Emu/g**	**Coercivity (G)**	**Retentivity (G)**
$CoFe_2O_4$	43.4	36.7	1460	19.5
$SnFe_2O_4$	45	2.3	186.8	0.54
$LiFe_5O_8$	89.6	29.5	171.9	7.69
650^{0}C				
$CoFe_2O_4$	46.5	41.4	654.1	16.8
$SnFe_2O_4$	89.6	1.76	171.6	0.3
$LiFe_5O_8$	92.7	27.3	134.7	8.3

Figure 1. XRD plots of samples (comparative view)

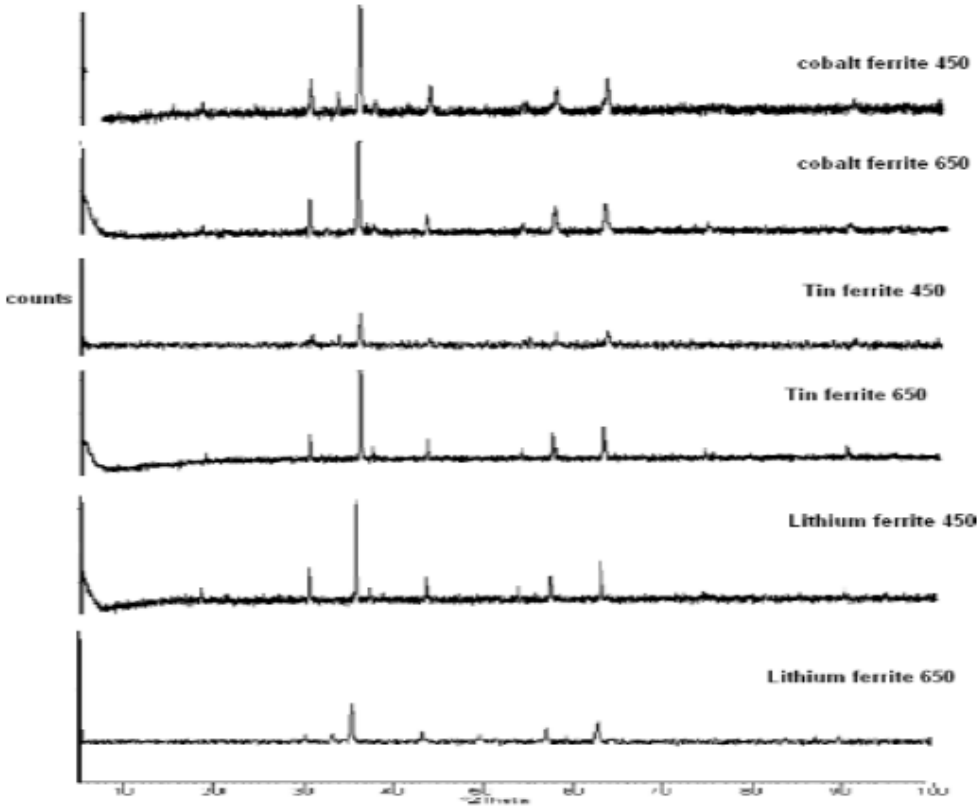
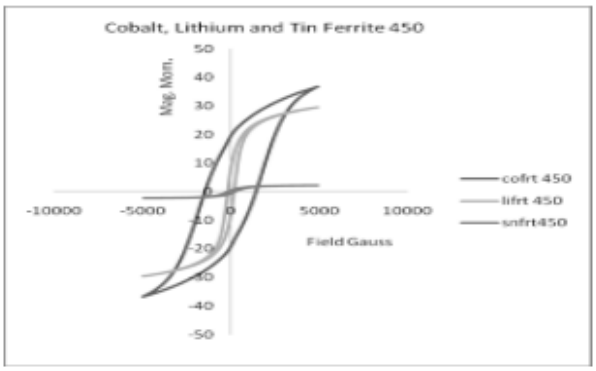


Figure 3 VSM plots of samples at 450℃

Figure 2 Particles sizes at 450℃ and 650℃



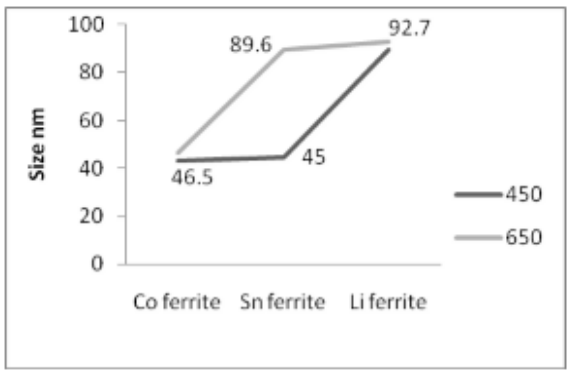
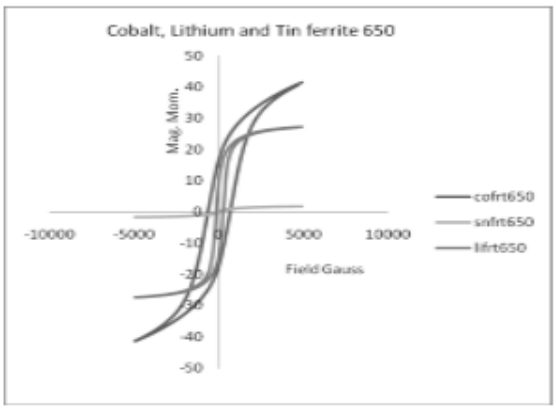


Figure 4 VSM Plots of samples at 650℃

Figure 5 Saturation magnetization of samples



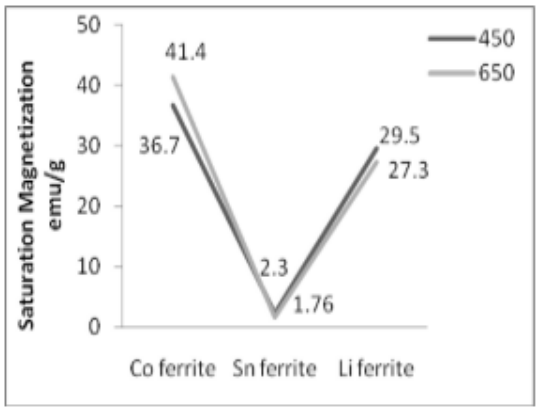


Figure 6 Coercivity of samples

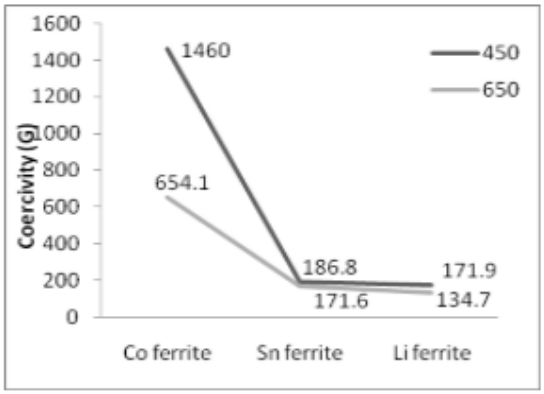
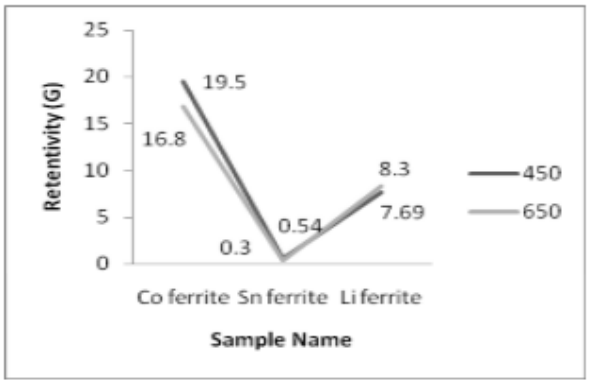


Figure 7 Retentivity of samples



4.CONCLUSION

We can conclude that lithium and tin ferrite have completely different trends in magnetic and structural and magnetic properties and their potential as the future smart materials is yet to be explored. In all the cases, we have found that phases were almost clear, but impurities were seen less in fraction at higher temperature. All the samples were sufficiently good, but contained less impurities at high temperature. This may be due to thermal breaking of oxides of them. Perhaps higher temperature of production is most suited for these ferrites.

