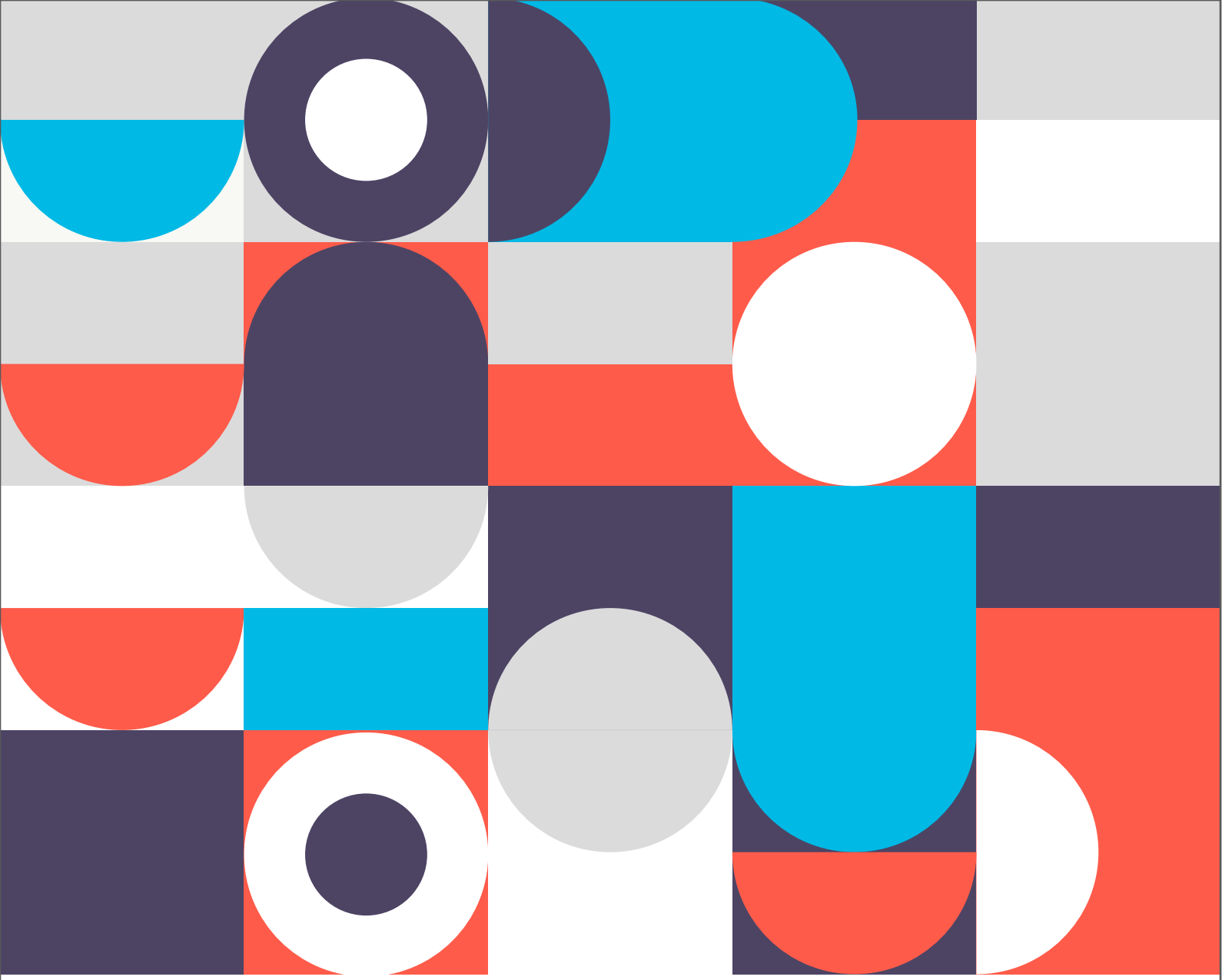

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The Academic Accountability in Higher Education; Rhetoric or Real

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Abstract

The need for accountability has always been figured in education sphere in general and higher education in specific. Despite the notions about higher education as an ivory tower, knowledge for knowledge's sake and academic freedom, higher education institutions are answerable to various stakeholders in terms of tax payers' money spent for quality education, research and community outreach activities. Accountability is much more explicit on stakeholders' agendas accounting for performance. Accountability is closely related to evaluation of efficiency, effectiveness, and performance, and requires proving that higher education has achieved the planned results and performance in an effective manner. Highlighting efficiency and effectiveness and emphasizing results are the basic characteristics of accountability in higher education.

This article analyses the various aspects of accountability in higher education viz. Marco and Micro Accountability, further it elaborates the types of accountability – Administrative, Financial and Academic. Academic accountability of teaching faculties includes Professional, Legal and Student Learning Accountability. Academics have to have worked mostly within the premises of these three accountability structures, often concurrently. The first system is rooted in the adherence to professional norms, the second system stresses in compliance with statutes and regulations which are demarked in the norms and standards of education enshrined in the administration documents whereas; the third accountability system is based upon effects demarcated in terms of student learning output.

Keywords

Accountability in Higher Education, Macro accountability, Micro Accountability, Financial Accountability, Legal Accountability, Professional Accountability, Results Driven Accountability-Students Learning Output Accountability.

Introduction

Education is key for development as it moulds the future by enabling individuals and societies with abilities, perceptions, knowledge and values to live and work in a sustainable manner. Higher education institutions hold the responsibility of developing human resources right from their inception and providing prospective professionals to all sectors of economy. Nations have been investing in higher education for generating relevant knowledge and honing essential skills for sustainable development. According to Higher Education Institutions sport the new ideas, develop roots and grow tall and robust. According to Yashpal[1], higher education widens the productivity of stakeholders', thus improving national capacity and delivering a competitive edge, by giving people access to knowledge and the necessary tools to accumulate and diversify it. Higher education helps in addressing the national challenges and priorities more diligently and sensitively. The research and development activities along with teaching at higher education institutions are major instruments for change in society and quality of life. The demands for high accountability and outcome based higher education are given great emphasis in the recent policy framework and efforts are being put to monitor the accountability of the institution and the accountability of the personnel in performing their roles and responsibilities.

Educational institutions need to exhibit accountability. Gnanam Committee Report (U.G.C., 1990)[2] acknowledges that the academic community both independently and cooperatively be made accountable in implicit and explicit terms to the society and the society is entitled to demand such answerability from them. The investment in education in terms of physical and human resources has been growing exponentially over the years. Accountability is a necessary aspect of the educational system. People seek education not only for gaining employment but to liberate their mind and to achieve the state of enlightenment, which makes man free from bondage. Educational institutions have an obligation to society because they are provided with the funds and resources by society.

Over the last decade, higher education institutions have been subjected to various accountability checks to maintain or improve the quality. The common parlance of these accountability systems and the processes is that higher educational institutions need to practice highly professional engagement in teaching, research and extension. Therefore, a lot of pertinent questions are coming forth in higher education such as;

- What is the typology of accountability in a higher educational context?
- Which are the major types to influence directly to the students learning output?
- How can academic accountability make higher education institution a "learning organization"?

Accountability in Higher Education- Typologies

Accountability has been used as an alternative expression for responsibility / answerability. Generally, accountability implies answerability to a person or organization that has imposed a target or expectation. In any organization, it is the human resources who define the success through their dedicated efforts. Once an individual is assigned responsibilities and the authority to perform a certain task, S/he is accountable for the task. So accountability literally means that the need to make one's actions satisfactory to some responsible body or agency as per the set standards or expectations. According to Robert[3] accountability means "the requirements to demonstrate reasonable actions to some external constituency or agency". In recent times various types of accountabilities in higher education have come to be discussed. But from a broader and analytical perspective, accountability in higher education may be considered in two forms, namely, Macro Accountability and Micro Accountability.

Macro Accountability refers to the responsibilities of the higher education system to the society represented by the students, parents and the government. Social responsibility of higher education is key here. This has to be clearly reflected in the vision and mission of the universities and should be translated into effective action plans for implementation across the campus. Educational institutions have an obligation to society because they are provided with the funds and resources by society. Gnanam[4] has argued "Macro accountability is difficult to measure and achieve as it involves normative judgment and connotation. The present objectives of the higher education system are framed in normative context and are

expressed in quantitative terms". In this context, the Indian Education Commission (1964-66) has formulated the objectives of Indian higher education system in the following words; 'Education should be developed so as to increase productivity, achieve social and national integration, accelerate the process of modernization and cultivate social, moral and spiritual values'.

University systems need to incorporate 'social responsibility' as a core component at all levels and encourage students, teachers and parents to actively take part in such activities throughout the academic year.

Micro accountability is concerned with the responsibilities and performance of each one of the functionaries within the academic system, including administration and various other bodies to the management as to what they have accomplished towards the overall objective of the university during a given point of time. According to Gnanam[4], micro accountability can be comprehended in three forms- Administrative Accountability, Financial accountability and Academic Accountability.

a) Administrative Accountability

The Vice Chancellor/ Provost of the University is both the academic and administrative head of the University and s/he presides over the meetings of all the important bodies of the University such as the academic council and executive committee. So the Vice Chancellor is expected to plan and execute academic and administrative programmes. Powar[5] has pointed out "The Vice-chancellor, therefore, needs to have personal involvement in all the activities of the university, and should visit all the departments, administrative units and examination centers regularly. There should be high accountability on the part of various managerial bodies of universities and colleges. They should not only take decisions but also implement them". To build administrative accountability into the system, definite goals should be set up for the university for a period of time, against which administrative performance could be evaluated.

Administrative accountability includes the active engagement of the administrative personnel in all sorts of managerial activities and provides administrative support for the successful implementation. Outcome based management system is the call of the government for higher

education, in which norms/standards/expectations/targets are collectively set and the appraisal systems are rigorously implemented.

b) Financial Accountability

The universities and colleges are largely financed by the central and the state governments either directly as through autonomous bodies in various forms, for e.g. UGC, ICAR, CSIR, AICT etc or? It means it is public money, which is being utilized for higher education. Hence, there has to be accountability of the educational system. The investment in education in terms of physical and human resources has grown tremendously. There has to be a mechanism for preparing meaningful and realistic budget estimates and for controlling and checking wasteful expenditure. Each and every person working in administration, teaching, research or extension should be subjected to accountability for efficient use of funds. From the viewpoint of enhancing the accountability of the educational system, it is necessary to improve the cost-effectiveness of investment of higher education. Swant & Dhonukshe[6] argued for a mechanism to improve the quality of education by using the financial mechanism and to let the inefficient departments, colleges and individuals be rooted out. Zero tolerance with regards to misuse of public money in higher education should be adopted and if necessary all such information should be placed in the public domain. Right to Information Act has increased the accountability of the system to some extent; however such practices need to be the integral part of university policy and governance.

c) Academic Accountability

Academicians form the fulcrum of the University and their role and responsibility determine the quality of higher education to a large extent. Their willful participation in the management and administration of the University is an essential pre-requisite for the success of the University. Among other things, academicians are also expected to help the University in preparing an action plan indicating the priority areas of activities for the academic year in the background of the academic plan prepared by the university, besides preparing the budget for the department. Teachers engage in teaching courses effectively and are involved in research and extension activities and perform other such incidental functions, which contribute to achieving the objectives of the university.

The teacher is the pivot of an education system. Imparting knowledge and evaluating students' performances are the primary responsibilities. According to Page and Thomas[7], teacher accountability is a "postulation of obligation for getting stated results in students". It is asserted that teachers' accountability likely touches their instructional practices, answerability and eventually the learning and development of students[8]. There are quite a number of studies on teachers' perspective about accountability[9-11]. They have acknowledged that although accountability has significant motivational consequences in terms of effort investment, perseverance, and commitment to students, it contains some personal costs for teachers such as hard work, sense of being evaluated, and spending more time for professional practices. Stiggins et al.[11] found that teachers' accountability correlated to their student achievement. Moreover, accountable teachers focus on their students' motivation, academic success[12, 13].

The New Education Policy demands from the teachers a higher performance and sense of dedication and devotion to their profession. Once the teacher is appointed and is confirmed, the immunity to accountability develops. Therefore, it is necessary to devise a suitable system of tools to enforce accountability for teachers. Each university should frame the norms for assessing the performance of teachers.

It is necessary to introduce some strictures for completion of the course syllabi, actual teaching performance in the classroom and laboratories and punctuality and sincerity in the evaluation of students' performance. It is necessary to introduce a proper mix of dissent and discipline in teaching community by providing the scope for improvement of ineffective teachers.

Types of Academic Accountability

Accountability suggests a statement of clarification of one's demeanor, a statement or explanation of reasons, causes or motivations. Kanika[14], enlisted the accountability of teachers as: Accountability towards the Learner; Accountability towards Community; Accountability towards Profession; Accountability towards Humanity and Values and Accountability towards Country. Betts et al.[15] move toward collective teacher accountability as a component of teachers' efficacy in their teaching preparations, internal locus of control,

commitment to all students' learning, and personal responsibility for students' learning outcomes.

In the field of higher education, there are three main types of accountability system: (a) compliance with regulations - legal accountability (b) adherence to professional norms - professional accountability, and (c) results driven - students learning output[16, 17]. Leveille[18] stated "Educators have worked mostly within three accountability systems, often simultaneously.

(a) Legal Accountability-Compliance with Regulations

Legal accountability is compliance with rules and regulations. This system demands compliance with statutes and regulations such as those embodied in the national educational system. In other words, educators are accountable for adherence to rules and accountable to the set norms and procedure. Individuals in the organizations tend to exhibit accountability in their work, if the consequences of non-performance are clearly stated and informed. Legal framework thus becomes a binding force for employees to perform.

b) Professional Accountability-Adherence to professional norms

The professional Accountability system is based upon loyalty to professional norms and practices. It is the responsibility towards one's self and colleagues. Though neither mandated nor required, the impact of the pervasive agreement on convinced principles and practices has done much to elevate education as a profession. Barton et al.[16] clarify this as "In this system of accountability, academics are responsible for adherence to standards of higher education and accountable to their peers; it is the responsibility to one's own profession and colleagues." This is also referred as professionalism. Individuals accept fully their professional standards and strictly follow them in real sense. Thus universities can become the community of professional learners.

c) Results Driven Accountability-Students Learning Output Accountability

This accountability system is based upon results, with results defined in terms of student progression and learning. The outcome based education, which requires a system of assessing the education performance monitoring task for results-based teaching and learning procedure. According to Barton et al.[16], this is the moral accountability which, is based upon

a sense of responsibility on students output; a feeling that one is responsible to ones' student community, eventually to the wide society. In this sense, social accountability of educational system is synonymous in this criterion.

It means teachers and the educational system should take responsibility for improvement in students' learning outcome and overall development to the potentials of their students. A major focus in higher education in the 21st century is, therefore, on learning outcome based education. With growing internationalization, the issue of accountability demands higher education institutions to perform not just a wheel that rotates but to do better in the competition and to produce best-talented students. The paradigm shift is moving from instructional oriented teaching to student-oriented learning, or in other words from "Teaching to learning". The students of higher education are going to be the direct contributors towards the social and economic development of the country therefore; they are the resources of the future society. Furthermore, Betts et al.[15] move toward collective academic accountability as a component of teachers' efficacy in their teaching rehearsals, internal locus of control, commitment to all students' learning, and personal responsibility for students' learning outcomes. Likewise, Stiggins et al.[11] found that teachers' accountability was positively linked to their student achievement. This is emphasized that teachers 'accountability expected to trace their instructional performs, responsibility and eventually their students' learning outcomes and performance[8]. Furthermore, accountable teachers focus on their students' enthusiasm, learning outcomes and academic success[12, 13]. Leveille[18] has argued "At present, accountability systems focus less on compliance and more on results. This changing discourse in accountability and emphasis on quality in teaching and learning etc. bring the students or learner at the central stage." It means teachers of higher education system should take responsibility for improvement in students' learning outcome and overall development to the potentials of their students.

Enhancement of Academic Accountability System in Higher Education

It is essential to nurture and promote academic accountability in higher education. Greater accountability of teachers will have to be emphasized. The degree of accountability can be perceived only when the functions and duties assigned to the individuals in the system are properly evaluated.

The following criteria may be considered for evaluating teachers and ensuring academic accountability system:

- Consistency and punctuality of teachers in taking classes and their availability in the department for the guidance of students;
- Classes-taught and the degree of the effectiveness of teaching as measured by the interest generated in the students and self-thinking process created in them;
- The quality of reference books used for teaching and reference and the quality of assignments given to the students;
- The course developed and innovative methods of teaching adopted;
- The honesty and neutrality with which the students are evaluated by the teachers and the whole-hearted participation of the teacher in all the evaluation processes of the university;
- Efforts of self-growth and professional development;
- General life enrichment and human resource development;
- Contribution in resolving social issues, institutional issues; exhibiting social responsibility.
- Number of papers published in reputed journals and research projects undertaken and research advisor;
- The position of teachers as revealed by student's evaluation of teachers;
- Contribution to the growth of the university, co-curricular activities, enrichment of the campus life, students welfare etc.;
- The contribution of the teacher to the design of curriculum, teaching methods, lab experiment, evaluation methods, preparation of resource materials, students counseling and remedial teaching; and
- The extent to which the teacher follows the code of professional ethics for higher education teachers as prepared by the legal authorities.

The performance of the teachers should be reviewed in the light of the above criteria by a committee of senior educators, an incentive should be given for better performance and disincentive for bad performance; further, enforcement of accountability may begin with the recruitment of teaching staffs who exhibit evidence of continuous academic interest. This may be followed by training and retraining of teaching staff from time to time to cope with

the curriculum and trends in educational fields. To motivate teachers to put their best, it may be useful to link 'emoluments and promotion', to 'performance'. Enforcement of accountability should begin with the recruitment of teaching staff that evidence of continuing academic interest and they should be supported by research and orientation of teachers about the responsibilities towards academics and administration[19].

Accountability has a close relationship with 'autonomy' as well, which means the power and freedom to act without any external control. It includes managerial freedom in performing a given responsibility. Now the teaching community tends to stretch this freedom without considering the fact that accountability and autonomy always go hand in hand.

The government and society should generate environments, which will drive teachers on productive and imaginative streaks. Academics should enjoy the freedom to innovate, to devise appropriate methods of teaching and activities relevant to the needs and concern of the community. Mammen[20] recommended that practitioners provide opportunities for teachers outside the classrooms to cultivate their skills through peer discussion and holding a special workshop /seminar to train them. It helps teachers to become better classroom leaders and contributes to students' learning outcome, employability and academic success. Therefore, once teachers' accountability is augmented, they try to improve their teaching techniques and strategies, offer help to particular students who need specific attention in an academic environment and seek to stimulate students in order to develop student autonomy. When the teacher accountability is augmented, they exercise effective and transformative leadership Thus, both characteristics of teachers will improve which in turn influences students' learning and academic achievement. According to Pandey[21] "A fine-tuned system of accountability must ensure that personal and professional development of the educators would continue, the mind and imagination retain the impulsiveness, experience extends in its assortment, and eventually the liveliness overspills in quickening power from the educators to the students." Essentially, self-realization is the best approach to accountability, which is linked with excellence and autonomy.

Conclusion

Accountability in education means an accounting of the performance with respect to the responsibility assigned to it. It implies the actual measurement of the responsibility fulfilled or performed by an institution. Academic accountability is an important factor for institutional effectiveness and quality education. Those educators who are highly accountable tend to exhibit the characteristics of academic leadership. Therefore, the academic leaders with a high degree of accountability can transform the learners and learning outcomes. Thus, cherishing academic accountability is the means for accomplishing quality in higher education.

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A Commentary on India's Dream of Becoming "A Five Trillion Dollar Economy by 2025"

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Abstract

At the outset, it may appear to be an overambitious dream of making India a Five Trillion Dollar Economy by 2025. The dream has taken a hit due to the current slowdown. But the slowdown in the economy is an aftereffect of demonetization and broad reforms in the field of taxation, credit lending, insolvency and meeting compliances taken in the past few years. Considering the strong fundamentals of the Indian Economy and vibrant demography led by a stable and determined Government, the slowdown seems to be cyclical and the dream of making India a 5 Trillion Dollar Economy should not be beyond reach. However, realization of this dream is subject to a lot of assumptions like continuity in economic policy, government stability, controlled inflation, fiscal deficit and current account deficit, increase in domestic investment and export, credit availability and a conducive tax environment.

Key Words

Indian Economy, GDP, 5 Trillion Dollar, Economic Slowdown

Introduction

For a large part of over 50 years since Independence, India remained an exemplar of an underdeveloped economy. India could barely be an economy worth $400 billion by 1996-97 (MOSPI, 2019). But since then the pace of growth has accelerated thanks to the effects of liberalization and changing demographic set up in terms of a population that was both young and restless. It took the next ten years for India to reach a mark of $1 trillion for its GDP in 2007-08. Precisely it took 60 years for India's GDP to reach $1trillion. But it took just

another seven years for the country to double its GDP in absolute terms. India crossed a $2 trillion GDP mark in 2014-15. Continuing the effect of acceleration India added another $800 billion to its nominal GDP by 2019-20 (MOSPI, 2019). With high growth rate in mining, manufacturing and services, the last addition in GDP has absorbed the effects of poor agriculture growth (Economic Survey, 2019). However, it was based on a strong public mandate for a stable and determined government along with growing acceptance of India's growth model around the World that gave courage to India's Prime Minister Narendra Modi to announce his dream of making India $5 trillion economy by 2025. Quoting from *Upanishad* at the World Economic Forum 2018 annual meet in Davos Mr. Modi assured the Global Business Leaders that India considers the World as a one big family with a common future. The theme of the meet 'Shared Future in a Fractured World' could not have been more suitable for India to announce its dream of $5 trillion economy and invite business leaders to invest in the world's fastest-growing economy and one of the largest consumption markets. Mr. Modi restated his vision in June 2019 at Niti Aayog-India's Think Tank's governing council meeting. But it was only July 2019 during the Annual Budget speech of India's Finance Minister Mrs. Nirmala Sitharaman that this dream was transformed into a target. Since then experts and policymakers have started taking sides with their optimistic and pessimistic opinions primarily influenced by their biases for and against the Modi government. In this entire discussion on achieving or failing to achieve $5 trillion GDP, it is important to consider the variables which will play an important role. Other than the dream or target that is set by the Modi government, what will decide its fulfillment is a set of variables like continuity in economic policy, government stability, controlled inflation, fiscal deficit and current account deficit, increase in domestic investment and export, credit availability for business and conducive tax environment.

Economic Factors

The International Monetary Fund (IMF) in July 2019 had cut India's real economic growth forecast from 7.5 to 7.2 percent for 2020-21, but it has restated that India's growth will remain very much above 7 percent, making it retain its record of fastest-growing economy in the world. From 2014-15 to 2019-20 India's GDP growth in nominal terms has been at an average growth rate of 8 percent. Assuming the same level of growth, along with the current level of inflation at around 3-4 percent and the foreign exchange rate around 70

per Dollar Government is expecting the GDP growth rate in nominal terms from 2019-20 to 2024-25 to be around 11.5 percent (Union Budget, 2019). The *Economic Survey* 2018-19 states that the headline inflation based on consumer price index (CPI) has been declining constantly in the last five years, from 5.9 percent in 2014-15 to 3.4 percent in 2018-19. Controlled inflation has been an outcome of focused policy decision on the part of the government during the last five years. Managing supply, curbing hoarding and black marketing, targeted subsidy and regulated market economy are a few of the many measures taken by the Central and the State government to keep inflation in control. CPI at 4 percent was expected to significantly boost domestic demand. However, on the contrary, due to lower returns the Indian industry is underutilizing its capacity by nearly 25 percent. Low consumer inflation and high demand can only motivate the industry to increase capacity utilization in the future and contribute to a high economic growth rate. The Reserve Bank of India is responsive to the situation of low consumption demand and has been lowering the interest rates since 2018. The government too recently has ensured that the rate cuts are passed on to the customers by lowering housing and auto loans, to begin with. These measures before the start of the festival season should push consumer demand on the higher side.

Another vital economic variable that is in favor of both the ruling government and the economy at large is the controlled fiscal deficit (Business Standard, 2019). The relationship between fiscal deficit and economic growth is very interesting and complex. To a large extent for a developing economy, it is advisable to maintain a certain amount of fiscal deficit through government borrowing to infuse additional investment in the economy. The investment made through borrowing should be in infrastructure and other capital heads. This will complement the domestic investment and increase production and growth in the long run. However, a rising fiscal deficit beyond acceptable limits will negatively affect GDP, as payment of interest in the coming years will drain out the resources which could have been invested in a more productive use. Also, a higher fiscal deficit will result in a fall of gross domestic savings and investment in the country further pulling down economic growth rate. In India, the Fiscal Responsibility and Budget Management Act (FRBM) 2003 enforced the government to maintain fiscal deficit around 3 percent of GDP. In the last few years, the Modi government has been successful in bringing down fiscal deficit from over 4 percent in 2014-15 to around 3.4 percent in 2018-19. This is commendable as the expenditure on capital

account has increased. Higher tax collections have helped the government to borrow less and invest more. For the current financial year, the 2019-20 government has kept a target of 3.3 percent. With a gradual reduction of 0.1 percent per year, it will be possible to achieve the FRBM target of 3 percent in the next few years. This will increase India's credibility in global markets and attract higher FDI's and other investments into the country. All this will considerably contribute towards higher economic growth of 11 percent per annum.

Similar to the fiscal deficit, the current account deficit is also an indicator that shows the economic stability of an economy. At 2.1 percent of GDP, India's Current Account Deficit (CAD) for 2018-19 is highest since 2013-14. In the last five years government was successful in keeping CAD in acceptable limits. CAD indicates the difference between the inflow and outflow of foreign exchange. An important reason for higher CAD is the widening of the trade deficit. In the last few years, India's exports have fallen due to lower industrial output and a shift in global demand from India and China towards other smaller economies in Asia. Also, higher crude oil prices have continued to keep import bill on the higher side. However, CAD is still considered to be in the limits indicating the government's ability to manage its balances in the current account of the balance of payments. At $400 billion-plus, India is 8th largest in terms of foreign exchange reserves which provides adequate protection to sustain a marginal increase in CAD. But if not controlled well, CAD is a big threat to economic growth. Higher CAD will put pressure on dollar-rupee rates. A depreciation of Rupee will pull down the country's prospects of a higher nominal economic growth rate. Already a 3 percent fall in Rupee in the last few quarters has forced the Indian economy to slip from 5th to 7th position in the World GDP ranking 2018. After the US, China, Japan, and Germany at the top four positions, UK and France have moved up the ladder at fifth and sixth positions respectively. While India's GDP in nominal terms slipped from $2.8 trillion to $2.72 trillion due to a weak Rupee against dollar. Depreciation of Rupee means increasing demand for foreign exchange within the country. This will put pressure on the import bill leading to a rise in CAD and also inflation. Both are negative factors for economic growth. For a $5 trillion GDP, it is least required to keep Dollar – Rupee rates at 69-70 till 2024-25. A breach upward i.e. above 70 per Dollar will dampen India's dream of becoming the 3rd largest economy in the World.

On the domestic front, the government needs to do a lot for raising sentiments of investors to remain committed to Indian markets. This is one area where not much progress has been done in the last few years. Investment as a percentage of GDP accounted for only 29.8 percent in March 2019. From 2004 to 2011 this rate was over 36 percent of GDP (RBI, 2013). A lower investment rate has pulled India's economic growth downwards in the last few years. The government was hoping to fill the deficit created by domestic investment from higher Foreign Direct Investment (FDI) and to a large extent it was successful. FDI to India increased from $45 billion in 2014-15 to a record high of $64 billion in 2018-19, with an aggregated FDI inflow of worth $286 billion in the last five years. High FDI not only balances falling domestic investment but also create the necessary supply of foreign exchange in the country and help in stabilization of foreign exchange rate. However, given India's increasing economic growth rate to over 11%, the inflow of FDI should not be considered just as a secondary source of investment. It is imperative to attract higher FDI over and above to high domestic investment.

Political Factors

Never in the history of India is the ruling government at the center so comfortable in its position to take bold steps. With a full majority in the lower house of the Parliament and with support from a few opposition parties in the upper house, the ruling government can take all measures required to make India's GDP jump up several points in the next five years. The government today also has support from international markets and political leadership. These factors can be used for increasing investment in India in a host of sectors like civil aviation, automobile, infrastructure, and agriculture. The central government led by India's largest political party is also ruling in over 20 states in the rest of the country. This makes it convenient for the central government to get its policies and intent executed well across the country through the state governments making a way for achieving a unified target of $5 trillion.

Challenges and Conclusion

The comfort on the economic and political front does not come without challenges. Major challenges in achieving a $5 trillion GDP dream are in the form of socio-economic and international factors. It is going to be a real challenge for the government to ensure that the

sentiment and confidence of people remain high and positive for a long period. Another major challenge is to protect the Indian economy from a demographic disaster. The signs of which are already visible in terms of widening gaps between education and industry. Lack of skilled workforce and rising unemployment will derail the progress towards $5 trillion GDP. Simultaneously, India needs to strengthen its foreign policy, especially concerning trade and commerce with the US and other economies to ensure export demand remains intact and rising. Inward foreign investment alone cannot make India a high GDP economy. It is important to focus on meeting international standards for expanding exports. Another international challenge is to ensure that the supply of crude to India remains available from alternative sources and at a reasonable price. Any disturbance in these international factors will affect the Foreign exchange rate on the higher side and thereby pull down India's economic growth rate.

The current economic growth rate of 5 percent in the first quarter of 2019-20 creates a reasonable doubt on the economy's capacity to achieve an above 11 percent nominal growth rate for the current financial year. It is high time the Government will have to take necessary actions to boost demand and investment at the same time. But in the process Government should not come under the pressure from industry and compromise on the structural reforms in the area of taxation, meeting compliances, ease of doing business, attracting foreign investment and others taken during the last five years.

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Critical Thinking: An Indispensable Dimension In The Course Of Sustainable Development

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Abstract

A world to become sustainable necessitates Critical Societies to be built. Critical Societies are a prerequisite for creation of just practices. A Critical Society is an assemblage of people that value and practice Critical Thinking. This is considered to be quite inconsequential now as selfish idiosyncratic goals have taken over the idea of living and sustaining together. The paper emphasizes the instinctive tendency of human beings to selfishly pursue things without bearing in mind the rights and needs of others. In order to deliberately deal with such issues and craft critical societies, Critical Thinking has to be thoroughly understood, practiced and has to be made an innate part of everyday life. Such a comprehensive definition and model for Critical Thinking has been provided by Richard Paul. This paper thus explores the idea of such a comprehensive conception of Critical Thinking so that critical societies can be shaped and sustainable human penchants are sought.

Key words

Critical Thinking, Paul's approach, Sustainable, critical societies, just practices, values

Introduction

The world's population is ever increasing and it is expected to reach the mark of 10 billion[1] very soon. The less developed countries in the race of catching up with the developed countries are increasing their consumption levels. The North/South economic divide and the unequal distribution of the consumption of the planet's natural resources between the world's populations are notable potential causes of tension. Faced with the above situation, the think tank known as the Club of Rome, advocated zero growth[2]. One can't reasonably campaign

for it as it would leave people in poverty. What one could do however, is 'ration' growth to ensure any further drain on natural resources to those who need it most[3].

The key questions that arise from the above context are:

1. Will the 10 billion men and women inhabiting our planet in 2100 be able to live as well as the 750 million people in industrialized nations do today?
2. Where should we focus our effort then?
3. What's worth trying now, and what do I need to prepare for?
4. What can help us to solve the environmental and other massive issues?

The only recourse to the above discussion is sustainable development. There has never been an important time in the human history for the quest of sustainable development. The concept seems to be a key for the all the monumental problems that the world faces today as it not only aims to reduce environmental degradation but also poverty reduction with an inclusive intention of peace and prosperity for the entire globe[4]. Achieving the Sustainable Development Goals (SDGs) require commitment from all; governments, private sector, civil society and citizens alike to make sure we leave a better planet for future generations

The next set of question that arises from the above context is:

1. How sustainable development goals can be taken forward as they are well planned, drafted and much looked forward to?
2. How can I as an individual make a difference to the above setting?

In order to answer the above question a strong need is felt on the part of all of us

1. To follow the implications of our actions
2. To take command of our thinking so that the implications can be tracked.
3. To develop and use our intellect so that we can take the actions in the veracious course.

In order to track implications as well as use our intellect we need to take command of our thinking process. When human thinking becomes primary interest in the society, critical societies develop[5].

Critical Societies

Critical societies are the societies that promote practices that are reasoned as well as fair[5]. These critical societies are involved in being reasoned, empathetic, autonomous, they examine beliefs, are open-minded, they think about the rights and needs of others. The emphasis of these critical societies is to cultivate intellect of people and thus make citizens aware of their interdependency with nature[5]. These critical societies have individuals that think their actions. The actions are product of thinking and when individuals think on their actions and when the actions don't affect the rights and needs of others then a critical society can develop. The actions that these individuals and together societies take would be sustainable actions. Sustainable actions will be actions that will be just and fair. This will affect the dimension of sustainability.

Critical Thinking

Before we begin the discussion on Critical Thinking and its significance in sustainable development certain questions smear around:

1. What is Critical Thinking and how can it be helpful in sustainable development?
2. What model can be espoused that is pertinent in achieving the extensive meaning of sustainable development?

The above enquiries can be retorted through the below confab.
Every bit in the nature has logic. Every action an individual takes has some logic. But again the questions arise as to

1. Do we ever question or examine our logic for doing various things at various points of times?
2. Do we examine our conduct?
3. Do we examine our thinking?

The answer is rarely. Say for the following instances:

A consumer acts unwisely and uncritically if he happens to see an advertisement on T.V. He never questions about the reliability of the claims that the ad makes or price it

charges or whether he really needs the product. He makes a decision many a times without being a rational human being.

As an individual am I thoughtful enough for my health? Superficially yes, essentially no. We often eat and do things that are harmful for our health. We don't scrutinize the effects of our eating practices and the way it affects our lifestyle. Even if we know that it affects our health we still prefer for unjustified reasons. We do have logic of doing things here but do we ever question and figure out whether it is justified or not? Even if we do, we dupe our mind saying that this is ok or this is not going to affect me so gravely.

As students we fail to understand the concepts at depth. We still believe that we know it very well. We superficially do lot of things in the class and the exams though we know it is not justified, though we know that we haven't understood it very well, though we know that the implications of this kind of shallow understanding won't be very far reaching.

As teachers we know that the classroom practices must be based on questioning and inquiry. Do we foster such practices? How many of the teachers actually like students asking questions while the class is active? According to research conducted by Almeida (2009), teachers spend up to 50% of class time on questioning and that they ask between 300 and 400 questions a day, while each student asks, on average, 1 question per week[6.] Even if teachers ask a huge number of questions per class, the questions posed are consistently of the same kind. Teachers ask typically low level questions, requiring mainly memory. Research indicates that questioning is second only to lecturing in popularity as a teaching method and that classroom teachers spend anywhere from thirty-five to fifty percent of their instructional time conducting questioning sessions[7].

As citizens too often we vote imprudently and uncritically, without taking the time to familiarize ourselves with the relevant issues and positions, without thinking about the long-run implications of what is being proposed, without paying attention to how politicians manipulate us by obsequiousness or vague and vacant promises.

As citizens we fail to examine our individual actions that may affect the natural resources. We use things thoughtlessly. Use of natural resources for extravagant purposes is a critical issue. The above examples are considered to be selfish acts because we fall prey to fast thinking. Dealing with complex mental challenges and drawing complex inferences requires the kind of deliberate, controlled, and effortful thinking characteristic of slow

thinking. Thus, what is required when trying to make a judgment is a conscious attempt to make our thinking more deliberate? [8].

Human mind is obviously engaged on pursuing selfish tendencies as highlighted above. It takes interest in self-indulgence and egotism[9]. Nevertheless, human beings have a strong capacity to think rationally, if thinking is taken seriously[10]. Thinking has to be evaluated consciously for its quality so that it can be transformed for better consequences in the form of decisions. On this view, as you can see; Critical Thinking as the goal which will achieve aims desired by the society and achieve sustainability. It is based on the skills, the insights, and the values essential to that end. It is a method of going about living and erudition that empowers us.

Assessing the dynamic relationship between Critical Thinking, Critical societies and Sustainable development

The concept of Critical Thinking has been evolving from the aegis of Socrates and various authors have worked into the area of Critical Thinking to define it. He contributed to ethics and consideration of thought. He considered critical thinking in the form of pursuing truth. He asked questions to dig beneath the thought processes. This helped the individuals to reflect on thinking processes. Ennis (1987) emphasized upon reasonable reflective thinking focused on deciding upon what to do[11]. Mcpeck (1988) as cited in Paul 1999 gave definition that revealed critical thinking as "the propensity and skill to engage in an activity with reflective skepticism". Siegel (1988) as cited in Paul (1999) defines it as "thinking moved by reasons". Such thinking may help here by allowing the individuals to question the actions that they perform. It develops the aspect of introspection of actions of oneself rather than others. It functions at the deepest level of thought to understand the thought processes. These individuals if they think collectively then critical society may emerge and help in sustainability.

When we attempt on the meaning of Sustainable Development Living within our environmental limits is one of the central principles of sustainable development. One implication of not doing so is climate change. According to sustainable development commission, the focus of sustainable development is far broader than just the environment. It's also about ensuring a strong, healthy and just society. Thus the just society can be created

with the help of Critical Thinking and each practice of an individual may result in a critical society i.e. A just society. This just society is the aim of sustainable development.