This type of materials needs further investigation in order to isolate trends in properties, so that they may be used to synthesize the materials with controlled properties in future.[12]

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Bianchi Type-III Cosmic String Coupled with Perfect Fluid in Bimetric Relativity

V. Mahurpawar
Associate Professor of Mathematics
Govt. Autonomous P.G. College, Chhindwara (M.P.), India

ABSTRACT

Five- dimensional Bianchi type-III cosmic string coupled with perfect fluid is considered in Rosen's bimetric theory of gravitation. It is observed that cosmic string couple with perfect fluid does not exist. Hence only vacuum model can be obtained.

Keywords: Bianchi type-III; cosmic string; perfect fluid; vacuum model; bimetric relativity.

1. INTRODUCTION

Rosen [6] has modified the theory of gravitation by introducing a second metric tensor Y_{ij} besides the Riemannian metric tensor g_{ij} at each point of space-time. Accordingly at each point of space-time one has two line elements-

$$ds^2 = g_{ij}\,dx^i dx^j . \quad (1)$$

$$d\varsigma^2 = \gamma_{ij}\,dx^i dx^j \quad (2)$$

The g_{ij} describe gravitation and interacts with matter. The back ground metric γ_{ij} has no direct physical significance but appears in the field equations. Therefore it interacts with g_{ij} but not directly wit matter. One can regard γ_{ij} as giving the geometric that would exist if there were no matter. ds is the interval between two neighboring events as measured by a measuring rod and a clock. The interval $d\varsigma$ n abstract or geometric quantity not directly measurable.

Rosen has proposed the field equations by bimetric relativity as-

$$K_i^j = N_i^j - \frac{1}{2}\delta_i^j N = -8\pi\kappa T_i^j \quad (3)$$

where $N_i^j = \frac{1}{2}\gamma^{\alpha\beta} g^{hi} g_{hj} \,|\alpha\,|\beta$ (4)

Here vertical bar (|) denotes the γ- covariant differentiation.

$$N = N_\alpha^\alpha,\ K = \left(\frac{g}{\gamma}\right)^{1/2} \quad (5)$$

$$g = det\ g_{ij}\ ,\ \gamma = det\ \gamma_{ij} \quad (6)$$

and T_i^j = Energy momentum tensor

equation (3) is obtained from Einstein field equation –

$$G_i^j = R_i^j - \frac{1}{2}\delta_i^j R = 8\pi\kappa T_i^j \quad (7)$$

Pursuing all the derivative o g_i^j of γ- differentiation. Using γ l derivatives does not change the physical contents of the field equations but it has some advantages. One can derive the Einstein field equations for empty space from the variation principle. Rosen [7] modified the version of bimetric relativity in accordance with perfect cosmological principle. In this new version the back ground metric γ_{ij} is considered as a space- time of constant curvature which has the same degree of maximal symmetry as that of the flat space-time. It is very interesting to note that "Black hole" a creation of general theory of relativity does not exist in Bimetric theory of relativity.

Wang Xing et al [8], R. Bali [2] studied Bianchi type -III cosmological models with bulk viscosity in general relativity. Bianchi type- III string cosmological model with time dependent bulk viscous was studied by Raj, Bali [2] the behavior of model with presence and absence of bulk viscous was discussed. Adhav et al[1] were studied both meson afield and masonic perfect fluid models and found that only vacuum models can be obtained. Ronghe and Mahurpawar[5] ,Mahurpawar[4] were studied four dimensional Bianchi type- III models taking the energy momentum tensors cosmic sting and cosmic string coupled with perfect fluid and conclude that there is no contribution of cosmic string and cosmic string coupled with perfect fluid.

In this paper I have shown that higher five- dimensional cosmic string coupled with perfect fluid does not exist in Rosen's biometric theory of gravitation. Hence a vacuum model is obtained

2. FIVE- DIMENSIONAL BIANCHI TYPE –III MODEL AND SOLUTIONS-

We considered here the five dimensional space-time described by Bianchi type-III metric-

$$ds^2 = dt^2 - A^2dx^2 - B^2e^{2\alpha}\,dy^2 - C^2dz^2 - D^2du^2 \quad (8)$$

where A,B, C and D are functions of "t" and α is a constant.

The flat metric corresponding to equation (8) is

$$dç^2 = dt^2 - dx^2 - dy^2 - dz^2 - du^2 \quad (9)$$

$$T^j_i = T^j_{istring} + \epsilon + v^j_i - \mathrm{p}g^h_i \quad (10)$$

$$T^j_{istring} = \rho u_i u^j - \lambda x^j_i \quad (11)$$

Where$\rho$is the rest energy density of the system of string, λ is the tension density of the string, we consider

$$= \rho_p + \lambda \quad (12)$$

Hereρ_p is the partial energy density attached to the string. The cosmological co-ordinate system is taken along x-direction i.e. $v_5\, v^5 = 1.u^i$ represents the five- velocities and x^j represent an anisotropic direction i.e. direction of string.

We have $u_i u^i = -x_i x^j = 1\ ,u_i x^j = 0$ (13)

εbeing the density p is the pressure . The components of energy momentum tensor for the cosmic string coupled with perfect fluid are-

$$T^i_i = -p + \lambda\ , T^2_2 = -p = T^3_3 = T^4_4 \text{ and } T^5_5 = \varepsilon + \rho \quad (14)$$

Rosen's Field equations (3) of biometric relativity for Bianchi type –III metric (8) with the help of (9) and equations (10) to(12) can be written as –

$$\frac{A_4}{A}_4 + \frac{B_4}{B}_4 + \frac{C_4}{C}_4 + \frac{D_4}{D}_4 = -16\pi\kappa - p + \lambda \quad (15)$$

$$\frac{A_4}{A}_4 - \frac{B_4}{B}_4 + \frac{C_4}{C}_4 + \frac{D_4}{D}_4 = 16\pi\kappa p \quad (16)$$

$$\frac{A_4}{A}_4 + \frac{B_4}{B}_4 - \frac{C_4}{C}_4 + \frac{D_4}{D}_4 = 16\pi\kappa p \quad (17)$$

$$+ \frac{B_4}{B}_4 + \frac{C_4}{C}_4 - \frac{D_4}{D}_4 = 16\pi\kappa p \quad (18)$$

$$\frac{A_4}{A}_4 - \frac{B_4}{B}_4 - \frac{C_4}{C}_4 - \frac{D_4}{D}_4 = -16\pi\kappa\,\varepsilon + \lambda \quad (19)$$

Using equations(15) to (19) we obtain

(20)

$$2\,\frac{A_4}{A}_4 = 16\pi\kappa p$$

$$2\,\frac{A_4}{A}_4 = -16\pi\kappa - p + 2\lambda + \varepsilon \quad (21)$$

Using equation (20) and (21) we get- (22)

$2\lambda + \varepsilon = 0$

By reality condition $\lambda \geq 0$ and ≥ 0i.e.$\lambda = 0 = \varepsilon$ (23)

With the help of equation (23) the field equations (15) to (19) can be written as

$$\frac{A_4}{A}_4 + \frac{B_4}{B}_4 + \frac{C_4}{C}_4 + \frac{D_4}{D}_4 = 0 \quad (24)$$

$$\frac{A_4}{A}_4 - \frac{B_4}{B}_4 + \frac{C_4}{C}_4 + \frac{D_4}{D}_4 = 0 \quad (25)$$

$$\frac{A_4}{A}_4 + \frac{B_4}{B}_4 - \frac{C_4}{C}_4 + \frac{D_4}{D}_4 = 0 \quad (26)$$

$$\frac{A_4}{A}_4 + \frac{B_4}{B}_4 + \frac{C_4}{C}_4 - \frac{D_4}{D}_4 = 0 \quad (27)$$

$$\frac{A_4}{A}_4 - \frac{B_4}{B}_4 - \frac{C_4}{C}_4 - \frac{D_4}{D}_4 = 0 \quad (28)$$

By Equations (24) to (28)

$= e^{1c^t}$ (29)

$= e^{2c^t}$ (30)

$= e^{3c^t}$ (31)

$= e^{4c^t}$ (32)

Using equations (29) to (32)

The line element (8) becomes-

$$ds^2 = dt^2 - e^{2c_1^t}dx^2 - e^{2c_2^t}e^{2\alpha}dy^2 - e^{2c_3^t}dz^2 - e^{2c_4^t}du^2 \quad (33)$$

By proper choice of coordinates this metric can be transform-

$$ds^2 = d\tau^2 - e^{2\tau}\,dx^2 + e^{2x}\,dy^2 + dz^2 + du^2 \quad (34)$$

It is observed that the equation (34) is free from singularity at $\tau = 0$

3. CONCLUSION

We have studied Five-dimensional Bianchi Type-III anisotropic cosmological model taking cosmic string coupled with perfect fluid an energy-momentum in Rosen's Bimetric theory of gravitation and we observed that there no contribution of cosmic string coupled with perfect fluid to this model so Bianchi type-III model is free from singularity at τ=0, a vacuum model can be found.

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Thermal Decomposition Kinetics and Mechanism of MN(II), NI(II) and CU(II) Complexes of 3-formylindole-2- Amino-5-Bromo Benzoicacid

Aby Paul*, Joby Thomas K, Reeja Johnson*****
**Research Division Department of Chemistry,
St.Thomas College (autonomous),Thrissur

ABSTRACT

Manganese(II), Nickel(II) and Copper(II) complexes of the Schiff base, 3-formylindole-2-amino-5-bromobenzoicacid were prepared and characterized by various analytical techniques such as 1Hnmr, 13Cnmr, infrared, mass, electronic spectroscopy, elemental, magnetic and conductance studies. Structural evalution established that a stoichiometry exists between the metal and ligand and the Chelates possess general formula [ML(Ac)(H2O)3]. Geometry of all the complexes was found to be octahedral Thermal decomposition kinetics and mechanism of the metal chelates were studied by TGA and DTA techniques. The TG curves of Mn(II) and Ni(II) showed a three stage decomposition pattern and Cu(II) complex showed a two stage decomposition pattern, which is supported by DTA data.

Keywords: Complexes; Kinetic; Themogravimetric studies.

1.INTRODUCTION

Transition metal complexes of Schiff bases have important technical applications. The thermal properties of metal chelates of a wide variety of chelating ligands were studied extensively by Wendlandt and co-workers[1-3] and Hill and co-workers[4,5]. Such studies on thermal decomposition and kinetics of metal chelates with Schiff bases have been done by many researchers[6-9]. In the present course of studies, synthesis, characterization and thermoanalytical data of three transition metal complexes of a novel potential Schiff base, 3-formylindole-2-amino-5-bromobenzoicacid (3FI2A5BBA) were carried out.

Non –isothermal methods have been widely used to study the kinetics and mechanism of thermal decomposition of solids[10,11]. This study therefore attempts to establish the mechanism of decomposition of [MnLAc(H2O)3], [NiLAc(H2O)3] and [CuLAc(H2O)3] from TGA and DTA experiments.

2.RESEARCH METHOD

The ligand 3-formylindole-2-amino-5-bromobenzoic acid (3FI2A5BBA) was prepared by refluxing an ethanolic mixture(1:1) of 2-amino-5-bromobenzoic acid and 3-formylindole for five hours. Yellowish crystals separated on cooling were purified by recrystallization from ethanol and characterized on the basis of analytical and spectral studies, mp 1550C. Samples of Mn(II), Ni(II) and Cu(II) chelates of 3-formylindole-2- amino-5-bromobenzoic acid(3FI2A5BBA) were prepared by adding ethanolic solution of the ligand to an aqueous solution of metal acetate in 1:1 ratio. The resulting solution was refluxed for about 3 hours, concentrated and cooled in an ice bath. The complex formed was filtered, washed with ethanol and dried in a vaccum desiccator.

Physicochemical techniques such as solution conductance, magnetic susceptibility measurements and spectral studies like 1Hnmr, 13Cnmr, infrared, mass and UV-Visible have been used to elucidate the structure and geometry of the complexes.

Thermogravimetric and differential thermal analysis curves were traced using a Shimadzu DT40 thermobalance in an atmosphere of static air. A constant heating rate of 100Cmin-1 and a sample mass of 5-10 mg were employed for the entire study. The mass loss considerations and X-ray diffraction data confirmed the products to the corresponding oxides. Mechanistic and non mechanistic calculations were performed with a Pentium IV computer using EXCEL and origin softwares. Evaluation of the mechanism of reactions from nonisothermal methods has been discussed by Sestak and Berggren[12] and Satava[13]. For evaluating kinetic parameters from mechanistic equations given by Satava, Coats and Redfern[14] following equation was used in the general form and the various g(α) values were substituted. This has been recommended to be one of the best solutions by several authors[15,16]. Along with the mechanistic equations, two non mechanistic methods suggested by Coats and Redfern and Horowitz[17] were also used for comparison.

$$\ln (\alpha)/T^2 = \ln AR/\varphi E - E/RT$$

where α = fraction of the compound decomposed at time T, φ, rate of heating in deg.min-1, R= Universal gas constant, A= frequency factor and E =activation energy

3.RESULTS AND ANALYSIS

Molar conductance, magnetic susceptibility and analytical data are presented in Table 1. The complexes exhibit molar conductance in the range 2-10(Ω-1cm2mol-1) indicating the non electrolytic nature.

Table 1 Microanalytical, magnetic and conductance data of transition metal complexes of 3-formylindole-2-amino-5-bromobenzoic acid (3FI2A5BBA)

Compound	Colour	M.P (^{0}C)	Metal% (Cald)*	C %	H %	N%	μ_{eff} (BM)	Ω **
3FI2A5BBA (LH)	Yellow	155	-	52.3 (56.14)	3.88 (3.21)	8.66 (8.18)	-	-
$[MnLAc(H_2O)_3]$	Grey	240	10.65 (10.81)	44.23 (44.44)	3.34 (3.73)	5.21 (5.50)	6.10	18
$[NiLAc(H_2O)_3]$	Grey	278	11.85 (11.50)	42.47 (42.10)	3.19 (3.70)	5.51 (5.46)	2.58	4
$[CuLAc(H_2O)_3]$	Green	340	12.37	41.28	2.01	5.02	2.00	15

***(Calculated values are given in parenthesis) ** Molar conductance in ($\Omega^{-1}cm^2mol^{-1}$)**

In the infrared spectrum of the ligand, the significant absorption frequencies appeared at 1610cm^{-1}and 1446cm-1 can be attributed to the stretching frequencies of the carbonyl bond of the carboxylic acid group. A strong band displayed at 1570cm^{-1}is a clear evidence for –C=N group. All the C-H vibrations of ligand appeared in the range 3050-3100cm $^{-1}$. The complexes exhibited slight deviations from the IR spectrum of the free Schiff base ligand. All the symmetric and asymmetric stretching vibrations of the carboxylate group in metal chelates changed into the lower frequency regions indicates chelation of the ligand to the metal atom through the carboxylate moiety[18]. All the studied metal chelates exhibited their characteristic stretching frequency for C=N group in the region 1540-1550cm^{-1} which falls to the lower region compared to the azomethine stretching frequency of the free Schiff base (1570cm^{-1}). These results also support the argument that one of the coordination sites of the bidentate Schiff base

ligand is the azomethine nitrogen[19]. New bands appeared in the IR spectrum of the metal chelates at ~ 510cm-1and 640-670cm^{-1} can be regarded as the presence of newly formed metal-nitrogen and metal-oxygen coordinate bonds respectively. In chelates, the presence of coordinated water is confirmed by the observation of a broad band at 3300cm^{-1}[20].

The sites of coordination of the Schiff base to the metal ions were further confirmed by recording the 1Hnmr and 13Cnmr spectra of the metal chelates. In the 1Hnmr spectra of all the metal complexes, the signal due to the carboxylic acid proton was absent, showing that one of the linkages by the ligand to the metal ion is through the carboxylate part of the Schiff base, after deprotonation. Also a noticeable shift for the azomethine proton peak to the downfield regions, suggests that second coordinating moiety of the ligand is the azomethine nitrogen. In the 13Cnmr spectra of all complexes, the peak due to the azomethine carbon atom in the metal chelates are shifted to downfield region which is an indication of the coordination through the C=N moiety. Even though two different carboxylate groups were present in the metal chelates, which originated from the ligand and the acetate respectively, considerable downward shift was noticed only for the signal of carboxylic acid carbon of the chelated ligand.