It is possible and quite effortless to live an automatic life. This automatic life is fast thinking, not based on reasoning and uncritical[12]. It is likely to live a life devoid of actually captivating charge of the individuals we are becoming; devoid of embryonic the skills and insights we are capable of. According to Richard Paul, if we allow ourselves to become unreflective persons — or rather, to the extent that we do — we are likely to do injury to ourselves and others, and to miss many opportunities to make our own lives, and the lives of others, fuller, happier, and more productive[12].

Thus, Critical Thinking is analysing and assessing thinking with a view to transform it. Broadly, it is said that behaviour is a product of thinking. Further behaviour is reflected in actions and many of our current practices are destructive. To achieve sustainability, we need to think. We need to reflect upon the activities and the behaviour that we adopt and consider ways that don't affect the rights and needs of others. We need to change our behaviour in order to avoid ecological problems, and be responsible to acting on what causes the problems. Critical thinking will help in determining what actions cause's problems and helps achieve inferences that will achieve clarity in the implications of the thought.

The answer to the second question is to choose a substantive conception of Critical Thinking

A substantive concept of Critical Thinking will help us to target both analysis of thought and assessment of thought and take into account the affective as well the cognitive dimension of thought. It not only emphasizes the intellectual skills and abilities but also intellectual traits, it also draws attention to the barriers to the development of critical thought, such as egocentric and Socio-centric thought.

Model that promotes the broad conception of Critical Thinking

Richard Paul's model on Critical Thinking incorporates all the above elements in an integrated manner so that the critical societies can be sought. It is based on strong theoretical and philosophical foundations of Critical Thinking. CT according to philosophers should focus on reflection, affective propensities to exercise cognitive skills. Richard Paul also

mentions the aspect of strong and weak sense of CT along with Intellectual Traits of mind. These traits point to affective propensities required to implement the skills[13.]

It mentions the usage of standards of thinking to assess the elements of reasoning to develop intellectual traits[8].

How can the above approach bring change in people's thinking and how can it help to build critical societies?

Standards of Thinking

According to Richard Paul, The Intellectual Standards are used to assess the quality of reasoning. Being able to think critically necessitates a thorough command of these standards, infused in all thinking. We use the Intellectual Standards as a guide to better and better thinking.

The Intellectual Standards include: Clarity which means that the thought should be an understandable thought, it should be close to the reality and should be truthful, it should be precise and relevant. The thinking should achieve depth, breadth, logicalness and fairness

To be accountable for one's actions one must be accountable for one's own thinking process. In order to take command of the thinking process and assess its quality one has to understand standards.

For example; say I am bullying someone or if I am manipulating things for my benefit and I don't consider the rights and needs of others. In that case if I can reflect on my thinking process then can always question me am I clear in my actions? Do I clearly know what is to be done in this situation? Is thinking accurate while I do the action?

Elements of Reasoning

We analyze many things during a day. It might be concepts, textbooks, decision that we took in past or to be taken into the future. We do the analysis implicitly but we don't know the structure of analysis so. There are parts of thinking through which we analyze things. These parts are purpose, questions, information, assumptions, point of view,

inferences, and implications. One usually does it implicitly. But conscious efforts are required to practice these explicitly. This analysis has to be assessed through the standards of thinking.

According to Richard Paul, The Elements of Reasoning (thought) tell us that the thinking that analyses or reasons has a purpose, it also is based on certain assumptions, looked into a point of view, collects information, has implications and generates inferences.

The last aspect of the model is the Intellectual Traits that are required for being the /fair-minded critical thinker. To cultivate the mind, we need command of these essential dimensions, and we need to consistently apply them as we think through the many problems and issues in our lives.

Intellectual Traits

According to Paul, consistent application of these standards of thinking to the elements of reasoning will lead to the development of Intellectual Traits like: Intellectual Humility which means that one should know what one doesn't know, intellectual empathy which means that one should be able to look from others point of view, intellectual autonomy which means that the thinking should be independent, intellectual integrity which means that the thinking should allow one to treat truth because its truth, intellectual perseverance which means that thinking should pursue and should be based on facts, information and data

The Outcome

Constant use of the intellectual traits produces a well-cultivated Critical Thinker who is able to:

- Think on the purpose before acting- because that is the intention with which any thought should begin
- Collect and assess relevant information
- Uncover assumptions governing the thought- assumptions are beliefs taken for granted. They usually reside in unconscious mind. These assumptions need to be justified and uncovered with sound evidence

- Raise necessary questions as well as inquire.
- Arrive at inferences that are based on facts, data and information
- Think within different systems of thought
- Communicate effectively with others in figuring out solutions to complex problem and
- Continuously use standards of thinking to assess elements of reasoning to cultivate intellectual traits

Conclusion

Research into Critical Thinking proves that thinking is a skill that needs to be cultivated and applied with effort. The human mind has to be trained to think consciously so that it can be developed and used for the right ends. If not, it will lead to distortions and blunders. The concept of critical thinking can give variety of insights in content development and create solutions of long held social and sustainable issues.

Thus, sustainable development doesn't need great names as "sustainable development" to make it successful and implemented. All it needs is little accountability that every being can take up. All it needs is common sense of not using things when not required. All it needs is hard work from each one of us. All it needs is not to wait for anyone to start and contribute towards it. All it needs is the change in the process of thinking: Critical Thinking.

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On Construction of Golden Section Octagon

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Abstract

The present author defines the golden section octagon as the eight – sided closed figure for which the ratio of the two adjacent sides (longer to shorter side) gives the value of golden number φ = 1.6180, unlike in regular octagon for which the ratio of the two adjacent sides gives a number 1. The few common shapes which involves golden ratio in its geometry are rectangle, triangle and pentagon. It is known that such shapes appear in all sorts of discipline, science, technology, art, architecture and in nature. Though the present work inspires from the shapes which are in existence, exact occurrence of golden section octagon in nature and other disciplines is not known. The main objective of this paper is to explore the method for geometrical construction of golden section octagon and study its property using the concept of golden ratio and golden sections.

Keywords

Golden section, golden octagon, golden ratio, Fibonacci Sequences

Introduction

Golden ratio is a special irrational number found by dividing a line into two parts such that the longer part divided by the smaller part of the line is also equal to the total length divided by the longer part of the line. The division of the parts of the lines has the approximate value equal to 1.6180. It is denoted by the Greek letter φ[1, 2].

This concept can be understood further by dividing the line in two parts as shown below. In this line, the line has two parts, AC and CB. Here, AC is larger part with reference to CB and also AB is larger part as compared to AC. These two parts can be in golden ratio if their ratio AC/CB and AB/AC gives 1.6180. There is an occurrence of various polygons whose adjacent

sides are in golden ratio if the ratio is approximately equal to 1.6180 can be called as golden section polygon. Such golden section polygons are rectangles, triangles and pentagon. More details of these shapes having golden section properties are discussed in the literature[3, 4]. In the present work, one of such golden section polygon, octagon having golden section properties is evolved and investigated which is unexplored elsewhere. The main objective of this construction method is (1) to obtain the general construction method which is applicable to any dimensions and any scale (n_1/n_2 = 1.6180) rather than specific cases such as two adjacent side of polygon has to be 8/5 = 1.6180, 13/8 = 1.6180 etc… and is achieved by measuring and drawing it. To make the method more valid for any general construction and geometrical parameters (2) To explore the geometrical properties new shape of golden section octagon (3) to enable the designers to use the shapes in the various designs.

$$\frac{AB}{AC} = \frac{AC}{CB} = \varphi \cong 1.6180 \tag{1}$$

Geometry and Construction

Construct an equilateral triangle ABC as shown in Fig. 1. Each sides of the triangle are named BA, AC and CB. On each of these line segments, obtain the points G, H, I, D, E, F in such a way (Procedure is given in Appendix I) that following property of the ratios on each of the line segments hold true for the constructed equilateral triangle.

$$\begin{aligned} \frac{AB}{BG} = \frac{AB}{AD} = \frac{AD}{AG} = \frac{BG}{BD} = \frac{AG}{GD} = \frac{BD}{DG} = \varphi \\ \frac{AC}{AH} = \frac{AC}{CE} = \frac{AH}{AE} = \frac{CE}{CH} = \frac{AE}{EH} = \frac{CH}{HE} = \varphi \\ \frac{BC}{BF} = \frac{BC}{CI} = \frac{BF}{FC} = \frac{CI}{CF} = \frac{BI}{IF} = \frac{CF}{FI} = \varphi \end{aligned} \tag{2}$$

Join line GE, DI, HF to complete the inside polygon GEHFIDG, makes golden section hexagon for which following holds true.

$$\frac{GE}{EH} = \frac{HF}{FI} = \frac{ID}{DG} = \varphi \tag{3}$$

The complete proof of Eq. 3 is given in[5].

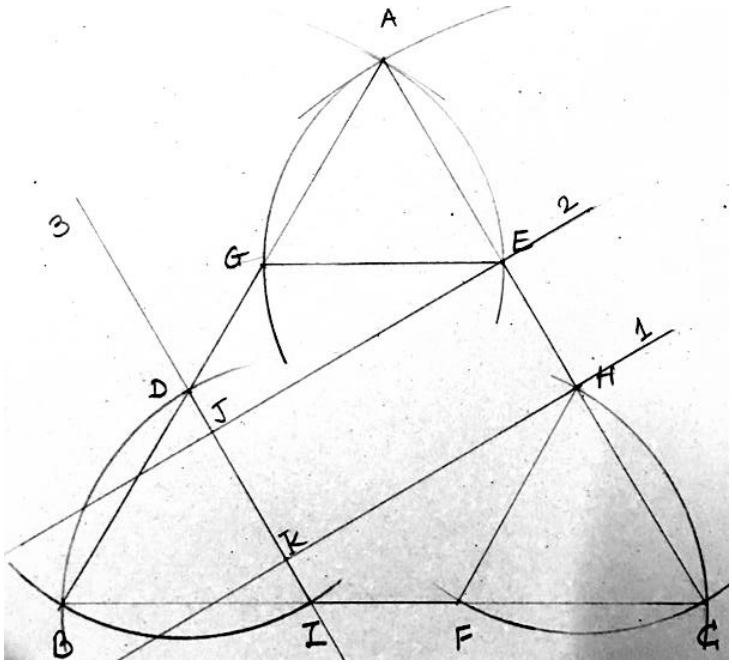

Figure 1: Golden Section on equilatral triangle

Take length GE and draw an arc from E of length GE passing through G and A. Repeat the similar procedure to draw the remaining arc seen in Fig. 1, as per the following Table 1 .

Sr. No.	Arc Length	From point	Points passing through	Covering Length
1	GE	G	E and A	AE
2	FH	H	C and F	CF
3	FH	F	C and H	CH
4	DI	D	B and I	BI
5	DI	I	B and D	BD

Table 1: Points for the Arc passing through A, B and C

For second construction phase, draw two parallel lines 1 and 2 passing through points E, J and H, K respectively. These lines are being noted as EJ and HK. By drawing the line, it is ensured that EH = JK. Draw a line passing through DJKI – line number 3, which also ensures DJ = KI.

Draw the perpendicular line from point M marked on the line 3. Mark M as the origin of this line to the point on the arc AG marked as L, which has the similar length as EH. EH = ML as shown in Fig. Line ML should remain parallel to lines 1 and 2. Repeat the process similar on the mirror side of the point M marked as N. Draw perpendicular line passing through N and projecting on the arc FC in such a way that ML = NO' = EH.

Bisect newly formed angles GEL and FHO'. Mark new bisection points on arc GL and FO' as P and Q, respectively. Bisecting angle procedure is performed to achieve the required angle in octagon. Now mark new points on arc AG and CF as R and S respectively in such a way that it has the arc length as PL = LR and QO' = O'S, respectively (Figure 2).

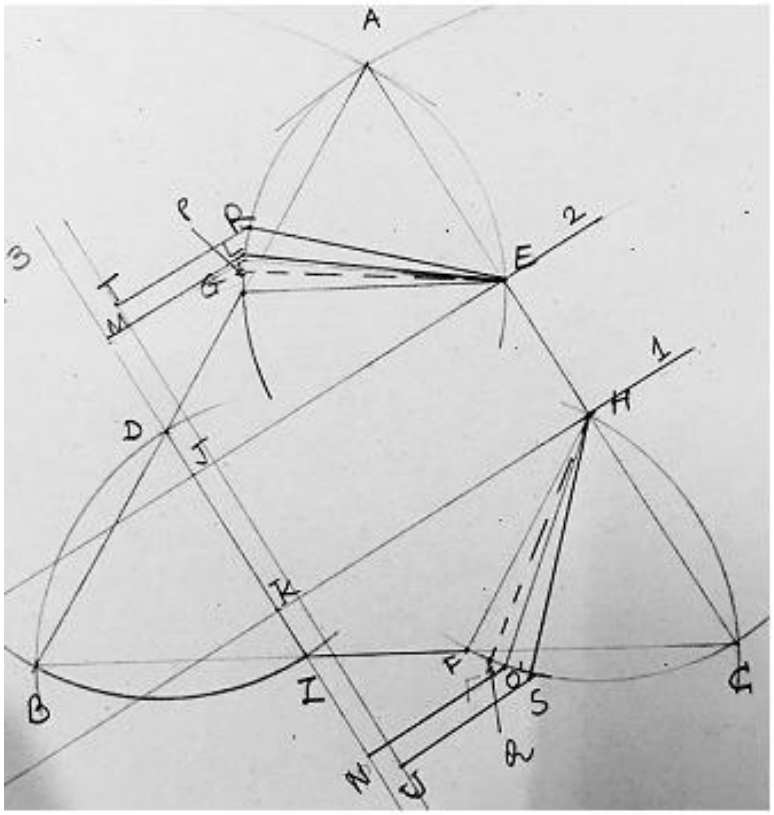

Figure 2: Constructing Golden Octagon

From R and S, draw parallel line such a way that it is parallel to the lines ML and NO'. Name these lines as RT and SU. Again, Points T and U are obtained in such a way so that it gives TR = EH and US = EH. Draw one line passing through T and U. Draw arcs named as 4 and 5 from T and U such as it has the length ER and HS, which also interacts line 1 and 2 respectively.

Intersection of the arc 4, arc BD and line 2 meet at the point V, similarly intersection of an arc 5, arc BI and line 1 meet at point W. Join VW. Also, join TV and UW. Complete ERTVWUSH, is golden section octagon as seen in Fig. 3. Some geometrical properties of golden section Octagon is observed and written as follows. VT/TR = φ, RE/EH = φ, HS/SU= φ, WU/WV = φ.

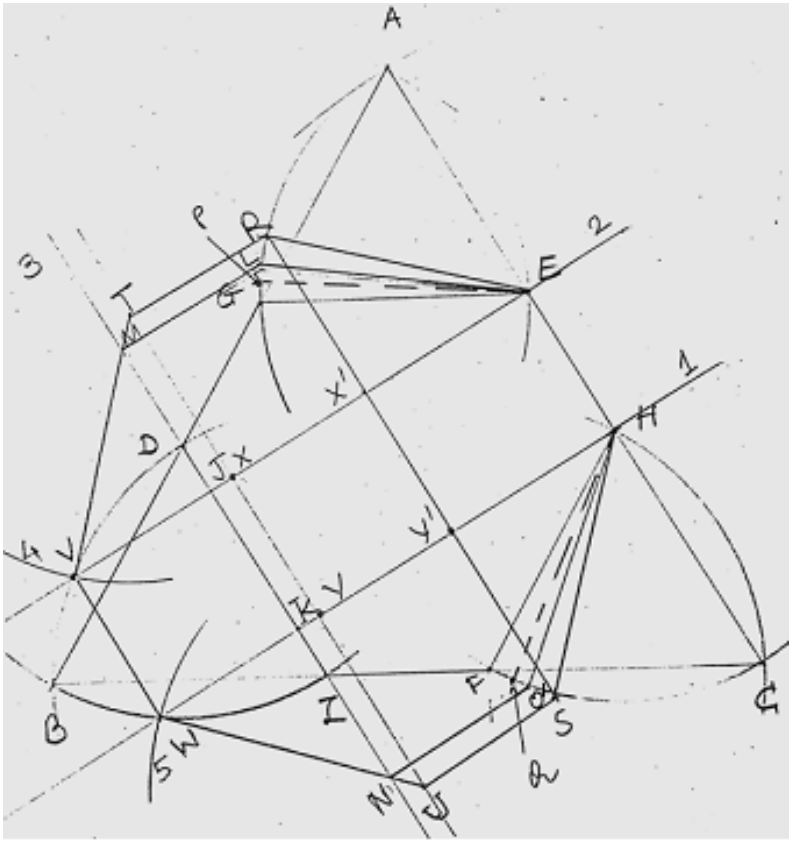

Figure 3: Golden Section Octagon

Properties of Constructed Golden Octagon

Constructed octagon is irregular, as the ratio of the longer side to shorter side should give golden number φ, since all the sides are incongruent. They also have incongruent angles, which mean that the measurement of all the angles of the triangles inside golden octagon is also incongruent. However, exterior angle of golden octagon is 135°, which the case for regular octagon is.

As shown in Fig. 4. , various interior angles of the octagon such as $\angle$VTR, $\angle$ERT, $\angle$TVW, $\angle$UWV, $\angle$USH and $\angle$HER gives 135°. The triangles are obtained by joining the opposite points and lines as shown in Fig. 4. The interior angles of the triangles are 34° and 56° for two incongruent triangles which are congruent alternatively. The ratio of these angles gives the value φ. The remaining angles for this triangles are 73° and 62°. (Fig. 4). For example, in fig. 4, these triangles are: OUS, OEH, OTR and OWV are congruent and have interior angle of 34°. Remaining two angles for this triangle is 73°. OER, OHS, OUW, OTV are congruent with each other and interior angle is 56°. Remaining two angles for these triangles are 62°. Here notation O is the central origin of the octagon.

The area of the Golden section octagon is given as below:

Assume the length TV = a and TR = b and RE = a, EH=b, due to symmetry, it also follows on the opposite side. HS = UW = a and US = b. Let us assume, TX = c and which is same as VX, same holds for other cases because of symmetry. Because of these the angle VTX and XVT are same and is 45°. It is presumed that angle TXV is 90°.

From the Fig. 4, it is seen that $\frac{a}{b} = \varphi \Rightarrow a = b\varphi$. From the trigonometry length c is given by,

$$c = b\varphi \sin 45^\circ$$
$$\therefore c = \frac{b\varphi}{\sqrt{2}} \quad (4)$$

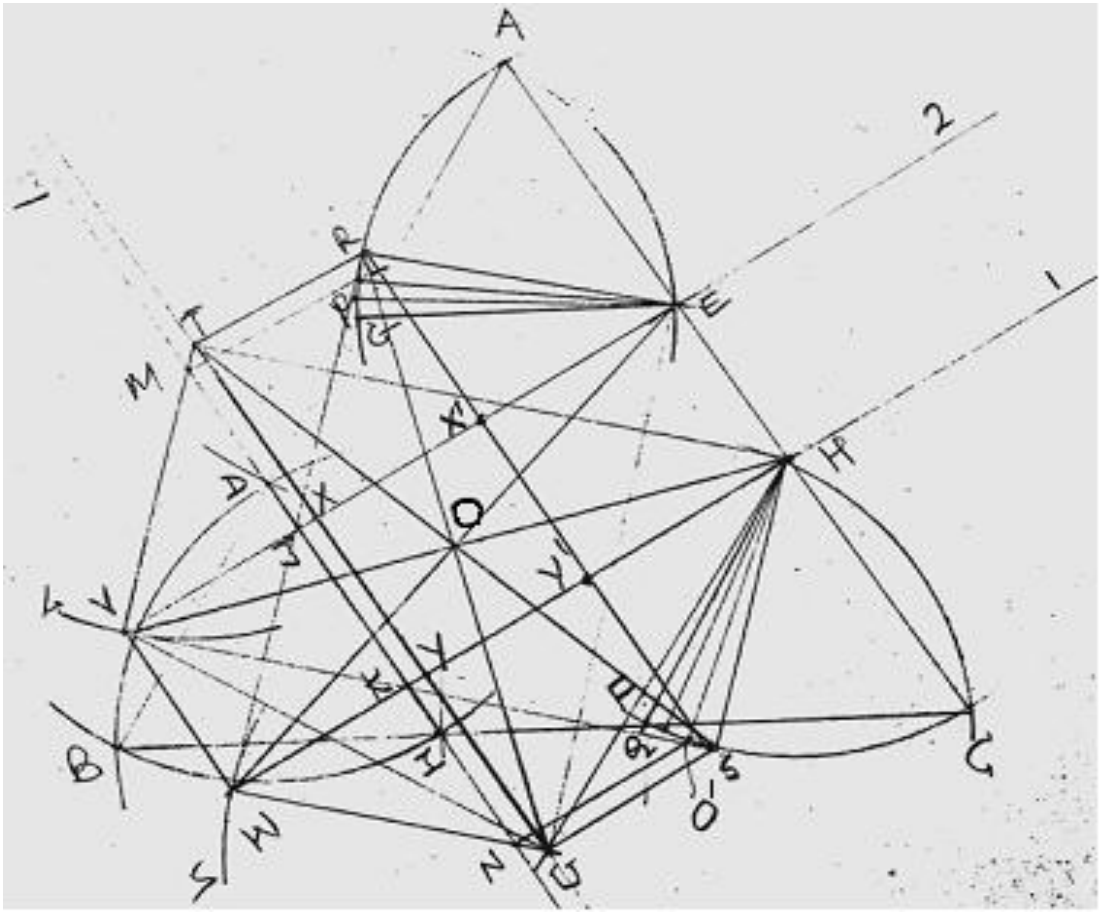

Figure 4: Properties of golden section octagon

Considering the trapezoid VTRE and WUOH, the area of these two trapezoids can be easily calculated by adding the area of two right angle triangles TXV and REX' and a rectangle TRXX'. One more area of the rectangle VEHW to get the area of the complete golden octagon, given as follows.

Total area of the golden Octagon

$$A = 2\left[\left(\frac{\varphi b}{\sqrt{2}}\right)^2 + \left(\frac{b^2\varphi}{\sqrt{2}}\right)\right] + \left[\frac{2\varphi b}{\sqrt{2}} + b\right]b \qquad (5)$$

The geometry of newly constructed golden section octagon without the construction line is seen in Fig. 5.

Conclusion

Systematic construction procedure for constructing the geometry for golden section octagon is presented in this article. The geometry is created using the concept of golden section and golden ratio in equilateral triangle. The exterior angle of the created geometry is 135° which proves and defines the shape of the octagon. The mathematical and geometrical properties are observed in the constructed golden section octagon. Golden section octagon design presented in this article is useful for engineers, artists, architects and mathematicians for drawing the various designs. The geometrical construction method presented here is applicable at any scale and valid for any construction and geometrical parameters.

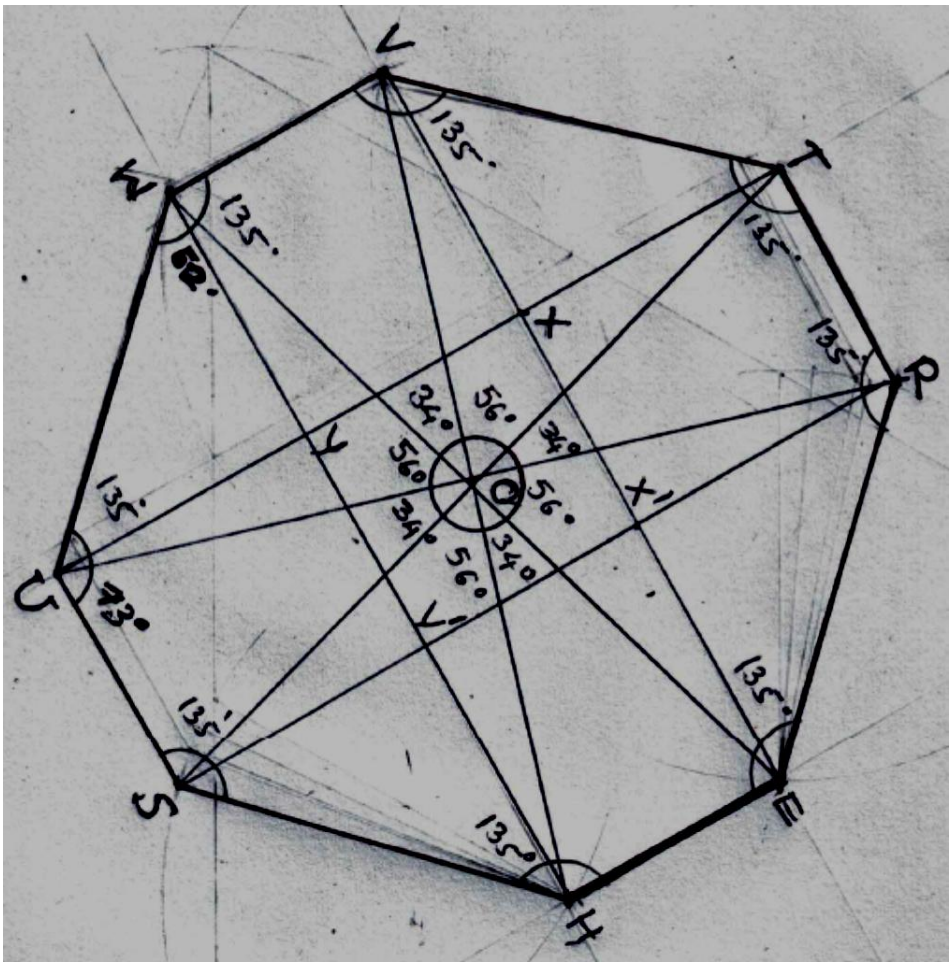

Figure 5: Golden Section Octagon

Appendix I – Procedure to obtain golden section on line

To obtain the point on the line AB such as the division of the longer line to shorter lines is in golden section, the procedure is given as follows.

Draw square of any size from the corner B on line of any length, assuming point A is not available. This line is 60^o to the horizontal line starting from corner B. Name this square as $BB_1B_2B_3$ as shown in Fig.6. Now divide the line B B_1 into half. Take the point at half a distance named B_4. Join $B_4 - B_2$ at right of the corner. Draw an arc from B_2 by taking length $B_4 - B_2$ from keeping compass point on B_4.

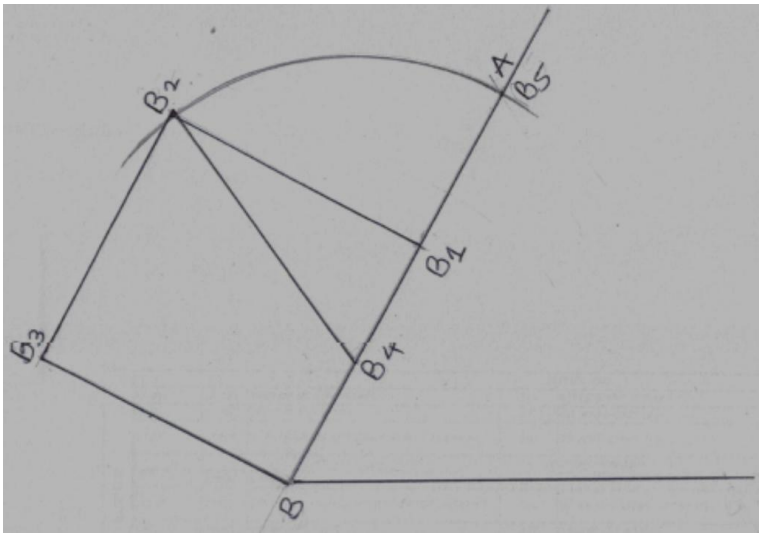

Figure 6: Procedure to obtain golden section on line

By doing this, it gives another point on inclined line going from B, named this new point B_5. We obtain, BB_1/B_1B_5 = 1.6180 and BB_5/BB_1= 1.6180. With this procedure we obtain the two divisions of lines which are in golden ratio. New point B_5 is the same as A in Fig. 1. The same procedure can be repeated for all other sides and the corners.

Another way to obtain the points which will divide lines in golden section is to simply measure the numbers following Fibonacci sequences. Such as if line is of 8 mm, take division of 5, and 3 on that line to obtain golden section. If total length is 13 mm, obtain division of 8 mm and 5 mm on the line to obtain the golden section, same is repeated from all corners and sides to achieve this ratio of division of line approximately equal to 1.6180.

Acknowledgement

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Quantitative and Qualitative analysis of Glucose and Fructose from Flower Nectaries

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Abstract

Nectar is important in pollination. Varied kinds of flowers show presence of different amount of nectars and sugars. The present study includes evaluation of sugar from the flowers collected from the campus of Navrachana University, Vadodara. The preliminary analysis revealed the presence of glucose and fructose in the samples. For quantitative assessments, spectrophotometric techniques were used. For glucose and fructose identification, anthrone and resorcinol methods were followed respectively. This study will thus help in understanding the basic chemical nature of nectar.

Keywords

Nectar, Glucose, Fructose, Spectrophotometer

Introduction

Nectar is sweet substance, produced by some plants to attract pollinators such as bees, butterflies and hummingbirds. Bees collect nectar and turn it into honey. In the process of nectar collection, pollinators accidentally transfer pollen from male flowers to female flowers. The nectar is the reward for several pollinators. The nectar is produced from sap of phloem by active secretion that results in a solution of sugars like sucrose, fructose and glucose in varied proportions depending upon the vegetative state[1]. The plant may secrete a little bit of nectar with high sugar concentration, or secrete more quantities but with low sugar concentration. These differences in nectar may vary depending on pollinator visitation[2].There are reports of estimation of individual sugars present in different nectars but relatively large volumes were necessary for the analytical methods used by most of the researchers[3,4]. Mostly

flowers of most plants secrete nectar sparingly, hence there is a need for simpler methods to quantify sugars. Other factor considered is types of secreted sugars: sucrose, glucose and fructose[5].The quantities of sugars may vary with the species.

Material and Methods

The following species were included in the present study. *Hibiscus rosa-sinensis* L. 'Yellow Wings' cultivar, *Hibiscus rosa-sinensis* L. , *Datura stramonium* L. , *Tecoma stans L.*, *Peltophorum pterocarpum* (DC.)Backer ex K. Heyne , *Heliconia psittacorum* Ruiz & Pay, *Ixora coccinea* L.

Herbarium specimens bearing collection number Bot/27819/aut are deposited in the herbarium of Botany Department, The M.S. University of Baroda. They were authenticated by Dr Padmanabhi Nagar, Associate Professor, Department of Botany, The M.S. University of Baroda. Nectar was collected from flowers in the morning by using glass capillaries. The collection was done carefully to prevent contamination with pollen grains [6]. The samples were collected in 1ml micro centrifuge vials, stored in refrigerator after dissolving in 75 % methanol[7].

Qualitative analysis of sugars

For the experiment TLC silica gel 60 F254 plates were purchased from Merck. A light reference line 2 cm above the base was marked. Concentrated solutions of standard and the sample were loaded on TLC plate using capillary tubes about 7-8 times and simply air-dried. The TLC chamber was saturated with the solvent prior to the experiment. TLC plates with loaded samples were placed in the chamber in upright position and covered and the solvent is allowed to rise till desired distance is achieved. The plates were taken out, dried in stream of warm air and gently sprayed with the spraying reagent. They were observed for the appearance and the Rf values were calculated accordingly.

Preparation of solvent system

Two solvent systems were used for identification of sugars [8]

- Chloroform:Acetic Acid:Water (3:3.5:0.5)
- Isopropanol: Distilled water (4:1)

The chamber was saturated half-an-hour prior to the experiment with the solvent.

Spraying reagent

1% aniline and 1% diphenylamine (both in acetone). Mixture of aniline, diphenylamine and 85% phosphoric acid were used as spraying reagent on the developed chromatogram. The plates were heated for few minutes for development of the band.

Quantitative analysis of glucose was done by Anthrone method [9].

Quantitative analysis of fructose was done by Resorcinol method [10].

Results and Discussion

Qualitative analysis of sugars All the nectar samples were analyzed for the presence of glucose, fructose and sucrose by comparison with the standard solutions of each sugar (Figure1).

Figure 1: Thin layer chromatography

Quantitative analysis of sugars

Glucose estimation Glucose was found to be present in all the samples. However the highest concentration was seen in *Ixora* followed by *Tecoma. Heliconia* however, showed the lowest levels of glucose (Figure 2).

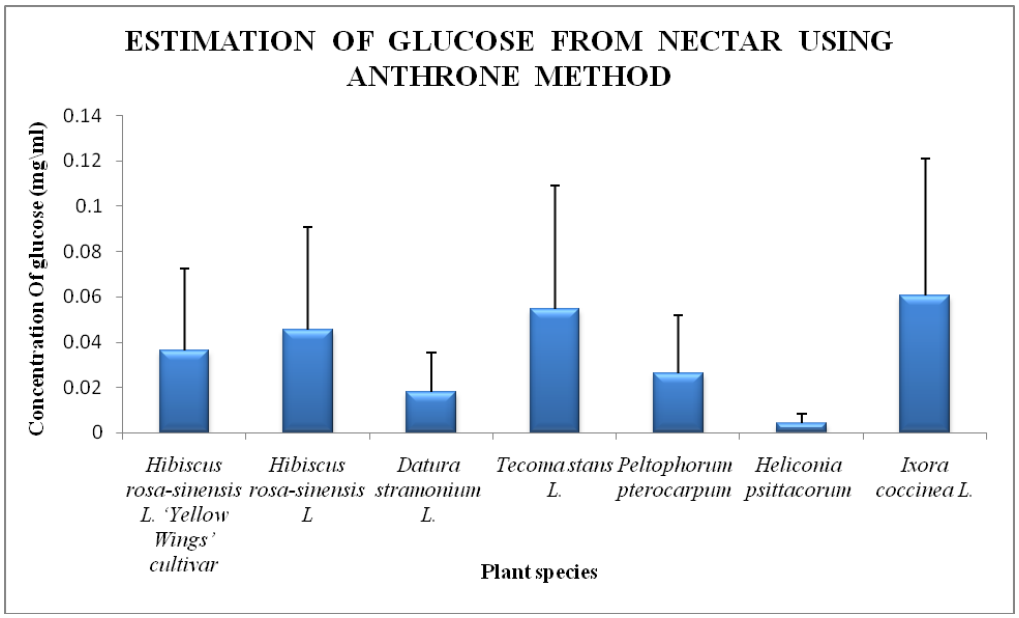

Figure 2: Quantitative analysis of sugars- *Glucose estimation*

Fructose estimation All nectar samples showed the presence of fructose. *Hibiscus rosa-sinensis* L. 'Yellow Wings' cultivar showed significant levels of fructose concentration while *Tecoma* had the lowest concentration (Figure 3).

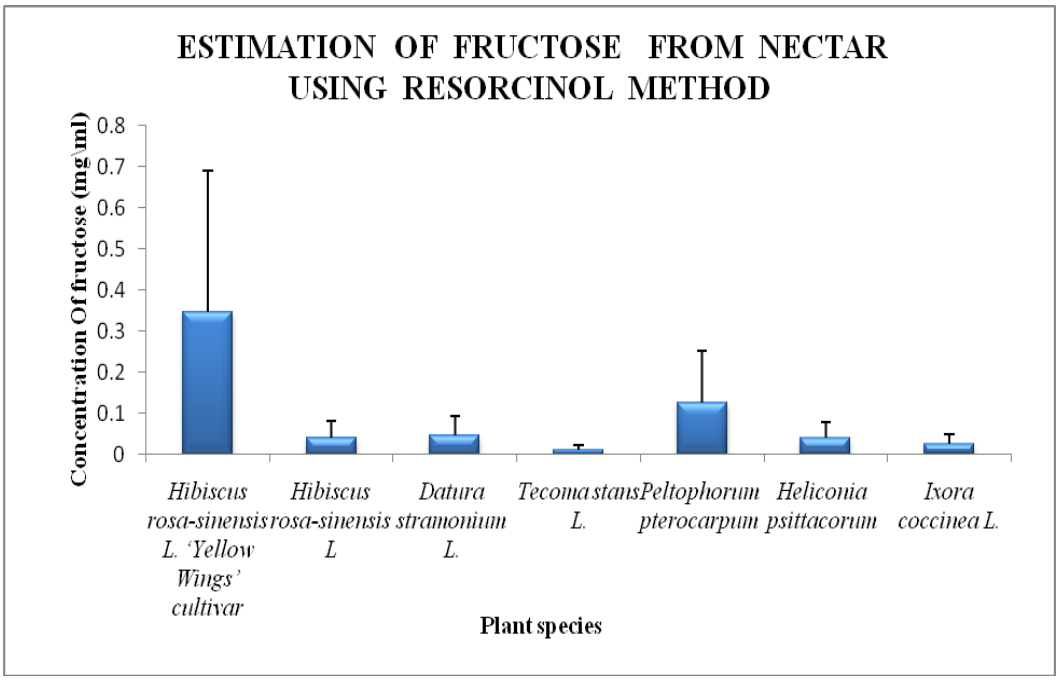

Figure 3: Quantitative analysis of sugars- *Fructose estimation*

All plants showed the presence of glucose and fructose but the content varied depending upon the plant species. The nectar of *Ixora* and *Tecoma* were rich in glucose while that of *Hibiscus rosa-sinensis* L. 'Yellow Wings' cultivar was found to be rich in fructose. The results suggest that similar studies can be employed for studies on other components of nectar.

Conclusion

The paper tries to understand nutritive value of nectar based on the quantitative assessment of the presence of glucose and fructose. All nectar samples are a good source of the sugars, glucose, fructose and sucrose in varying proportions, proving that nectar is a good source of nutrition after being converted into honey. The present study can be expanded further to detect the presence of other chemical constituents of nectar, thus establishing the importance of different chemical constituents of nectar and increasing its edible value.