In the mass spectrum of the Schiff base, the M+ peak was absent. The base peak observed at m/z 144 can be assignable to the fragment [C9H8N2]+ formed by the loss of bromobenzoic acid part of the ligand.

Electronic spectrum of the Schiff base was characterized by two intense bands lying at 27548cm^{-1} and 37735cm-1. The intense peak observed at 28571cm $^{-1}$ can be attributed due to $\pi \rightarrow \pi^*$ transition. The electronic spectrum of the Mn(II) complex revealed a band at 24800 cm-1 which support the presence of Mn(II) in an octahedral geometry [21]. The effective magnetic moment value of Cu(II) chelate was 2.0 BM, which is in agreement with the value found for octahedral copper complexes [22]. The electronic transitions in the Ni(II) complex gave three intense bands at 14200, 18864 and 24243cm-1, which can be assigned to 3A2g(F) → 3T2g , 3A2g(F) → 3T1g(F) and 3A2g(F)→3T1g(P) transitions respectively. In the octahedral field, Cu(II) chelate is expected to display a band in the electronic spectrum which can be assigned due to 2Eg→2Tg electronic transition. In the present case, the same signal appeared at 20100cm^{-1}. In addition to this, a band with high molar extinction coefficient was observed at 27640cm-1, assignable to the Laporte forbidden LMCT band. The magnetic moment value and the electronic spectral data thus confirmed the octahedral geometry of the Cu(II) chelate. On the basis of the above results, the structure of the ligand 3FI2A5BBA was confirmed and shown in the Fig.1. From the spectroscopic and magnetic studies octahedral geometry can be assigned to all these complexes of 3FI2A5BBA (Fig. 2)

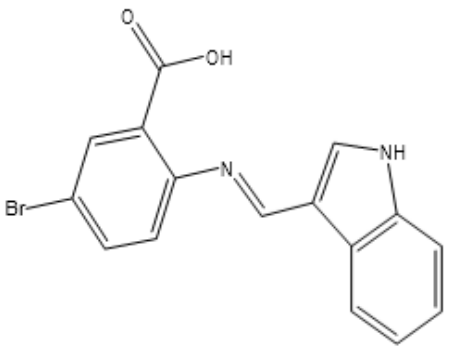

Fig. 1 Structure of 3FI2A5BBA

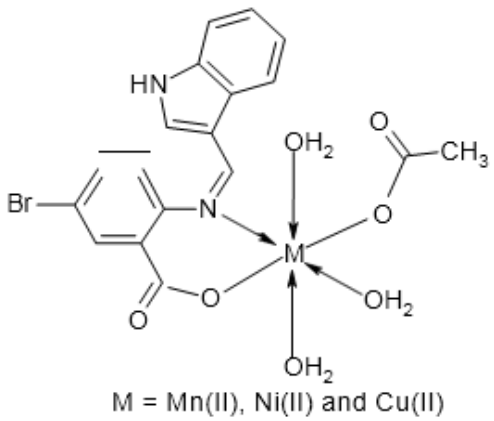

Fig.2 Structure of the metal complexes

3.1 Thermal studies

The TG curves of Mn(II) and Ni(II) complexes show a three stage decomposition pattern which is supported by DTA data (Fig.3 and Fig.4) . The first stage decomposition of both the Mn(II) and Ni(II) complexes consist of the removal of the coordinated water molecules. The second stage in both cases has two sub stages. The two sub stages of second stage decomposition of Mn(II) complex is quite overlapping and overall mass loss may due to the removal of indole and bromo parts of the ligand. In the case of Ni(II) complex the first substage(IIa) is due to the loss of indole and azomethine moieties of the Schiff base. The bromine part of the ligand is lost in the second substage(IIb). The loss of three water molecules and acetate part, indole and bromo part of the ligand takes place in the first stage decomposition pattern of the copper complex (Fig.5). The Cu(II) complex exhibits a well clear two stage decomposition pattern where the second stage may be due to the loss of the rest part of the ligand. In the third stage decomposition pattern of both Mn(II) and Ni(II) complexes there is a loss of acetate part and the rest of the ligand moieties.

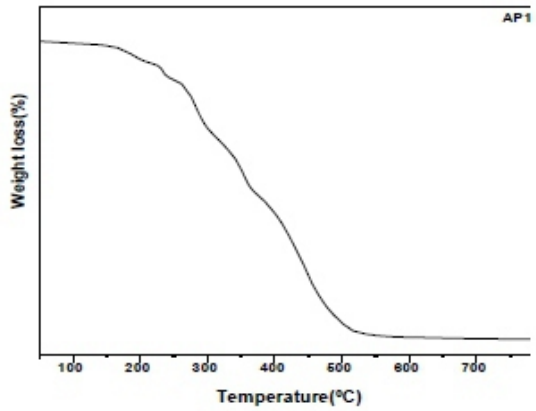

Fig.3 TG curve of $[MnLAc(H_2O)]_3$

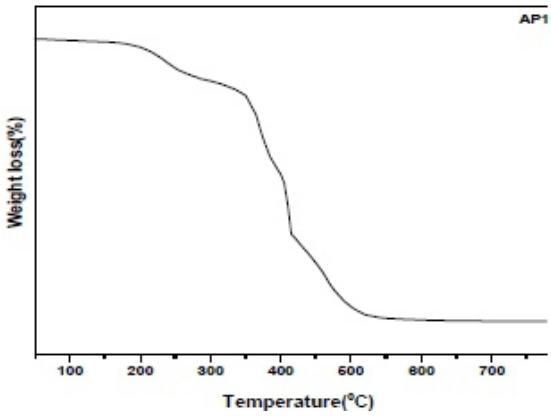

Fig. 4 TG curve of $[NiLAc(H_2O)]_3$

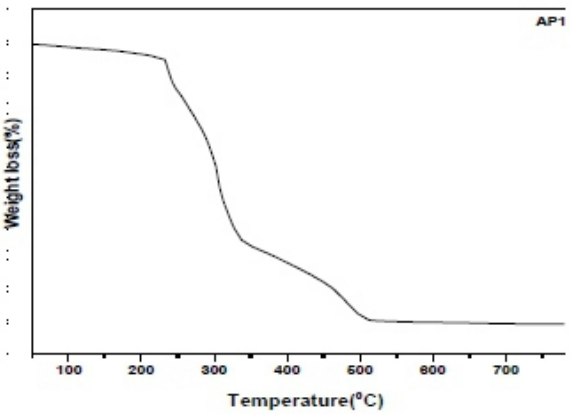

Fig. 5 TG curve of $[CuLAc(H_2O)]_3$

3.2 Decomposition Kinetics

Thermal decomposition data of the three metal chelates are represented in Table 2. Data from independent pyrolytic experiments are also given in this table. The non-isothermal TG curves have been subjected to mathematical analysis using the integral method of Coats-Redfern and the activation parameters have been evaluated for all these complexes. The most suitable parameters were selected with the aid of correlation coefficient which is shown in Table 3 and 4. The mechanism of decomposition has been established from the TG data using the nine mechanistic equations in comparison with the integral method (Coats and Redfern). The kinetic parameters obtained show maximum correlation between F1 mechanism, (Mampel equation i.e. $-\ln(1-\alpha) = kt$) based on random nucleation with one

nucleus at each particle and the Coats-Redfern equation with n=1, for the second and third stage decomposition pattern of manganese complex. Similarly the values of kinetic parameters obtained from various mechanistic and non mechanistic equations, particularly the Coats-Redfern equation, revealed that IIa and III stages of decomposition of Ni(II) chelate follows R mechanism, phase boundary reaction, cylindrical symmetry (n=1/3), whereas IIb stage of decomposition obeys equation V; Mampel equation with random nucleation. It is observed that the F1 mechanism based on Mampel equation gives maximum correlation for the first and second stage decomposition of [CuLAc(HO)]. Thermal decomposition studies established the relative stability of these complexes follows the order $[MnLAc(H_2O)]_3 < [NiLAc(H_2O)]_3 \leq [CuLAc(H_2O)]_3$.