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Notorious Radicals and Their Fate

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Abstract

Organic chemistry has been an essential part of our civilization. In this article, we talk about one of the four intermediates in organic chemistry – "the radical". The evolution of radical from being termed as notorious to a versatile intermediate in organic transformations to generate complex molecular architectures and natural products has been discussed. We attempt to explain herein some basic aspects of radicals in the domain of organic synthesis through examples reported over the years from our laboratory.

Key words: Radicals, homolytic fission, vinylogous carbonates, intramolecular cyclization, Baldwin's rule

What alchemy was to the ancient civilization, chemistry is to the modern world! Organic chemistry has been a boon and has improved all facets of our lives, namely, agriculture, health, energy, textile and technology. For instance, eyesight is feasible due to a molecule present in our eyes, retinal, which undergoes structural change, in turn helping us in vision. Fragrance always has a significance, be it the smell of flowers such as roses, jasmine, or of fruits like oranges and lemons. The salivating truffle taste is due to a sulfur containing molecule whereas the vanillin gives the vanilla flavour we cherish in ice creams and cakes (figure 1).[1] Moreover, dyes such as Indigo, which has been a major part of our Indian history, is an organic molecule. All our five senses have been related to organic chemistry in one way or the other!

Numerous examples of organic compounds in nature make us believe that it is indeed possible to mimic it. To understand as well as replicate the structures and functions of nature,

organic chemistry and its tools have been studied and built over several years. The reactivity of organic molecules (mainly carbon containing compounds) can be ascertained if the intermediates can be studied broadly.

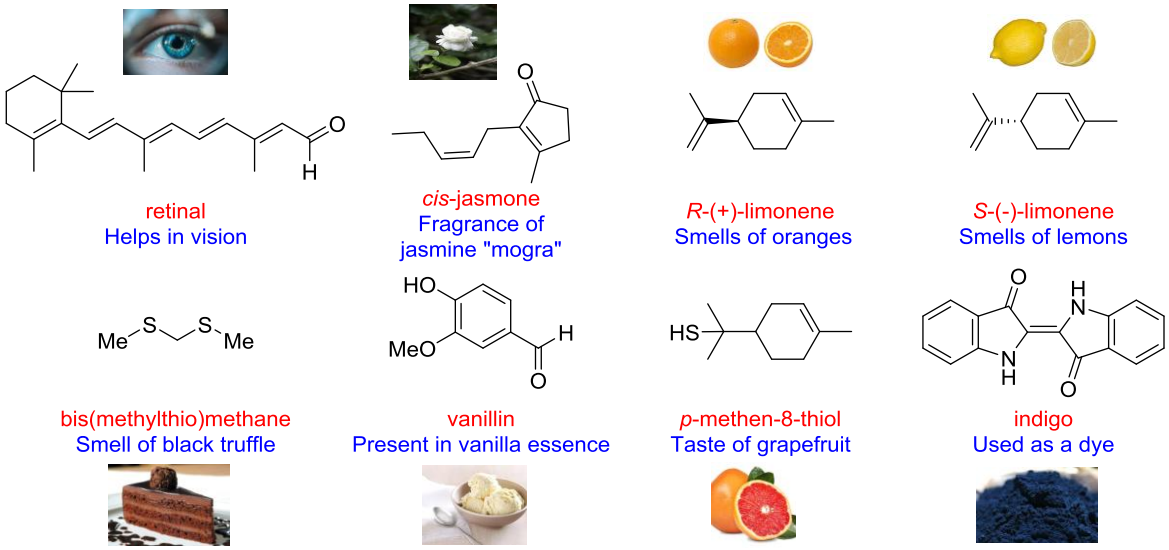


Figure 1: Organic molecules influencing our senses[1]

The primary intermediates in organic chemistry are cations, anions, radicals and carbenes (figure 2). They help in predicting and realizing synthesis of complex natural products, which are biologically significant. If you recall, in school, we are mainly taught about the ionic reactions, which involved the cations and the anions, and their reactivity and stability. They can be obtained by a heterolytic fission of a chemical bond, e.g. A in A–B allows B to take both the bonded pair of e⁻s, thus A becomes positively charged (cation) and B becomes negatively charged (anion). The 'book keeping' of electrons during the bond breaking process is denoted by a spear headed arrow.[2]

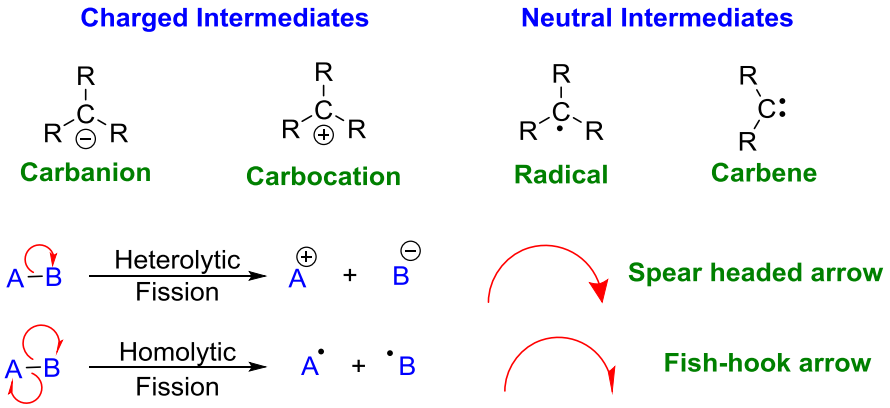


Figure 2: Reactive intermediates and their formation[2]

However, there is an alternative possibility for bond fission in which both A and B in A–B retain one e^- each. In this scenario, the intermediates $A^\bullet$ and $B^\bullet$ are both neutral and are called radicals. This homolytic fission is denoted by a 'fish-hook' arrow. Since their valency is incomplete, they look for options of completing it by a reaction, which many a times appears to be random. For several decades, the scientists thought that chemistry of radicals is quite mysterious! If looked at platonically, we may perceive them to be harmful. Free radicals are known to get generated in combustion of fuel in an engine. Did you know that melanin in our skin helps in preventing generation of free radicals by protecting us from UV rays of the sun? Do you know why green tea is considered good for weight loss? The current hypothesis is that it contains anti-oxidants, which have free radical scavenging capability. However, at school level, the knowledge of radicals that we got was of halogenation and ozone layer depletion. We studied that reactions of radicals are uncontrollable as they seem to be unstoppable until all the reactants are consumed. In fact, even in the early part of the 20th century, scientists largely focused on the ionic reactions (involving cations and anions) alone as they were far better controllable. Although, Gomberg was able to isolate triphenyl radical in 1900, it was not until 1930 that chemists could find enough evidence to accept that a trivalent carbon species existed.[3-4] Organic chemists had not taken appropriate risks for taming the notorious radicals. Perhaps, this was the time when the word "radical" got a negative connotation in English language! With the influx of courageous and innovative chemists came strategies with which the stability and reactivity of the radicals were studied. The initial breakthroughs on 'taming' radicals fruitfully were in the domain of polymer chemistry. Synthesis of polymers with different properties and hence diverse uses quickly caught the imagination of the industry in the middle of 20th century. Industrialization can be attributed to the progress in the synthesis of various polymers and textiles such as polystyrene, Teflon etc. *via* radical chemistry, in turn enabling the faith in these intermediates. Radicals became as important and sought out in the world of polymer chemistry as "Harry Potter" is to the wizarding world! Sustained efforts over the years on taming radicals to carry out well defined and controlled reactions finally yielded fruits, when organic chemists could tweak their substrates in such a manner that the radical reactions progressed only at the reactive centres and nowhere else. It was a great turning point and it led to 'mainstreaming' of this ephemeral intermediate. The developments in the understanding of the radical chemistry was so rapid that today, organic chemists confidently

plan the total synthesis of complex natural products using radical based reactions in key steps. But, it was not until the total synthesis of hirsutene by Curran in 1985 that we saw an efficient use of a cascade (a series of reactions, *vide infra*) radical cyclization.[5-15] Now, let us try to understand how and why radicals behave in a certain way and how they were tamed.

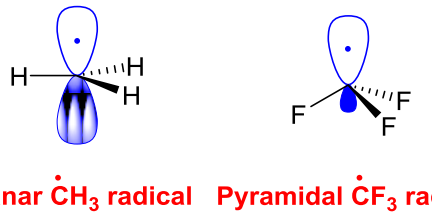
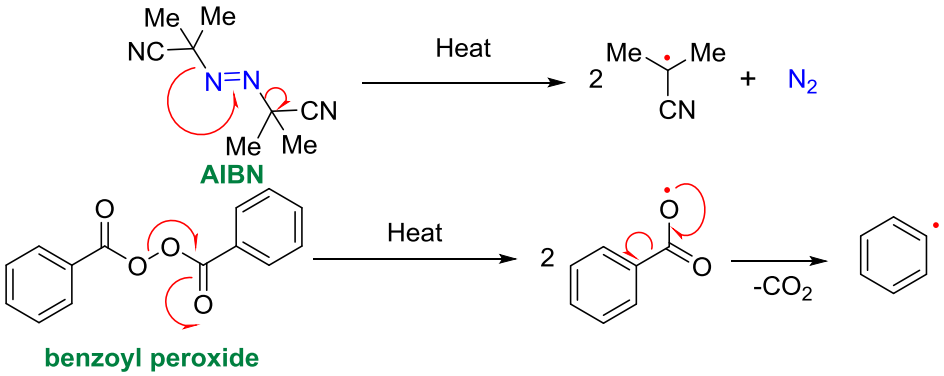


Figure 3: Structure of carbon centred radicals[1]

The radical, in specific, carbon radical is a species, which is trivalent and contains a single electron in the *p* orbital. It is electron deficient in nature. Its geometry is mostly planar but could occasionally be pyramidal due to certain substituents present on it (figure 3).[1]

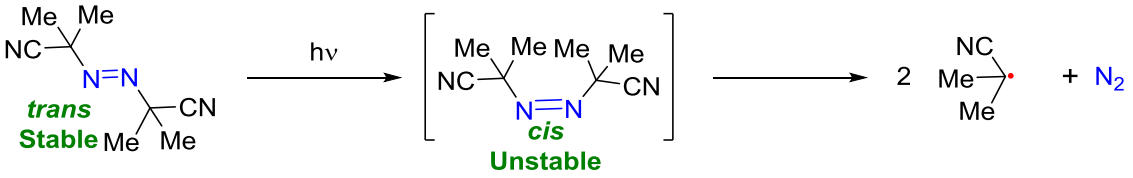


Scheme 1: Radical generation by thermolysis[2]

There are two ways of generating radicals by homolytic cleavage of covalent bonds:

1. **Thermolysis:** Most covalent bonds are strong and require high temperature (> 800 ^{o}C) to cleave them. But some molecules have weaker covalent bonds, which can be cleaved homolytically at <150 ^{o}C (Scheme 1), *e.g.* Azobisisobutyronitrile (AIBN), benzoyl peroxide, triethyl borane etc. In AIBN, generation of N_2 is the driving force for the homolytic C-N bond cleavage. On the other hand, in benzoyl peroxide, initial homolytic cleavage of O-O bond generates $PhCOO^{\bullet}$, which readily loses stable CO_2 leaving behind $Ph^{\bullet}$ radical.[2]
2. **Photolysis:** Weaker covalent bonds have the tendency to break when shown to light. For instance, AIBN produces radicals by converting into its *cis*-isomer, which is unstable and

hence cleaves C-N bond to generate radical and N_2. Expulsion of N_2 is entropically favoured process.[2]



Scheme 2: Radical generation by photolysis[2]

Thus, radical reactions can be initiated both by heat as well as light. Homolytic bond cleavage has been studied extensively and is dependent on the bond dissociation energy (energy required for the formation of that radical) (BDE).[16]

Bond	BDE (kcal/mol)	Bond	BDE (kcal/mol)	Bond	BDE (kcal/mol)
CH_3-H	105	F-H	136	PhS-H	83
CH_3CH_2-H	100	Cl-H	102	$(CH_3)_3Si$-H	93
$(CH_3)_2C$-H	98	Br-H	87	Bu_3Sn-H	78
$(CH_3)_3$-H	96	I-H	71	PhCOO-OOCPh	60
CH_2=CH-H	111	H_2NCH_2-H	84	$HOCH_2$-H	96
HC≡C-H	133	HO-H	119	H-H	104

Table 1: Bond dissociation energies (BDEs) of various molecules[16]

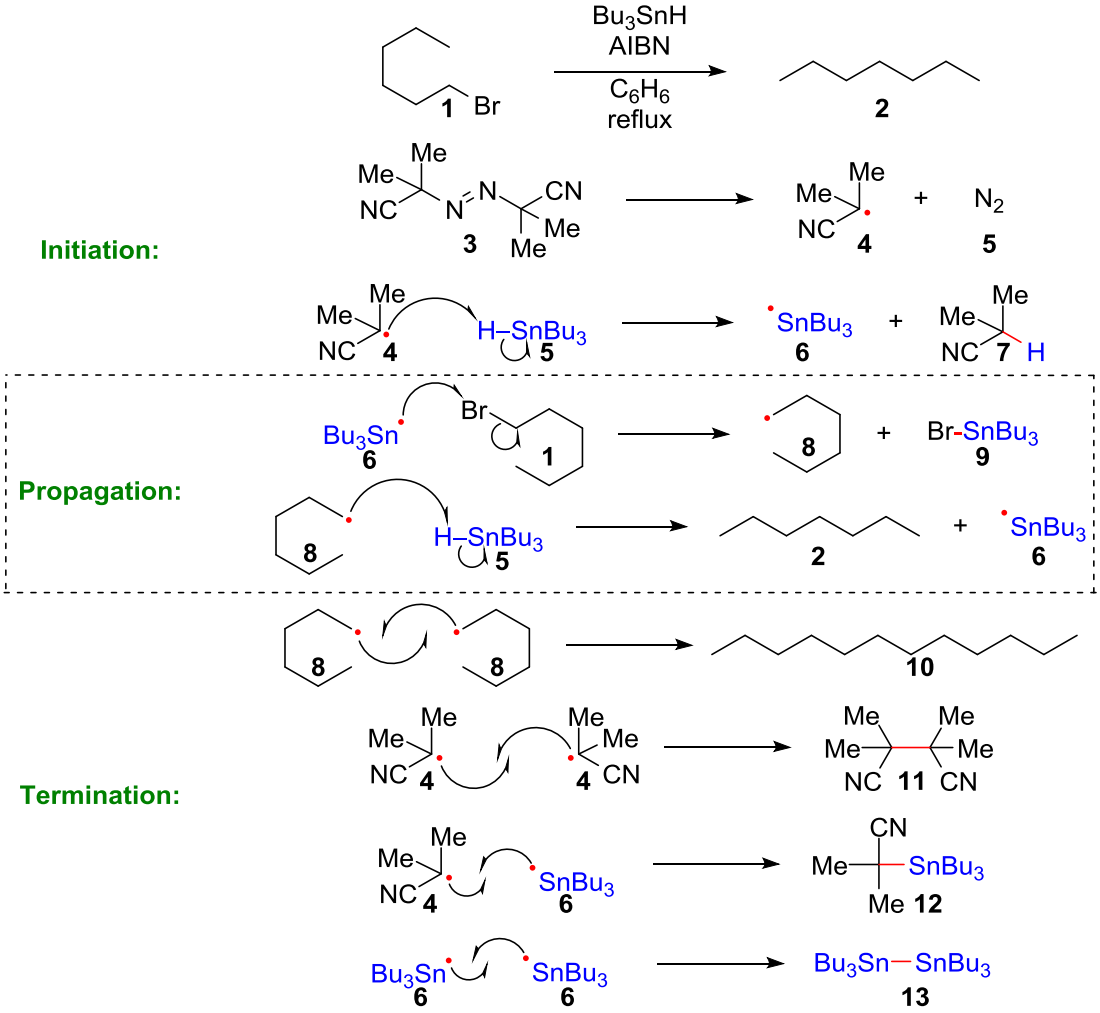
Table 1 shows the BDE of various radicals. If you observe closely, as the branching in carbon chain increases from methyl, ethyl, isopropyl to *tert*-butyl, the BDE slightly decreases – lower the BDE, easier cleavage. More the substitution on the radical carbon, more stable is the radical. This is similar to the property of cations (inductive effect and hyperconjugation). Allylic radical is more stable than vinylic (ethylene). Special mention must be made of PhS-H, Bu_3Sn-H and $[Ph(CO)O]_2$, which play key roles in most of the radical reactions, due to their low bond dissociation energy. As mentioned previously $[Ph(CO)O]_2$ undergoes

thermolysis or photolysis of O-O bond pretty easily and is one of the most frequently used initiators like AIBN.

A successful radical transformation can be attributed to the following steps *viz.*

a. Initiation
b. Propagation
c. Termination

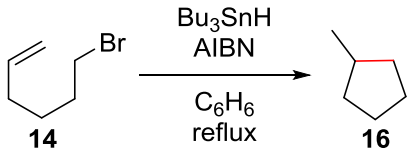
These processes are present in all the radical reactions, without any exceptions. Let's understand these steps with radical reaction of 1-bromohexane (**1**) using $^{n}Bu_3SnH$ and AIBN to furnish the *n*-hexane (**2**) as the product – a reduction reaction.



Scheme 3: Reduction of organic halide using radical reaction

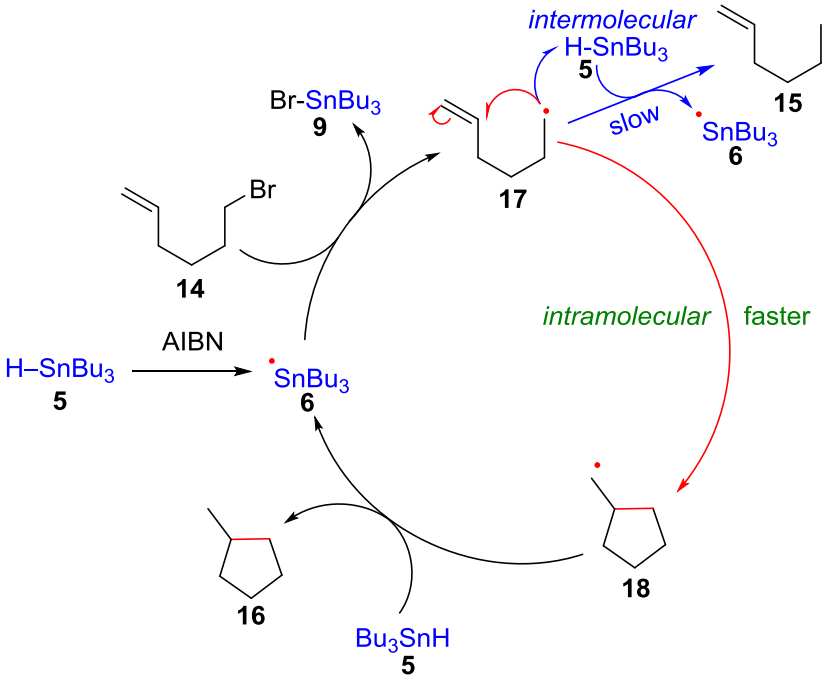
If you observe the temperature, benzene (C_6H_6) is being refluxed, which implies that the temperature is that of the boiling point of benzene i.e. 80 ^{o}C. AIBN (**3**) undergoes thermolysis at around 56 ^{o}C generating a rather unreactive radical $^{\bullet}C(CN)Me_2$ **4**. However, it can abstract

a weakly bonded hydrogen atom from $Bu_3Sn–H$ (**5**) to generate $Bu_3Sn^{\bullet}$ **6** (Scheme 3).After initiation, one must identify the next weak covalent bond, which in this case happens to be C–Br bond. Thus, the $Bu_3Sn^{\bullet}$ **6** starts a chain reaction, wherein it reacts with bromide **1** to generate hexanyl radical **8** along with Bu_3SnBr **9**. The hexanyl radical **8** abstracts a hydrogen from $Bu_3Sn–H$(**5**) enabling the regeneration of $Bu_3Sn^{\bullet}$**6** along with the hexane (**2**).These two steps keep repeating until all of the 1-bromohexane (**1**) has been consumed. This is called the propagation stage of the mechanism. Finally, various radical intermediates 'quench' by bonding with one another, known as the termination of the radical process.



Scheme 4: Intramolecular radical cyclization

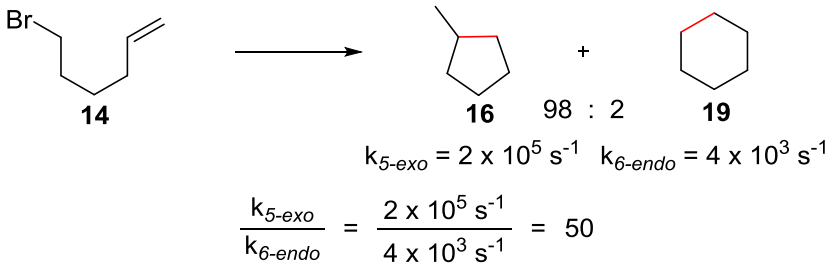
Consider the reaction of 6-bromohex-1-ene (**14**) under similar conditions i.e. using Bu_3SnH (**5**) and AIBN (**3**) in refluxing benzene (Scheme 4). Interestingly, while the difference between the two starting compounds is only that of an olefin, the outcomes change dramatically! What one observes in this reaction is not formation of the hex-1-ene (**15**) but methylcyclopentane (**16**) as the major product. So how do we rationalise the outcome of this reaction? Which step in the radical mechanism is different? Let us breakdown the steps again.



Scheme 5: Mechanism of intramolecular radical cyclization

As in the earlier case, the initiation step is the same. At the propagation stage, once the $Bu_3Sn^{\bullet}$ **6** reacts with the 6-bromohex-1-ene (**14**) to generate hex-1-enyl radical **17**, it undergoes a faster *intramolecular* (within the molecule) cyclization process to give cyclopentylmethyl radical **18** rather than the *intermolecular* hydrogen abstraction from Bu_3SnH (**5**) to furnish hex-1-ene (**15**) (Scheme 5). You would appreciate that an intramolecular process should in general faster due to proximity than an intermolecular reaction, which is diffusion controlled. Also note that a weaker π-bond is broken and a stronger σ-bond is formed during this radical cyclization step. Cyclopentylmethyl radical **18** then abstracts an H from Bu_3SnH (**5**) to furnish the product **16** and regenerates $Bu_3Sn^{\bullet}$ **6** (propagation).

But the story doesn't end here! On more careful analysis of the reaction, it was revealed that a very small quantity of cyclohexane **19** was also obtained along with the methylcyclopentane **16**, which is the major product. Arguably, cyclohexane **19** would be thermodynamically more stable product of the two (Scheme 6).[17]



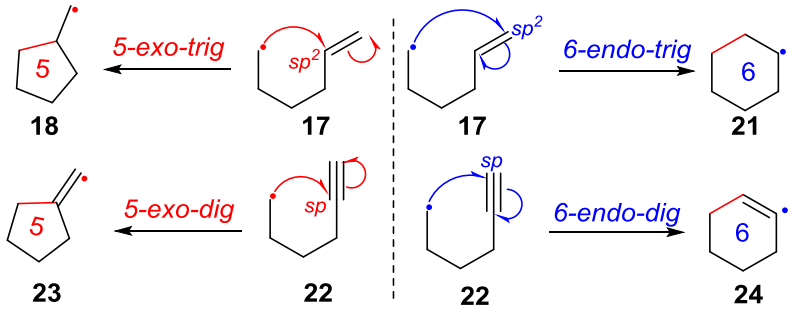
Scheme 6: Kinetics of radical cyclization reaction[17]

Measurement of rate of this reaction showed that methylcyclopentane formation is indeed 50 times faster than cyclohexane. Why is this so? Are there any principles, which govern this or related processes? Is this the only instance when selective formation of one ring over the other is seen? Baldwin observed that this phenomenon is not unique and this kind of selectivity for formation of one ring size over the other (here, five-membered ring formed easily as compared to six-membered ring) is quite common. While explaining this empirical observation of relative facility of ring forming reactions, he said, "The physical bases of the rules lie in the stereochemical requirements of the transition states for the various tetrahedral, trigonal, and digonal ring closure processes." While detailed discussion of these aspects would be out of the scope of the present article, these observations made by Baldwin way back in 1976, are still found to be useful by synthetic chemists, particularly in planning synthesis of cyclic compounds.[18]

An empirical basis to predict the relative facility of ring forming reactions are now referred to as Baldwin's rules. They are used for all *intramolecular* cyclizations – cationic, anionic or radical. The nomenclature of the rules captures three aspects related to the reaction, namely:

1. The size of the ring formed.
2. Whether the bond that broke is inside (*endo*) or outside (*exo*) the smallest ring formed.
3. The hybridization of the carbon being attacked – *sp* (*dig*onal), sp^2 (*trig*onal) or sp^3 (*tet*rahedral).

Now let us try to get the nomenclature for the radical cyclization of 6-bromohex-1-ene (**1**) to give methylcyclopentane (**16**) and cyclohexane (**19**) (*cf.* Scheme 6). As per Baldwin system, formation of methylcyclopentane involves a *5-exo-trig* radical cyclization. How do we arrive at this nomenclature?



Scheme 7: Nomenclature of Baldwin's Rules[18]

The cyclization of the hexenyl radical **17** involves formation of five membered ring – hence *5*. The hexenyl radical **17** undergoes *intramolecular* addition in such a way that the breaking bond is *exo*cyclic (i.e. outside the ring) to the ring that is formed – hence *exo*. The geometry (hybridization) of the carbon atom undergoing ring closure reaction is *tri*gonal (sp^2) – hence *trig* (Scheme 7). Now, can you guess what will be the nomenclature for cyclohexyl radical **21** formation process? Six-membered ring is formed, the breaking bond is inside the ring (*endo*cyclic) and the carbon atom undergoing ring closure is sp^2 hybridised i.e. has trigonal geometry – hence it will be a *6-endo-trig* radical cyclization.

What if we replace the olefin in the above example with the alkyne as in the case of radical **22** leading to radicals **23** or **24**? The reactions would be said to involve *5-exo-dig* (leading to methylenecyclopentenyl radical **23**) and *6-endo-dig* (leading to cyclohexenyl radical **24**) radical cyclization reactions, respectively.

The empirical rules provided by Baldwin are summarised in Table 2. To assess the favourable mode of cyclization, the boxes that are green and ticked are termed to be feasible, whereas, the boxes that are red and have a cross are known to be not feasible.

Ring Size	*endo*			*exo*		
	dig	***trig***	***tet***	***Dig***	***trig***	***tet***
3	✓	✗	✗	✓	✓	✓
4	✓	✗	✗	✓	✓	✓
5	✓	✗	✗	✗	✓	✓
6	✓	✓	✗	✗	✓	✓
7	✓	✓	✗	✗	✓	✓

Table 2: Baldwin's Rules for Ring Closure[1]

For example, a *4-exo-trig* cyclization would mean that a four-membered ring formation, with the bond that broke being outside the ring and sp^2 hybridization at the carbon centre on which the attack took place. According to Table 2, this cyclization is favourable, hence could occur.

For more than a decade, our group has been engaged in developing strategies for the synthesis of *oxa*- and *aza*-cycles using a functional group called *vinylogous* carbonates/carbamates. Since we would be using this term often, let us understand what we mean by *vinylogous*.

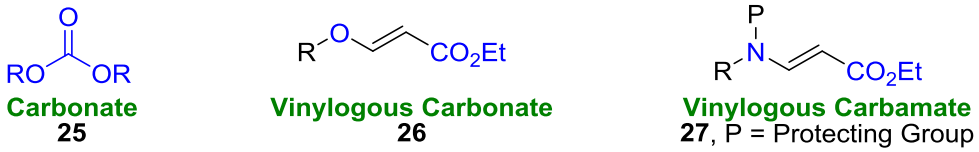
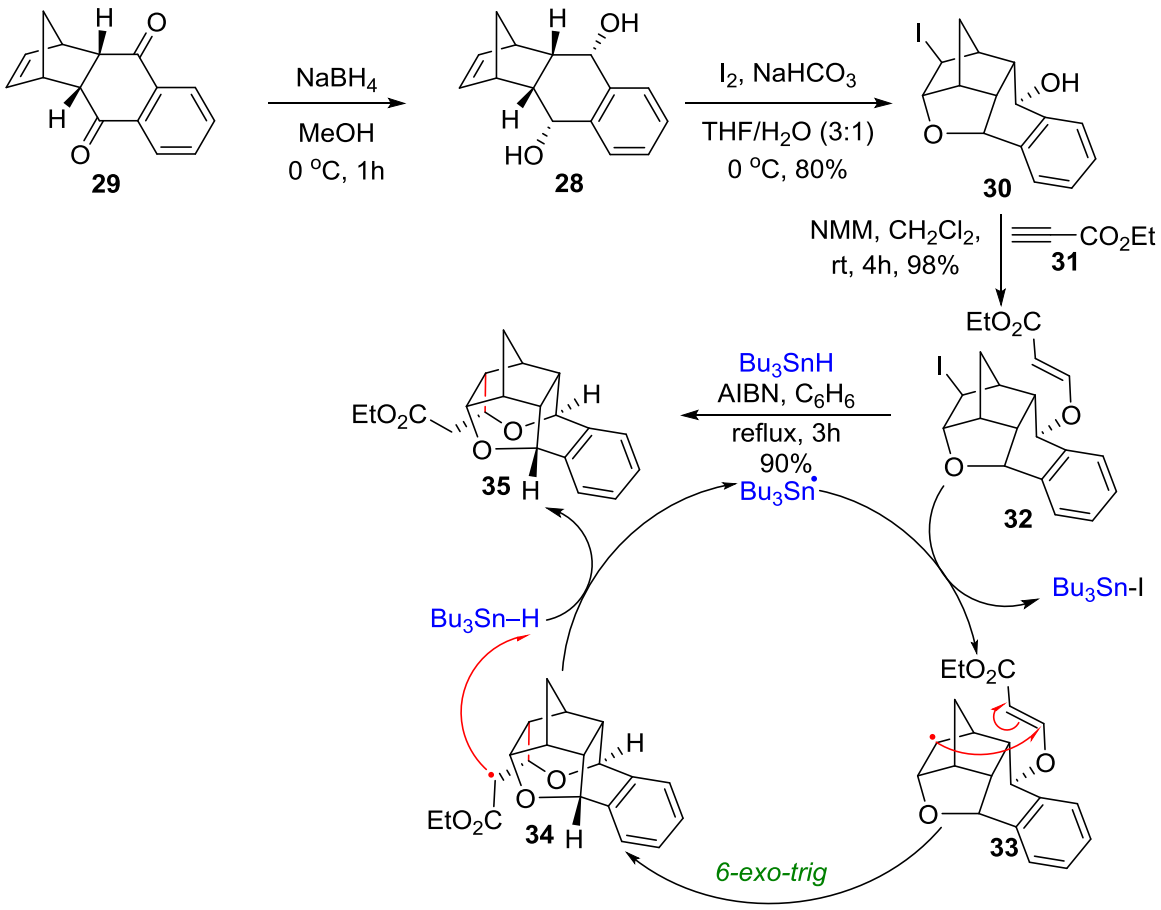


Figure 4: Carbonate and vinylogous carbonate/carbamate

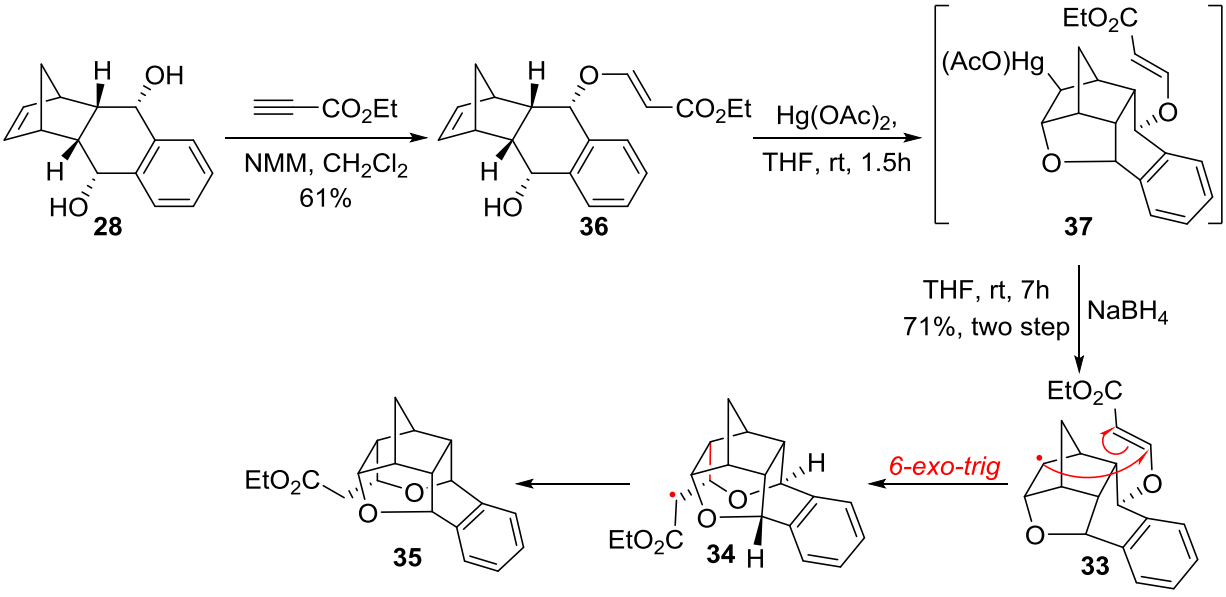
You already know that the functional group present in RO–CO–OR **25** is called as carbonate. Imagine a vinyl group inserted between oxygen and CO of the carbonate to give a compound like **26**. The functional group in this compound **26** would be referred to as vinylogous carbonate – recollect term '*homologous* series' for alkanes – you inserted a CH_2 to get higher alkane – so this is somewhat similar to that wherein we have inserted vinyl (CH=CH) group! In a similar manner the functional group in compound like **27** would be referred to as *vinylogous* carbamate. Of course, these compounds **26** and **27** can also be called as *β*-alkoxy acrylate and *β*-amino acrylate, respectively. The push-pull ability of this group is what

attracted us towards its reactivity as an acceptor and led us to explore its utility in radical reactions.

Oxa-bowls and cages are unnatural products with interesting structural features. Though symmetrical *oxa*-bowls and cages were synthesized easily, our objective was to synthesize the unsymmetrical *dioxa*-cages utilizing the radical cyclization strategy. We began with the synthesis of diol **28**, which was readily obtained by reduction of the Diels-Alder adduct **29**. Iodoetherification reaction on the diol **28** using iodine and aq. $NaHCO_3$ gave the iodo alcohol **30**. Reaction of the alcohol **30** with ethyl propiolate (**31**) in the presence of *N*-methyl morpholine (NMM) resulted in the formation of the vinylogous carbonate **32** *via oxa*-Michael addition of hydroxy group to ynoate moiety. Once the vinylogous carbonate **32** was available, it was subjected to radical cyclization conditions using Bu_3SnH and AIBN in refluxing benzene (Scheme 8). During the reaction, the C–I bond cleaves homolytically to give the radical **33**. This radical undergoes an *intramolecular 6-exo-trig* cyclization with vinylogous carbonate (*cf.* Baldwin's rules of cyclization, Table 1) to give new radical **34**. The radical **34** then abstracts a hydrogen from $^{n}Bu_3SnH$ (**5**) to give the *oxa*-bowl **35**, regenerating $^{n}Bu_3Sn^{\bullet}$ (propagation). The fate of the radical cyclization was determined by the topology of the substrate and hence, is extremely specific.[19]



Scheme 8: Synthesis of *oxa*-bowl *via* radical cyclization to vinylogous carbonate[19]

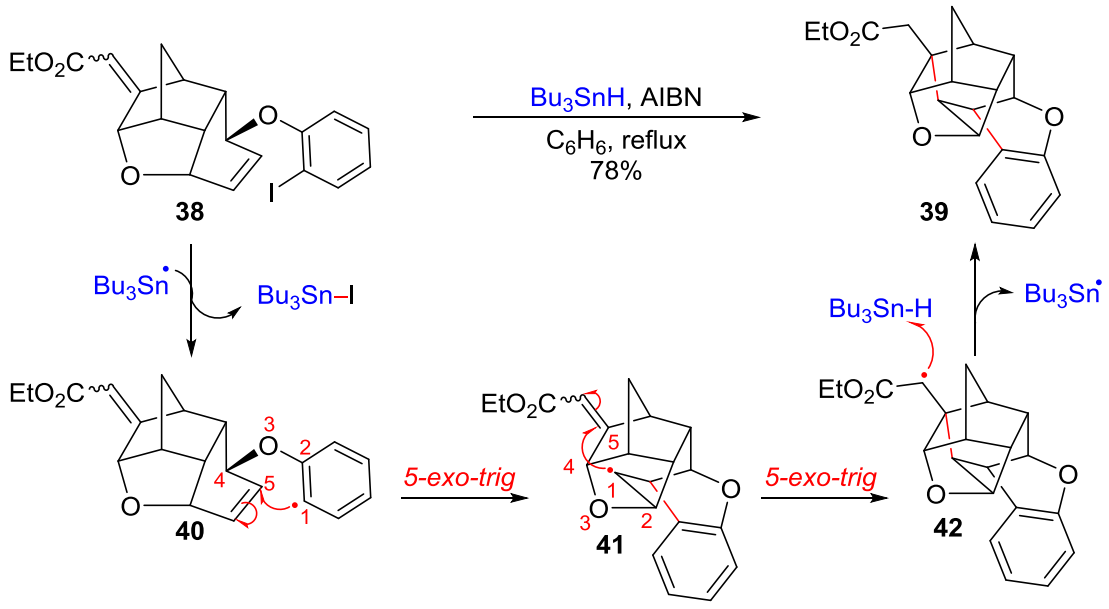


Scheme 9: Synthesis of *oxa*-bowl by oxy-mercuration-reduction[20-

As with other reactive intermediates, whatever be the method of its generation, once formed, the fate of the radical is the same. Thus, when the vinylogous carbonate **36** (generated from the diol **28** by reaction with ethyl propiolate) was subjected to treatment with [$Hg(OAc)_2$], it resulted in the formation of the intermediate **37** *via* oxy-mercuration (Scheme 9). When this intermediate is reacted sodium borohydride ($NaBH_4$), it generated radical **33**. This radical will undergo a *6-exo-trig* cyclization to furnish the di*oxa*-bowl **35**. This reaction in a way further supports that the mechanism of the reduction step of oxy-mercuration – reduction protocol for the synthesis of alcohols/ethers that you would have studied earlier, indeed involved a radical intermediate and not an ionic mechanism.[20]

At this juncture, we started wondering if it is necessary to generate radical from halide alone or one generated as the product of one cyclization can participate in another cyclization. In another words, can a radical cyclization be followed by another if one more olefin is situated correctly within the same molecule?