Table 2 Thermal decomposition data (0C) of Mn(II), Ni(II) and Cu(II) complexes of 3FI2A5BBA

Complex	Stage	Temp range in TG	Peak temp in TG	Peak temp in DTA	Loss of mass %		
					From TG	Cald.	From Pyrolysis
$[MnLAc(H_2O)_3]$	Ia	76-231	194	199			
	Ib	231-241	233	237	10.35	10.61	-
	IIa	241-301	276	281			
	IIb	301-396	346	350	38.09	38.31	-
	III	396-531	416	425	35.71	35.57	
					84.15	84.49	84.5
$[NiLAc(H_2O)_3]$	I	120-255	220	222	10	10.53	-
	IIa	255-385	365	370	27.35	27.88	-
	IIb	385-410	405	408	15.09	15.39	-
	III	410-505	465	472	33.12	31.64	-
					85.56	85.43	85.37
$[CuLAc(H_2O)_3]$	I	6-352	280	287	58.85	59.46	-
	II	352-987	422	428	22.41	22.01	-
					81.26	81.47	81.41

Table 3 Kinetic parameters of the decomposition of Mn(II) and Ni(II) complexes of 3FI2A5BBA from TG using non-mechanistic equation (Coats-Redfern) and its correlation with mechanistic equation

Complex (Stage)	Non-mechanistic/ mechanistic equation	Kinetic parameters*				Order (n)	Mechanism of decomposition
		E	A	ΔS	r		
$[MnLAc(H_2O)_3]$ Stage IIa	Coats-Redfern	185.11	$1.51x10^{15}$	40.6	0.9982	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	185.11	$1.51x10^{15}$	40.6	0.9982		
Stage IIb	Coats-Redfern	133.46	$7.69x10^{8}$	-80.86	0.9963	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	133.46	$7.69x10^{8}$	-80.86	0.9963		
Stage III	Coats-Redfern	140.16	$4.53x10^{7}$	-105.29	0.9800	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	140.16	$4.53x10^{7}$	-105.29	0.9800		
$[NiLAc(H_2O)_3]$ Stage IIa	Coats-Redfern	60.24	$1.34x10^{2}$	-210.48	0.9686	1/3	R_2 mechanism. Phase boundary reaction. Cylindrical symmetry
	Equation VIII	62.10	$1.03x10^{2}$	-212.64	0.9658		
Stage IIb	Coats-Redfern	390.36	$1.54x10^{28}$	287.88	0.9974	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	390.36	$1.54x10^{28}$	287.88	0.9974		

Stage III	Coats-Redfern	57.48	$1.2x10^8$	-97.79	0.9993	1/3	R_2 mechanism. Phase boundary reaction. Cylindrical symmetry
	Equation VIII	64.22	$2.63x10^8$	-91.258	0.9984		
$[CuLAc(H_2O)_3]$ Stage I	Coats- Redfern	109.7	$4.99x10^7$	-102.66	0.997	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	109.7	$4.99x10^7$	-102.66	0.997		
StageII	Coats-Redfern	93.98	$1.71x10^4$	-170.9	0.985	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	93.98	$1.71x10^4$	-170.9	0.985		

***E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$**

4. CONCLUSION

- Novel heterocyclic Schiff base 3-formylindole-2-amino-5-bromobenzoic acid (3FI2A5BBA) and its metal chelates were synthesized
- Structures of the ligand and chelates were established by various analytical methods and it was proved that 1:1 stoichiometry exists between the ligand and the metal ion. Octahedral geometry was suggested for these chelates
- The thermal behavior of metal complexes shows that the lose of hydrated water molecules occurs in the first step, immediately followed by decomposition of ligand molecules in the subsequent steps.
- Thermal data showed degradation pattern of the complexes. TG and DTA studies also guided to derive the thermodynamic, kinetic and reactivity behavior of these materials and metal-ligand interaction.
- Thermal decomposition studies established the relative stability of these complexes follows the order [MnLAc(H2O)3] < [NiLAc(H2O)3] < [CuLAc(H2O)3].

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The Kinetic Study of the Solvent Effect of Polyhydric Alcohol on the Thermodynamic Extensive Properties of the Catalysed Solvolysis of Propionate Ester

Sushma Kumari[1], Rakesh Kumar Ranjan [2] and R . T. Singh [3]

[1] Research Scholar, Department of Chemistry, V.K.S.University, Ara, Bihar, India.

[2] Research Scholar, Department of Physics, V.K.S.University, Ara, Bihar, India.

[3] Professor and Formerly H.O.D. Chemistry & the Dean of the Faculty of Science, V. K. S. University,Ara,Bihar, India.

A B S T R A C T

The changes observed and evaluated due to the solvent effect of a dipolar protic or dipolar aprotic solvent on the thermodynamic extensive properties of solvolysis of the propionate ester have been found responsible for changes in its biochemical and medicinal properties.With a view to highlight the effect of a polyhydric alcohol (dipolar protic solvent) on the extensive thermodynamic properties of propionate ester, the kinetics of alkali catalysed hydrolysis of ethylpropionate was studied in aquo-glycerol reaction media.

From the enhancement observed in DG values with simultaneous decrease in the values of DH and DS* of the reaction, it is inferred that the organic co-solvent glycerol acts as entropy controller and enthalpy stimulator solvent for alkali catalysed hydrolysis of ethyl propionate.*

The numerical value of Iso-kinetic temperature of the reaction which comes to be nearly 286.0 (below 300) indicates that there is weak but considerable solvent-solute interaction in the aquo-glycerol reaction media.

Key words: Extensive properties, Trihydric alcohol, Dielectric effect Solvation and desolvation, Weak solvent -solute interacion

INTRODUCTION :

Though different kinecists[1-2] of the kinetic field have reported the effect of different solvents on the rates, mechanism and the thermodynamic properties of hydrolysis of simple esters, but, a little attention has been paid towards the studies of solvent effect of polyhydric alcohol on the rate, mechanism and extensive thermodynamic properties and solvent-solute interaction for alkali catalysed solvolysis of ethyl propionate. In order to highlight the above noted facts, it has been proposed to study the kinetics of alkali catalysed hydrolysis of ethyl propionate in aquo-glycerol reaction media.

EXPERIMENTAL & CALCULATION :

The kinetics of alkali catalysed hydrolysis of ethyl propionate was carried out separately in the different aquo- organic co-solvent media (aquo-glycerol) prepared by adding different volumes of glycerol (20 to 80%). The strength of the solution was kept 0.1 M with respect of NaOH and 0.05 M with respect to the ester. The reaction was found to follow the second order kinetic equation and the evaluated values of specific rate constants have been recorded in Table - I. For studying the effect of change of concentration of organic component (glycerol), the variation of log k values of the reaction with its mol % in the reaction media has been enlisted in Table - II. Using Arrhenius equation, the iso-composition and iso-dielectric activation energies values of the reaction were evaluated and are recorded respectively in

Table - III & IV. The thermodynamic activation parameters such as ΔH*, ΔG and ΔS* have been evaluated using Wynne-Jones and Eyring[3] equation and their consolidated values have been shown in Table - V. For studying the mechanism of the reaction, the evaluated number of water molecules associated with the transition state of the reaction at different temperatures have been depicted in Table - VI.

RESULTS AND DISCUSSION :

Effect of Solvent on the Specific Rate Constants of the Reaction:
In order to highlight the effect of the solvent on the specific rate constant values of the reaction, the log k values were plotted against the mole % of the organic co-solvent glycerol (their values from Table - II) as shown in Fig. - 1, and were found to follow decreasing trends. However, the depletion found in the rate with increasing mole % of the organic co-solvent (glycerol) at all the temperatures follow smooth path following two intersecting straight lines at about 16.25 mol % of glycerol having different numerical values of the slope (of similar nature) before and after the point of intersection (at about 16.25 mol % of glycerol in the reaction media). From the plots, it was found that with increasing the temperature of the reaction, the degree of depletion in the rate constants of the reaction becomes steeper.

However, the possible rate depleting factors in the rate can be listed as follows:

(i) decrease in the bulk dielectric constant value of the medium,
(ii) decrease in the polarity of the reaction media on adding less polar glycerol to it

The above noted two depleting factors are quite in operation and this is quite in agreement with the theory of Hughes and Ingold[4] that the rate ought to decrease with decreasing dielectric constant of the reaction media. Such decrease in rate constant with increasing proportion of the organic co-solvent like glycerol has been reported earlier by Laidler and Landskroener[5], Akanksha & Singh et al[6]. and Singh & Hafizee et al..[7] In recent years, Singh, R.T. and[8] Kumar & Singh et al. have[9] also reported similar observations and inferences on the effect of solvent on the specific rate constants of catalysed solvolysis reactions. However, the decrease observed in the specific rate constant values with different numerical values of slopes may be attributed partly due to the dielectric effects of the reaction media and partly due to solvation changes taking place in it (aquo-glycerol reaction media).