To test this idea, we synthesized ether **38** wherein an iodide is present on phenyl moiety along with two different types of olefins. When this iodide was subjected to radical cyclization using Bu_3SnH and AIBN in refluxing benzene, the dioxa-cage **39** was obtained as the product, which is devoid of both the olefins indicating that two cyclizations have indeed taken place. So how do we explain formation of the product?

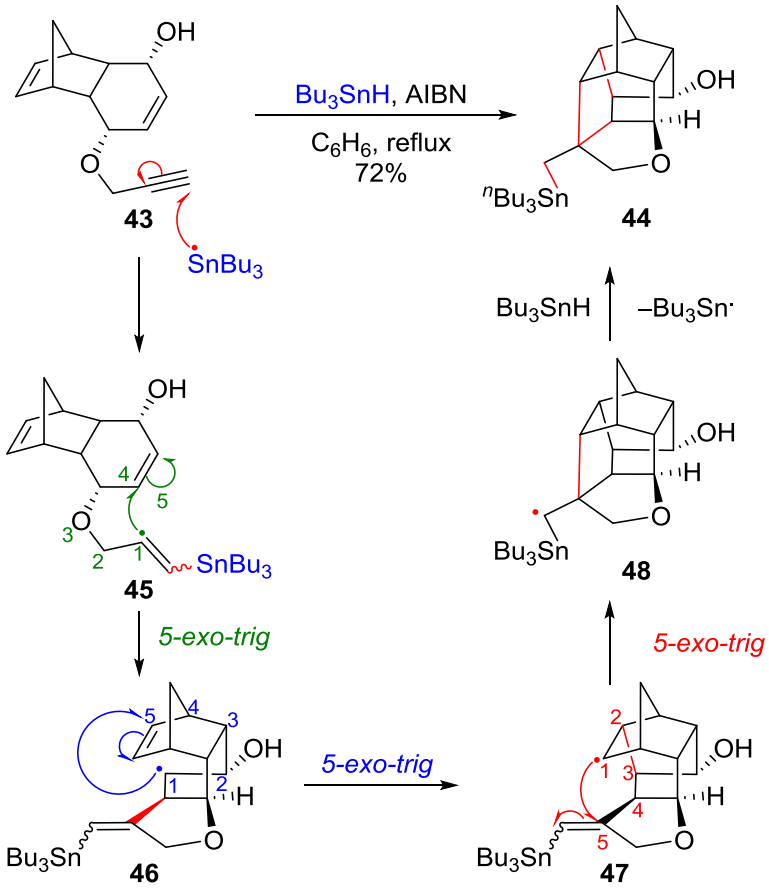


Scheme 10: Sequential radical cyclization for the synthesis of *oxa*-cage[21]

The $Bu_3Sn^{\bullet}$ cleaves the C–I bond to give transient radical **40**. It is in a suitable position to undergo a *5-exo-trig* cyclization with the C=C double bond present in the vicinity. Why did

aryl radical not cyclize on the olefin bearing ester, which arguably is better acceptor? Does it have to do with the relative ease of cyclization – a *5-exo-trig* cyclization is lot more facile than *7-exo-trig* cyclization – and it is a kinetic outcome? No, the reason is the topology of the molecule – the stereochemistry of the molecule precludes approach of the radical to the olefin bearing ester. The newly formed radical **41**, has the olefin bearing ester appropriately positioned for another *5-exo-trig* cyclization, which readily takes place to furnish the radical **42**. This intermediate is now reduced by the $Bu_3Sn–H$ in turn giving $Bu_3Sn^{\bullet}$, which propagates the reaction further (Scheme 10). This study helped us synthesize a unique framework, which would've been very difficult to synthesize otherwise.[21]

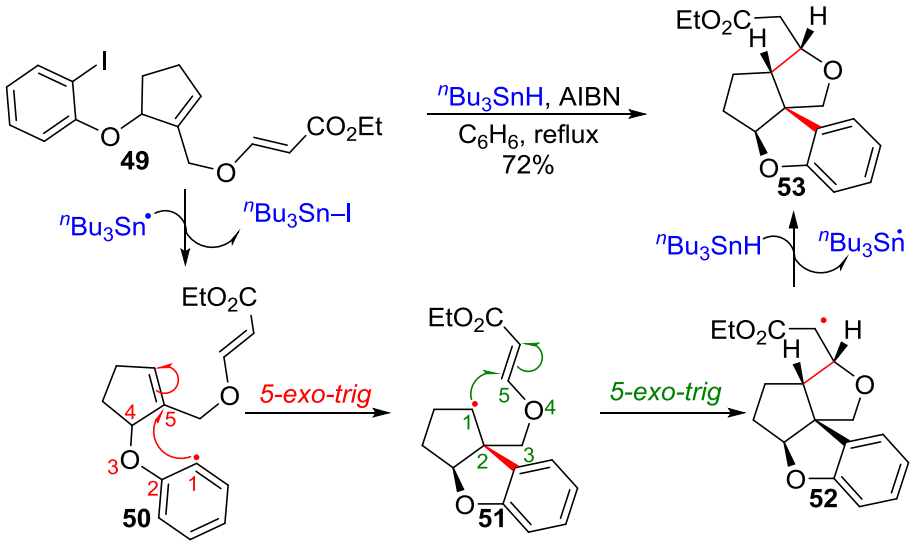
In the quest to dive deeper in the radical cyclization, we decided to move away from acrylates little bit and add more non-conjugated olefins instead in the molecule. Thus, we subjected propargyl ether **43**, which has an alkyne and two olefins, to radical cyclization conditions. The reaction indeed resulted in the consumption of starting material and resulted in the formation of a complex looking cage compound **44**. So how did this product form? It is appearent that lots of bond making/bond-making has taken place – most importantly, all the π-bonds in the starting compound have magically vanished! As you know, in science, there is no magic but only logic! So can we explain it logically?



Scheme 11: Tandem radical cyclization for the synthesis of *oxa*-cage[22]

Unlike previous cases, wherein tin radical would abstract an iodide, here due to absence of any C-X bond, the $^{n}Bu_3Sn^{\bullet}$ radical adds to weakest bond i.e. to the alkyne moiety generating a vinyl radical **45**. The vinyl radical **45** undegoes a very facile *5-exo-trig* radical cyclization to grenerate new radical intermediate **46**. Due to the topology of the molecule **46**, the radical entity comes in close proximity with the double bond located just above it. Not just that, but if the radical adds to olefin, it would result in a very facile *5-exo-trig* cycliazation! Naturally, this intramolecuar process takes place rather than its reduction with Bu_3SnH and thus, new radical **47** is generated. But the story does not end here! Note that an olefin is just located beneath the radical in the intermediate **47**. Can you count the location of the radical from the olefin if it was to undergo cyclization? In principle, you would get many answers, but as per Baldwin, one should remember to count the '*smallest ring so formed*'! So it is again a *5-exo-trig* radical cyclization that follows on the intermediate **47** resulting in the formation of the radical intermediate **48**. Finally, this radical abstracts hydrogen from Bu_3SnH to give the cage compound **44** – and not to forget regenerate $Bu_3Sn^{\bullet}$ to keep radical cyclization going (propagation) (Scheme 11)!

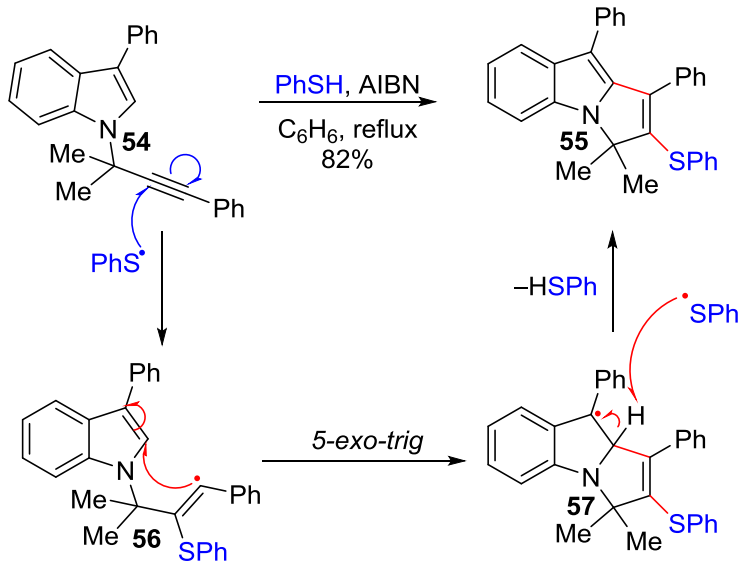
Can you count how many different steps were invovled in this process? Let's count: i. intermoelcular $^{n}Bu_3Sn^{\bullet}$ addition to alkyne; ii. *5-exo-trig* radical cyclization; iii. *5-exo-trig* radical cyclization; iv. *5-exo-trig* radical cyclization; v. intermoelcular hydrogen abstration. When a series of steps of such type occur one after the other in a reaction, it is termed as "*cascade reaction*" (*a.k.a. tandem reaction*). It is one of the unique transformations, wherein the successive cyclization is dependant on the outcome of the previous cyclization due to structural proximity of the reactive species.[22]



Scheme 12: Synthesis of angular triquinanes by tandem radical cyclization[23-24]

Another structurally interesting class of molecules that we were curious to synthesize were triquinanes. The idea of tandem/cascade radical cyclization was explored in the synthesis of linear triquianes in 1980's.[15] Many natural products bearing linearly or angularly-fused carbocyclic triquinane motifs from terpene family were isolated and synthesised using various methods. However, synthesis of heteroatom containing angular triquinanes had not been explored much. To proceed in this endeavour, we prepared *o*-iodophenyl cyclopentenyl vinylogous carbonate **49** and subjected it to radical conditions of Bu_3SnH/AIBN in benzene (Scheme 12). As you would have guessed by now, the initial step sill involve generation of $Bu_3Sn^{\bullet}$ radical, which in turn will furnish the phenyl radical **50**. This phenyl radical **51** adds to the cyclopentenyl double bond in a *5-exo-trig* manner forming a benzofuran skeleton **51** in a stereoselective manner. The radical **51** thus formed, undergoes one more *5-exo-trig* cyclization **52** – this time to vinylogous carbonate moiety, to stereoselectively form *dioxa*-triquinane **53** in good yield.[23-24]

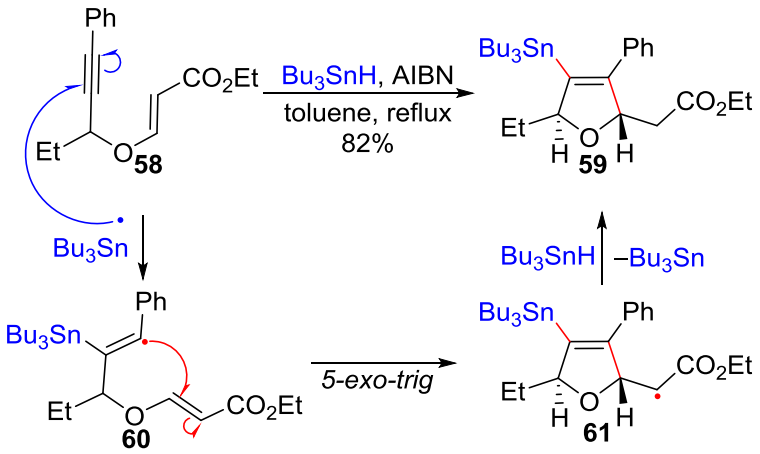
It may seem as if Bu_3SnH is the only reagent used for initiation of radicals. It is primarily so because in general, it does not react rapidly with the reactive intermediates generated, allowing them to participate in further cyclization processes as opposed to direct reduction. There are other reagents as well, which are used frequently while developing a successful radical cyclization, one such example being thiophenol (PhSH). As is visible from its BDE, thiophenol generates $H^{\bullet}$ and $PhS^{\bullet}$ quite easily.



Scheme 13: Synthesis of *N*-fused indole using radical cyclization[25]

Relying on this fact, we attempted a radical cyclization reaction on *N*-propargylated indole **54** using excess PhSH/AIBN rather than Bu_3SnH/AIBN. Interestingly, we observed formation of the *N*-fused indole **55** in good yield (Scheme 13). Initially formed $PhS^{\bullet}$ adds across the C≡C triple bond specifically, such that the vinyl radical **56** thus formed is stabilized by the Ph substituent. This vinyl radical **56** adds to the C=C double bond of the indole to give radical **57**. Unlike previous cases, here instead of reduction of the radical **57**, $PhS^{\bullet}$ abstracts a hydrogen atom from the carbon next to nitrogen and forms the product, *N*-fused indole **55**. The last step is attributed to ability of $PhS^{\bullet}$ to abstract a hydrogen easily as well as the fact that indole regains aromaticity if hydrogen is abstracted. [25]

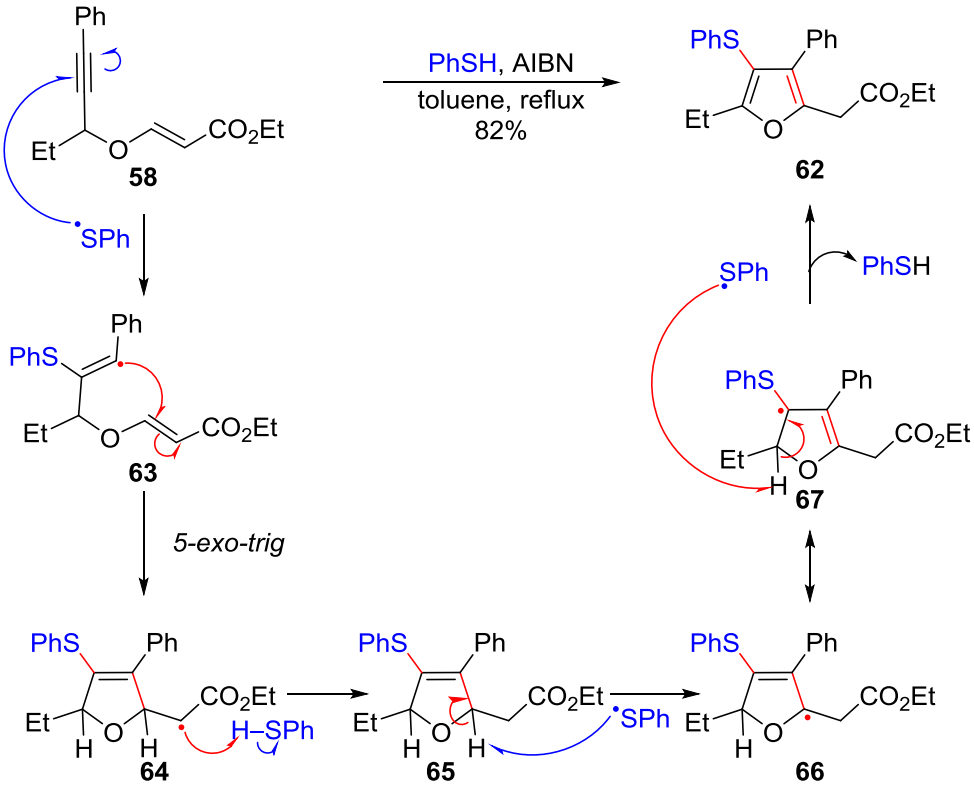
Till now, we came across radical cyclization wherein radicals were added onto isolated alkenes, vinylogous carbonates, alkynes or a heterocycle as in the case of indole. We planned synthesis of tetrahydrofuran **59** by addition of $Bu_3Sn^{\bullet}$ to propargyl vinylogous carbonate **58** (Scheme 14). Indeed, we observed synthesis of dihydrofuran by the addition of $Bu_3Sn^{\bullet}$ on the internal alkyne **58**, which in turn forms vinyl radical **60**.



Scheme 14: Synthesis of tetrasubstituted dihydrofuran by tributyltinhydride addition[26]

It then proceeds *via* a *5-exo-trig* cyclization to the vinylogous carbonate forming radical **61**, which is quenched by Bu_3SnH to give tetrasubstituted dihydrofuran **59** in good yield.

You may ask, when we add thiophenol PhSH to the same propargyl vinylogous carbonate **58**, will we get a molecule that is like dihydrofuran **59**? The only way to find the answer was to carry out an experiment. Interestingly, when we subjected vinylogous carbonate **58** to radical–



Scheme 15: Synthesis of tetrasubstituted furan by thiophenol addition[26]

cyclization with excess of PhSH/AIBN in refluxing toluene, we got tetrasubstituted furan **62**! So how did we get the furan? After carrying out mechanistic investigation, we got a fair idea as

to how reaction proceeds. To cut the long story short, let us very briefly explain what happened in this reaction. Addition of thiyl radical to alkyne gives radical intermediates **63**, which undergoes a *5-exo-trig* radical cyclization to furnish the radical **64**, which in turn undergoes reduction to form the dihydrofuran **65** (Scheme 15). However, the reaction does not stop here and the PhS$^{\bullet}$ picks up a hydrogen α to the oxygen and β to the ester, forming intermediate **66**. The intermediate **66** can be written as its resonance structure **67**. The PhS$^{\bullet}$ picks up another hydrogen, forming an aromatic molecule furan **62**.[26]

In conclusion, we have demonstrated over the years that tandem radical reactions of vinylogous carbonates have tremendous potential to be used in the synthesis of various types of complex heterocycles. It requires judicious planning, diligent execution and considerable effort – just like in the story of the thirsty crow and the scarce water in the clay pot! One by one, as the crow adds stone inside the pot, the water level keeps rising, ultimately making it reachable for it to drink and quench it's thirst. Radical reactions can be straightforward if thought out well and have helped in evolving the chemistry from something that was not dependable to the key reactions in the synthesis of complex molecules.