Effect of Solvent on the Iso-composition Activation Energy (EC) of the Reaction :
On perusal of the data mentioned in Table - III, it is observed that the value of iso-composition activation energy of the reaction go on decreasing from 80.45 kJ/mol to 49.19 kJ/mol with increasing concentration of glycerol from 20 to 80% (v/v), in the reaction media.

The depletion EC values of the reaction in aquo-glycerol media may be due to either of the following three causes :

(i) The transition state is solvated and the initial state is desolvated,
(ii) The transition state is less desolvated than the initial state, and
(iii) The transition state is more solvated than the initial state.

Among these three factors, the first factor seems to be operative in this case as from the values of thermodynamic activation parameters of the reaction in Table - V, both Δ H* and ΔS* values of the reaction are found to decrease with increasing proportion of glycerol in the reaction media (DH* values decreases from 77.70 kJ/mol to 46.81 kJ/mol and Δ S* values decreases from –35.71 J/K/mol to –144.69 J/K/mol at 30°C).

Regarding effect of solvent on the EC value of reaction, similar findings and their interpretations have been reported earlier by Singh & Parween et al[10], Pathak & Singh et al[11]. and also recently by Choubey & Singh et al.[12].

Solvent Effect on the Iso-dielectric Activation energy (ED) of the reaction :
From the values recorded in Table - IV, it appears that ED values of the reaction go on increasing with increasing dielectric constant values of the aquo-glycerol reaction media. The ED value is 61.85 kJ/mol at D value 50 and increases to 80.67 kJ/mol at D value 65. The enhancement in the ED values with increase in D values of the reaction media is in accordance with depletion in EC or Eexp values of the reaction with increasing mol % of glycerol in the reaction media. These findings and conclusions have been found in support of the earlier reports of Wolford[13], Priyanka and Singh et al[14]. and recent reports of Singh & Hafizee et al[15].

Solvent Effect on Thermodynamic Activation Parameters of the Reaction :
From Table - V, on perusal of the values of thermodynamic activation parameters, namely ΔG*, ΔH* and ΔS*, it is observed that ΔG* values (free energy of activation) of the reaction increases with simultaneous decrease in its ΔH* and ΔS* values. At 30°C, ΔG* values have been observed increasing from 88.52 k cal/mol to 90.65 k cal/mol with increasing concentration of glycerol from 20 to 80% (v/v) in the reaction media. Though this enhancement is not very large, however, it is quite considerable and acceptable too. In order to highlight the effect of changing concentration of the organic content (glycerol) in the reaction media, ΔH*, ΔG* and ΔS* values have been plotted against the changing mol % of glycerol in the reaction media and their plots are shown in Fig. - 2, 3 and 4 respectively.

From the plots of ΔG* values against mol % of glycerol as shown in Fig.-3, it is found that ΔG* values go on increasing non-linearly with gradual addition of glycerol in the reaction media. This finding is indicative of desolvation of reactants as explained by Elsemongy et al[16].

So far as the variations in ΔH* and ΔS* are concerned on observing their values from Table - V and their plots against mol % of glycerol as shown in Fig. - 2 and 4, it is interestingly found that both of them decrease linearly with gradual addition of glycerol in the reaction media.

From the thermodynamic relation:

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

it can be easily concluded that increase in ΔG* values with simultaneous decrease in both of ΔH* and ΔS* values is only possible when ΔS* values decreases more than ΔH* value. From such findings, it is inferred that in presence of glycerol in the reaction media, the alkali catalysed hydrolysis of ethyl propionate becomes entropy controlled and enthalpy stimulated reaction.

Moreover, non-linear variation in ΔH* and ΔS* values with increasing mol % of glycerol as shown in Fig. - 2 and 4 respectively, gives information of the fact that specific solvation is taking place in aquo-glycerol solvent systems similar to that as reported in the past by Saville et al[17]. Similar solvent effect on thermodynamic activation parameters and their explanations have been found in support of the earlier reports of Singh & Priyanka et al[18]., Singh & Navendu et al[19]. and also with the recent reports of Kumar & Singh et al[20].

Solvent Effect on Iso-kinetic Temperature and Solvent-Solute Interaction in aquo-glycerol Media:

The value of the iso-kinetic temperature of the reaction was evaluated by using Barcley- Butler[21] relationship which is expressed as

$$dm\ (\Delta H^*) = b\ dm\ (\Delta S^*)$$

It is a straight line equation representing the relationship between enthalpy and entropy of activation values of the reaction. 'b' is known as iso-kinetic temperature. From the values of ΔH^* and ΔS^* values available in Table - V, the plots of ΔH^* versus ΔS^* at 30°C were made which is shown in Fig. - 5. From the slope of the straight line of the plots, the value of the kinetic temperature was evaluated to be 286.17 ≈ 286.0 (below 300). Thus, in the light of Leffler's guidelines [22], from the numerical values of the iso-kinetic temperature (which is below 300), it can safely be inferred that there is appreciable change in the structure of the reactant or in the solvent or in both the reactant and solvent due to weak but considerable interaction between solvent and solute present in the aquo- glycerol reaction media in the similar way as reported earlier by Singh & Singh et al.[23], Pathak & Singh et al.[24] and recently also by Kumari & Singh et al.[25] and Singh & Singh et al.[26].

Effect of number of water molecules of the reaction media on the Mechanism of the Reaction:

The number of water molecules associated with the formation of transition state or activated complex has been evaluated by plotting log k values of the reaction against log [H2O] values as shown in Fig.- 6 in the light of relation proposed by Robertson[27].

$$\log k = \log ko + n \log [H2O]$$

From Fig. - 6, it is apparent that at each temperature two straight lines intersecting each other at log [HO] value approximately 1.485 having different values of slopes are obtained.

From the slopes of the plots of log k versus log [HO], the evaluated values of number of water molecules associated with the activated complex of the reaction are noted in Table - VI. From Fig. - 6 as well as from Table - VI, it is clear that the number water molecules associated with the transition state increases from 0.246 to 0.757 with increase in temperature above 20 to 40°C befor log [H_2O], value 1.485 which corresponds to 55.0% of water concentration in the reaction media.Similarly, in case of above 55.0 % of water concentration in the reaction media, the number of water molecules associated with the transition state in its formation increases from 0.601 to 1.218 with rise of temperature from 20 to 40°C. Overall, the number of water molecules involved in the formation of the activated complex of the reaction increases from 0.246 to 1.218 with rise of temperature From 20 to 40°C.

According to observation and findings of Robertson et al.[24] it has been suggested that number of water molecules associated with the transition state is fairly high for unimolecular reaction while that for bimolecular reaction will be very low.

Hence in the light of principle of Robrtson et al.[28], it may be inferred that with rise in temperature of the reaction, the mechanistic path of the reaction changes from bimolecular to unimolecular in aquo-glycerol media. From above noted findings about the increasing number of water molecules associated with activated complex, it may be inferred that in presence of glycerol in the reaction media and with rise of temperature of the reaction, the structure of water is changed from its dense form to bulky form at equilibrium.

$$(H_2O)d \text{ ----------} (HO_2)b$$

Earlier Kumari & Singh et al.[29], Singh & Hafizee et al.[30] and recently Singh & Lal et a.[31] and Sharma& Singh et al.[32] have also reported similar findings and their interpretations for effect of solvent on the mechanism of the catalysed solvolysis reactions in different aquo-organic co-solvent reaction media

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Table – I Specific rate constant values of Alkali Catalysed hydrolysis of Ethyl propionate in water – Glycerol media. K x 10^3in (dm) ^{3}mol $^{-1}$ min^{-1}

Temp in °C	% of Glycerol (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	71.37	65.07	60.06	57.39	53.96	50.1	45.57
25°C	120.67	109.72	99.59	92.92	82.66	74.17	64.24
30°C	208.64	185.18	163.38	149.18	127.29	109.62	89.85
35°C	346.66	301.86	257.81	220.5	190.5	147.86	120.59
40°C	579.83	492.85	419.08	338.17	283.53	225.48	164.74

Table – II Variation of log k values of the reaction at different temperatures with mol % of glycol in water- Glycerol media

% of Glycerol (v/v)	Mol % of Glycerol	3 + log k values				
		20° C	25° C	30° C	35° C	40° C
20%	5.81	1.8535	2.0816	2.3194	2.5399	2.7633
30%	9.56	1.8134	2.0403	2.2676	2.4798	2.6927
40%	14.12	1.7786	1.9982	2.2132	2.4113	2.623
50%	19.79	1.7588	1.9681	2.1589	2.3434	2.5299
60%	27.01	1.7321	1.913	2.1048	2.2799	2.4526
70%	36.54	1.6998	1.8702	2.0399	2.1699	2.3531
80%	49.67	1.6587	1.8078	1.9535	2.0813	2.2168

Table – III Evaluated values of Iso-composition Activation Energy (EC or Eexp) of the reaction in water- Glycerol media.

% of Glycerol (v/v)	20%	30%	40%	50%	60%	70%	80%
E_C value in KJ/ mol	80.45	77.14	73.78	67.92	63.79	56.38	49.16

Table – IV Evaluated values of Iso – Dielectric Activation Energy (ED) of the reaction at different desired 'D' values of the water – Glycerol media.

D values	D = 50	D = 52.5	D = 55	D = 57.5	D = 60	D = 62.5	D =65
E_D values in kJ/mol	61.85	65.6	67.7	71.14	73.93	77.73	80.67

Table – VI Values of the slopes of the plots of log k versus log [H_2O] at different temperatures.

Temperature in° C	Slope – l When log [H_2O] values is below 1.485	Slope – ll When log [H_2O] values is below 1.485
20° C	0.246	0.601
25° C	0.371	0.71
30° C	0.505	0.931
35° C	0.694	1.032
40° C	0.757	1.218

Table - V Consolidated Values of Activation parameters (DH*, DG* and DS*) of the reaction in water-Glycerol system at different temperatures. DH* and DG* in kJ/mol, DS* in J/K/mol

% of Glycerol (v/v)	Mole % of Glycerol	Δ H* in kJ/mol	20 0 C		25 0 C		30 0 C		35 0 C		40 0 C	
			Δ G*	Δ S*	Δ G*	Δ S*	Δ G*	Δ S*	Δ G*	Δ S*	Δ G*	Δ S*
20%	5.81	77.7	88.1	-35.6	88.4	-35.84	88.5	-35.71	88.7	-35.81	88.9	-35.69
30%	9.56	76.39	88.4	-41.85	88.6	-41.71	88.8	-41.02	89.1	-41.2	89.3	-41.21
40%	14.12	72.11	88.6	-56.11	88.9	-56.17	89.1	-56.2	89.5	-56.4	89.7	-56.23
50%	19.79	66.4	88.7	-75.97	89	-76.98	89.5	-75.05	89.9	-76.23	90.3	-76.23
60%	27.01	60.25	88.8	-97.51	89.3	-97.62	89.8	-97.43	90.3	-97.44	90.7	-97.38
70%	36.54	55.48	89	-114.4	89.6	-114.43	90.1	-114.4	91	-115.4	91.3	-114.5
80%	49.67	46.81	89.2	-144.8	89.9	-144.73	90.7	-144.7	91.4	-144.9	92.1	-144.8

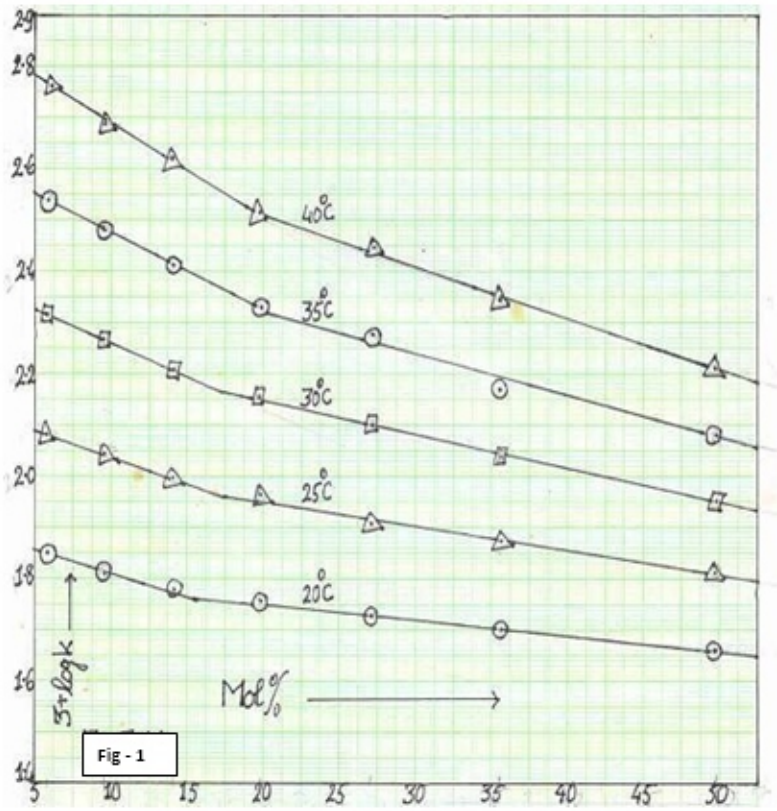


Fig - 1

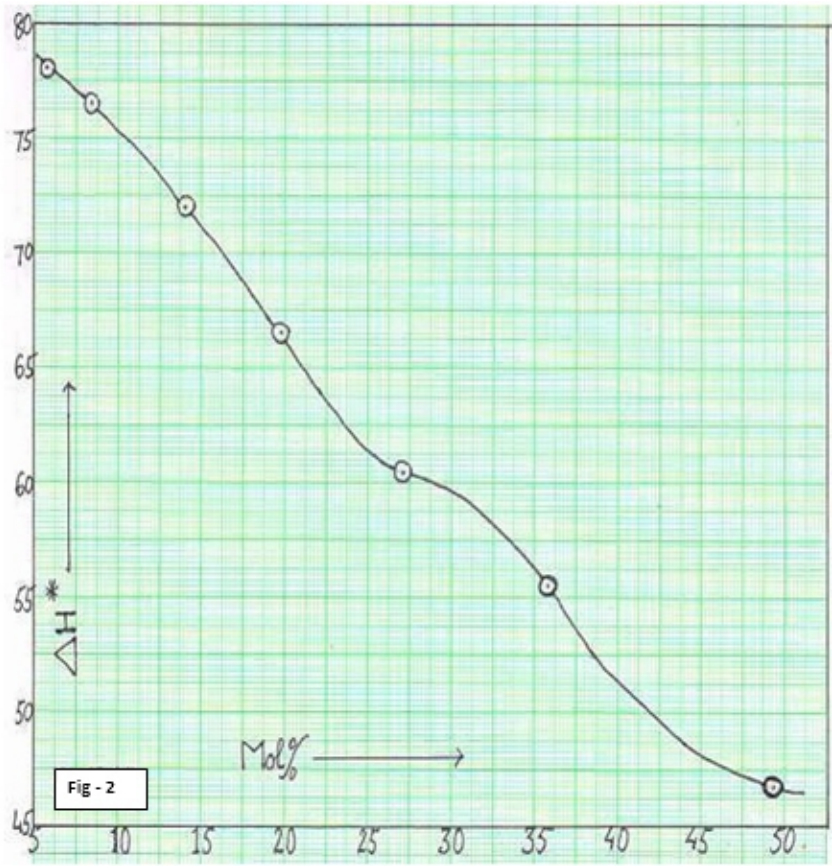
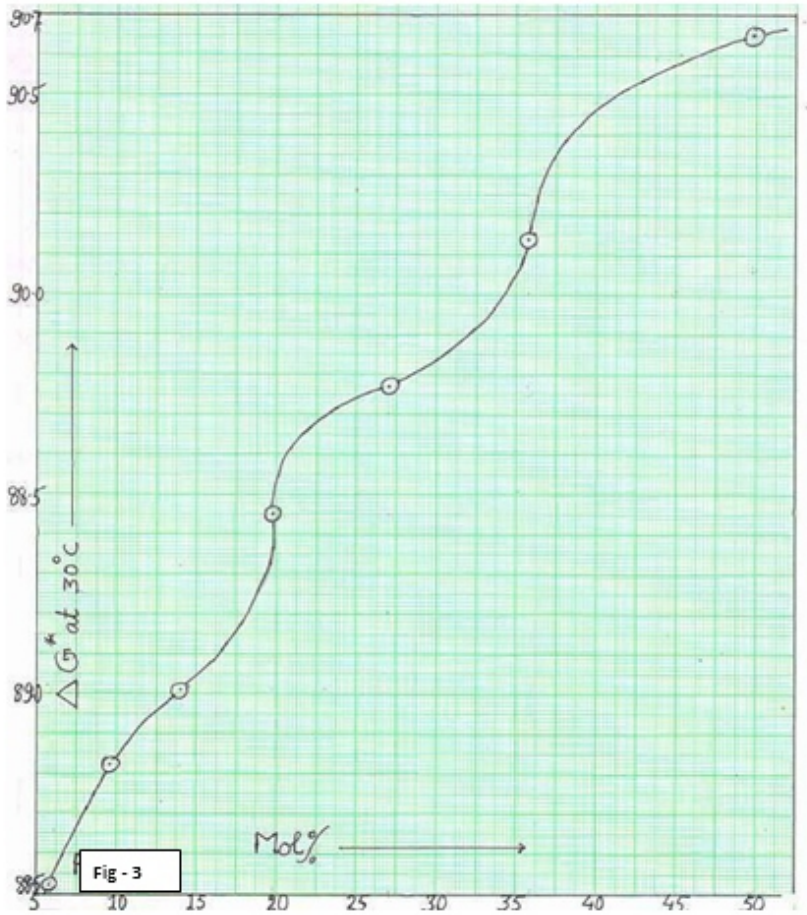


Fig - 2


90.5
90.0
88.5
89.0
ΔG^* at 30°C
Mol%
5
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35
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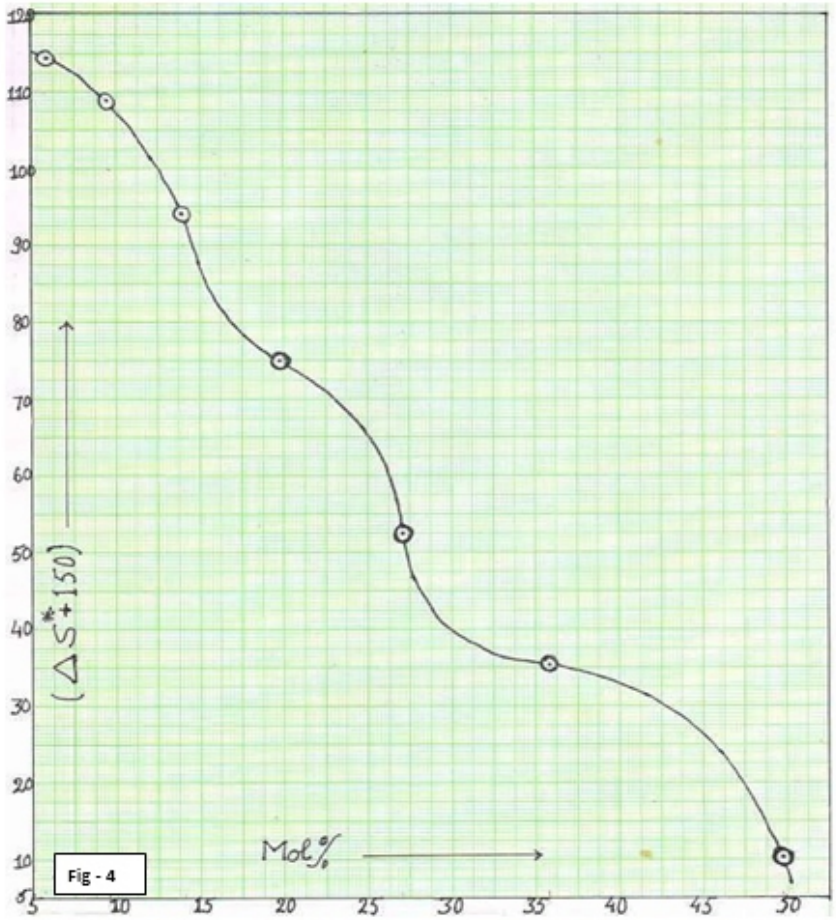
Fig - 3


110
100
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$(\Delta S^* + 150)$
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Fig - 4

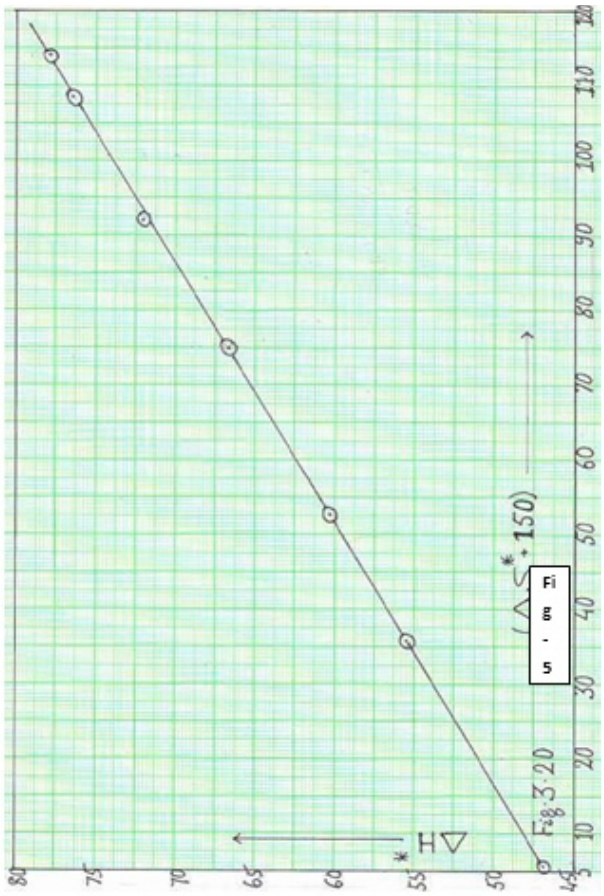
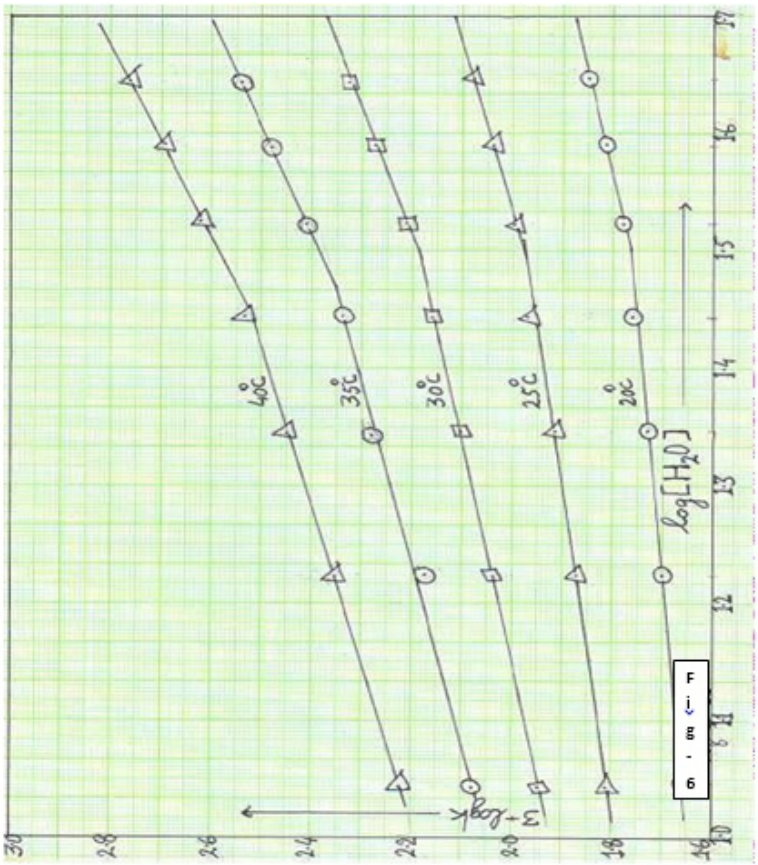


Fig. 5
Fig 3.20


40°C
35°C
30°C
25°C
20°C
log[H2O]
Fig. 6

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