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Critical Thinking Integrated with Instructional Scaffolding Approach in Physics Classroom

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Abstract

The Case Study presents critical thinking with instructional scaffolding as a novel pedagogical approach in teaching a physics course. The approach is described in detail with the help of examples in introductory physics.

Keywords

Instructional scaffolding, physics learning, critical thinking, pedagogy

Introduction

Many students who scrape through Physics and Mathematics in their 12th Board Examination and still join Engineering stream find it very difficult to cope up with the physics syllabus in the first semester of their engineering education. We have come to realize that they attempt to learn the subject by rote without actually understanding the subject. The issue becomes more difficult for the students who do not come from English medium background. While there may be numerous ways to tackle this problem, we chose to improve critical thinking skills of students from scratch to an acceptable level. The first step towards this was to help the students break up a physics problem – say projectile motion – into simple easily understood steps that will logically lead the students to solve the problems in physics with understanding. This breaking up of a problem into simpler logical steps that leads up to the solution is what we define as ‘scaffolding’. We have found that this method works very well in classrooms the downside being that it takes much more time.

It is a question mark whether it is worthwhile spending more time helping students master what they are expected to learn which may end with teaching less content, or is it better to just deliver the content in the stipulated time as is being done presently. These are questions that need more discussion especially when lack of mastery and true understanding is creating a gap between what the job market needs and the capability of our fresh graduates.

Methodology

We consider the methodology of scaffolding from the following two points of views:

1. Critical thinking based on asking right questions, analysis and narration.

2. Logical step by step progression.

We will demonstrate this with an example. Below is a typical question to test the understanding of projectile motion[1].

Problem 1: "A stone is thrown from the top of a building upward at an angle of 30.0° to the horizontal and with an initial speed of 20.0 m/s. If the height of the building is 45 m,

(a) How long does it take before the stone hits the ground?

(b) What is the speed of the stone just before it strikes the ground?"

A question of this nature should be analyzed thoroughly in the classroom so that students start to read questions carefully.

Critical Thinking:

Questions to be asked a priori-

a. In the above question the height of a building is given as 45 meters and the fact that a stone is thrown from the top of the building presumes that somebody is standing on top of the building and throwing the stone. Should we not consider the height of the person's fist at the moment the stone leaves his fist?

b. Nowhere in the question is it clarified that the ground on which the building is standing is horizontal!

c. Should we expect the stone to come to rest when it hits the ground or should it bounce a few number of times before coming to rest? The latter possibility exists if the stone is round in shape.

d. What would happen if the ground where it lands has a downward slope?

e. What are the unstated assumptions in the question?

With the help of above questions we will restate the given problem accurately without any ambiguity. In the process, we will also get rid of the story form of the problem.

Restatement of the problem-

A person is standing/sitting on the top of a building. He throws a stone at an angle of 30.0° to the horizontal and with an initial speed of 20.0 m/s. The height of the building is 45 m. Ignore the vertical distance from the person's hand to the top of the building and assume the stone to be round in shape.

The stone rises to a certain height after being thrown and after some time falls on the ground taking a parabolic path throughout its journey. Assume that the ground on which it falls is flat. The stone most likely bounces a few times before it comes to a halt unless the ground is muddy wherein the stone can get embedded when it strikes. In any case, since the question is to find the speed of the stone and the time when the stone hits the ground for the first time, ignore the motion of the stone after it hits the ground for the first time.

We now give the narration and scaffolding for the above problem. By going through this part, *step by step the student will be able to solve the problem completely to the end.*

Narration and Scaffolding:

a. Narration- The first step would be to draw a sketch/graph and put all the available information in it. This is required to understand the information given vis-à-vis what needs to be determined. Also placing coordinate system helps one to start writing equations of motion with vector components of parameters like velocity, acceleration, displacement with 'plus' or 'minus' sign whichever is appropriate.

Instruction- Sketch an appropriate diagram depicting the situation. Clearly mark x (horizontal) and y (vertical) axes and the origin. Mark 'A' as the starting point, 'B' as the highest point and 'C' as the point at which the stone hits the ground. Write coordinates of points A, B and C. Call the coordinates of point A as (x_0, y_0).

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b. Narration- The next step is to find out what the velocity components of the ball are in the horizontal and vertical direction. What do we mean by resolving vectors? Why do we resolve them?

Remember, the velocity vector makes an angle of 30° with the horizontal. The ball thrown at this angle will not go straight up. It will go to a certain height in a parabolic path after which the ball starts descending downwards again in a parabolic path before it hits the ground. This parabolic motion is considered as a superposition of two straight line motions one in the horizontal direction (along x-axis) and the other in the vertical direction (along y-axis). Point to be noted is that only gravitational acceleration acts on the ball in the vertical direction and no acceleration acts on the ball in the horizontal direction.

With this understanding, one can proceed to write equations of motion of the stone in x and y directions as the parabolic motion is a superposition of two straight line motions in x and y

directions. The relevant equation of motion is $s = ut + \frac{1}{2}at^2$. In this equation one needs to take into account (i) displacement, (ii) velocity and (iii) acceleration with appropriate sign depending on the coordinate system you have chosen.

The displacement should be measured with respect to the starting point.

Now the velocity vector given in the problem is at 30° with the horizontal, which is neither in the x-direction nor in the y-direction. So one needs to find what is the effective velocity in x and y directions when the actual velocity is given at 30° with the horizontal (x-axis). The effective velocity of the stone along x and y directions can be found by resolving velocity vector along x and y directions. In other words, if you find projection of the velocity vector on x and y axes, what you get are the effective velocity vectors/velocity components along x and y directions. It is these velocity components that need to be plugged in the above equation of motion. You need to use your knowledge of trigonometry to write these components[2].

Remember, the velocity of the stone along x-axis remains unchanged and that along the y-axis changes due to gravitational acceleration.

Instruction- The stone is thrown at an angle of 30 degrees with a speed of 20 meters per second. Therefore, resolving the velocity vector into its horizontal and vertical components we get

$v_{x0} =$----------

$v_{y0} =$----------

Equation of motion for x and y distances are given by

$x - x_0 =$----------

$y - y_0$ = ----------

Eliminating t from the above two equations, one can write y in terms of x as:

y = ----------

The value (coordinate) of y when the stone hits the ground = ----------

$\therefore$ From x - y relation, the value of x at which the stone hits the ground

= ----------

Use equation of motion for x and find at what time, the stone will have the x value calculated in above step.

Using equation of motion for y, find out v_y at the time stone hits the ground (as calculated above).

---

v_x at the time when the stone hits the ground = ----------

Calculate $v = \sqrt{v_x^{\,2} + v_y^{\,2}}$ at the time when the stone hits the ground.

Answer -

The stone hits at the ground at ---------- seconds and its velocity at that time is ---------- (units ------).

Now we present a second problem based on projectile motion. This time we don't give scaffolding to the students. We expect the students to do critical thinking and ask right questions *a priori* to themselves. Then they may restate the problem without any ambiguity. This will then be followed by narration on self scaffolded steps to be taken to solve the problem.

Problem 2: "A monkey escapes from the zoo and climbs a tree. After failing to entice the monkey down, the zookeeper fires a tranquilizer dart directly at the monkey. The monkey lets go at the instant the dart leaves the gun. Show that the dart will always hit the monkey, provided that the dart reaches the monkey before he hits the ground and runs away."[3]

a. Is it possible that the dart will not hit the monkey? If so, under which conditions?

b. What happens if the dart is fired with less speed keeping the angle same? What happens if the dart is fired with more speed keeping the angle same?

c. Give a comment on the vertical distance from the ground where the dart hits the monkey in each of the above cases, as discussed in c.

d. Explain the situation if there is a moderate breeze parallel to ground in horizontal direction flowing with constant velocity. Does the breeze affect the maximum height achieved by the dart?

Expected understanding

For answering problem 2, the students have to understand that the dart follows projectile motion and the monkey follows a vertical straight line motion as a case of free fall. The solution requires understanding of two components of velocity v_x and v_y of the dart. They need to work out the time at which both of them will have same coordinates. The difference will come only in the vertical distance from the ground if the speed is changed. In case of breeze flowing in horizontal direction, it is again v_x that gets affected. Once again it can be shown that there will be difference in the vertical distance where the dart hits the monkey.

Analysis

The case presented above is just an example. There can be numerous ways to make them more interactive, meaningful and interesting. We didn't perform any statistical analysis but graded their answer sheets and also took feedback from them. Following are the observations that we made.

Some fast learners showed reluctance to undergo this trial at least the scaffolding part (Problem 1). Their reaction was so as they thought that they are capable to solve the problem in 3-4 lines much ahead of the class then, why explain in so many detailed steps which appeared mundane for them. However most of these students couldn't answer the subsequent problem and the critical thinking questions. Hardly any of them could get 100% score.

Most of the slow learners, who generally are numb at any problem posed to them, could start attempting the problem 1 with the help of scaffolding provided to them. Those who required our questions just as a support could make good progress and complete substantial part of the solution. However, to them as well, Problem 2 and the critical thinking questions were not possible to answer.

Overall, scaffolding and narration while solving such problems can make rote learning unnecessary. We expect that with enough practice the students will be able to do this kind of exercise for themselves having experienced the value of the approach. Further we expect, students learn to do critical thinking and narrative in their mind quickly and directly proceed to do calculations/analysis in a logical manner. Writing logical steps is also important because the evaluator needs to understand the clarity of the thought process of the student even if there is a mistake in the calculations.

Recommendation

The instructional scaffolding approach should be implemented for all important concepts and problems based on them. The basic design of the scaffolding pertaining to classical mechanics can be as follows.

1. First students should be given time to imagine situation described in the problem and if possible should be asked to draw a sketch on it. While drawing sketch, many questions should surface if the students do critical thinking themselves. They can be asked to restate the problem as they have understood.
2. The narration then should start by small and basic steps which can give students enough time to dig out information like physical quantities involved units and differentiate as to which of them are given and which are to be obtained by solving the problem. They should be asked to define reference frame and the origin.
3. The questions that follow can then revoke their understanding of physics principle involved.
4. The students can then work out the numerical solution to the problem.
5. A handful of problems can then be given as exercises with scaffolding approach and slowly the scaffolds can be removed depending on the students' progress.
6. Once all the similar questions are answered by the students without scaffolds, the questions that can challenge their higher order thinking skills (HOTS) should be posed in the form of a new problem at advanced level.
7. Summary - After the scaffolded assignment is completed by each student independently, it can be graded. The student can then be given a tutorial sheet based on similar kind and twisted problems but without scaffolding. Their answers should be checked. Ideally, students should be taking up Tutorial assignments based on different concepts only after they achieve mastery in a given conceptual topic. Some deadline can be set up by the instructor for the submission of all the assignments (scaffolded as well as final tutorial sheet without scaffolding). The fast learners may be taking up new assignments earlier as compared to the slow learners but finally one can expect that each student would have achieved some level of mastery in each topic.

We believe this approach should build confidence in weak students and if their perseverance and hard work is consistent, they can make remarkable progress in Physics course grades and in their overall understanding of the subject. The recommended systematic steps and the challenging questions asked during critical thinking process should also engage the fast learners as they realize that there is plenty of gaps for them to improve upon, understand and move deep ahead in the subject. These fast learners then can be guided to advanced level reference books and can be asked to solve higher level problems. They can be encouraged to do hands-on or computational projects based on the contents of the course. Finally, they can also be asked to review one research paper based on the contents of the course and made to explain their understanding in a written or oral presentation. They should also be motivated to do research project based on the contents of the course.

Although the recommendations mentioned above sound idealistic, if implemented properly, they may be real. The main point is that it cannot be one semester's task for the teacher and students. If the mastery on basic topics is achieved during high school education itself, it would be easier to develop learning approach at advanced level.

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Evaluation of various Bankruptcy Prediction Models

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Abstract

Bankruptcy Prediction Models plays a critical role in Loan Appraisal System for Banks and Financial Institutions across the globe. The study focuses on evaluation of various bankruptcy models available across literature. With plethora of choices among the models, it is interesting to evaluate various models with the perspective of end user and further construction of new models. History and evolution of Bankruptcy Prediction Models are discussed and evaluated. More than 50 Models from the US, UK, Greece, Cyrpus, India, etc. are studied since 1928. It is concluded out of 13 parameters to select the model; Transparency and Accuracy are of utmost importance to the end users. If Logistic Regression, Decision Tree Analysis, Multivariate Discriminant Analysis and Artificial Intelligence are used simultaneously then it can prove to be better in overcoming the weakness of Transparency and Accuracy.

Keywords

Bankruptcy Prediction Models, Artificial Neural Network, Logistic Regression.

Introduction

The lending has become very complex and bankers need to consider domestic and international markets in depth. The focus has been shifting from Balance Sheet to Cash Flow analysis for lending. Securitization of loans by banks and investment banks has standardize approach for evaluating credit risk. Also, with the increase its geographical reaches across the globe, bank need to have objective and standardize approach for evaluation. With the introduction of technology, modern lending techniques adopt sophisticated methodology to evaluate the

probability of repayment and quantifying the risk. The major development has been in the field of credit rating, portfolio management, neural network and neural and intelligent knowledge-bases system. Two governing factors for lending are credit culture and credit standard. There has been a tremendous growth in the area of Credit Risk Evaluation; tools are broadly based from Statistics, Operations Research and Financial Market Based models. Statistics and Operations Research includes Survival Analysis, Neural Networks, Mathematical Programming, Deterministic and Probabilistic Simulation, Stochastic Calculus and Game Theory while Financial Markets based model includes Arbitrage Pricing Theory, Option Pricing Theory and Capital Asset Pricing Model. All these methods help the appraisal officers to predict whether the borrower will be able to repay or not. Monitoring performance after lending is even more critical, lending institutions are interested in prediction bankruptcy beforehand to take measures for further losses. Hence, Bankruptcy Prediction Models are very important aspect for any bank or Financial Institution. All of these were extensively studied, refined, tested if effective under various conditions and profitably implemented. These models need to undergo various constructs/variables; identify the variable and derive the relationship by using mathematics and statistics, simulation and other relevant technique to authenticate the relationship. Lastly, the models need to be tested upon and verified for outcome. In case of Credit Risk, models undergo the process which verifies the relationship through classification of the tools or techniques employed, the sector or the domain of application, and last the products on which the models shall be applicable[2].

There is a plethora of prediction models across the globe; it is developed considering various factors highly sensitive towards its background. The model construction is based on the data selection, tools/techniques, country, sector, etc. In an interesting interaction narrated in the article by Ajit Balakrishnan, founder Rediff.com quoted as "If you reject a consumer loan application and the consumer asks why her loan was rejected, you will get into regulatory trouble if you say, 'I don't know, the algorithm did it". His expression brings a strong conviction on the requirement of transparency in the method of loan evaluation for the customer. It is highly desirable to include the transparency trait in selecting the right model[3].

History and Major Advancement of Bankruptcy Prediction Models

In 1928, Wall and Duning created the first example of real linear multivariate discriminant analysis through a ratio index, a weighted combination of several different ratios with the weights randomly selected to predict bankruptcy[4]. Later in 1932, Fitzpatrick investigated the differences between ratios of successful industrial enterprises with those of failed firms [5]. Smith and Winakor investigated the trends of twenty-one accounting ratios, analyzed the mean of each ratio up to ten years prior to the occurrence of the financial difficulty and concluded that the ratio of net working capital to total assets was the most accurate predictor of failure[6]. In 1942, nearly 1000 companies were analyzed spanning the period 1926-1936 by using ratios, viz., Current ratio, net worth to total debt, and net working capital to total assets[7]. Hickman found net profit to sales and the times-interest-earned ratios were the best predictors of default. In 1966, Beaver's model analyzed 79 failed companies between 1954 and 1964 by using 30 variables tested across 6 groups of financial ratios. A year before the bankruptcy was predicated 87% accurately and five year before at 78% by using Multivariate Discriminate Analysis (MDA) concluded single ratio known as best performing ratio Cash Flow/Total Debt Best Value[8]. From 1968 to 1980 was the era of multivariate discriminant analysis. In 1968, Edward Altman had come up with the now famous bankruptcy model known as Z-Score model. Altman's Z-Score model was introduced to incorporate the quality of ratio analysis as an analytical technique wherein a multiple discriminant statistical methodology was employed and set 5 ratios were introduced. The data of 66 companies equally distributed amongst bankrupt and non-bankrupt in the year 1964 were selected. With the use of Multivariate Discriminant Analysis (MDA) the accuracy results were 95%[9]. With the use of linear programming technique, a model was derived which was a useful tool for bank auditors, loan officers, and examiners with a meaningful measure of the loan portfolio's quality (Orgler, 1969).

Working further on Beaver's prediction model in 1972, Deakin extended the model by adding the element of probability and could produce better results. Total 14 Financial Ratios were selected for MDA technique to predict bankruptcy improved to 90% from 78% of Beaver's Prediction model before 2 years of bankruptcy[10]. In the same year, research focusing on the small business failure prediction used a dataset of 42 bankrupt companies which borrowed from

Small Business Association and Robert Morris Associates reduced the ratios to 7 through MDA technique. It could predict 39 out of 42 bankrupt firms with accuracy rate of 93%[11]. Total 230 companies both failed and non-failed used Failing Company Model (FCM) developed through MDA technique that quantify probability with accuracy rate of 93-95%,[12]. In 1977, Altman's model was criticized in terms of predictability and accuracy was presented[13].

The valuation of an asset is also a yardstick to predict the failure, a major breakthrough in the option valuation was presented in the public domain in 1973. One of the parameters of valuation lies in the discount of bonds based on the probability of default. In such a framework the default process of a company is driven by the value of the company's assets, and the risk of a firm's default is therefore explicitly linked to the variability of the firm's asset value[14,13,15], . Zavgren and Friedman used Logistic Regression for US based companies extracted from COMPUSTAT predicted bankruptcy using 7 financial variables. Prediction rate before 5 years of bankruptcy was just 12% while just before a year it was 98%[16]. The Hazard Model is preferred over static model theoretically; it corrects for period at risk and allows for time-varying covariates. It used financial ratios and converted to natural log, the results showed 95% accuracy in prediction[17]. By using 8 Financial Ratios of Bankrupt companies in Belgium used Logistic Regression Model resulted with 67% for business termination category and 91% for audit report model[18]. In an interesting study on comparison between sector focused and general prediction models, it was found that the Spanish companies general or unfocused prediction models are superior to focused (sector specific) models[19].

Discussion: Criteria for Bankruptcy Prediction Model

The quest to find a universal bankruptcy model will be really difficult due to variety of complications and factors involved in the data. Bankruptcy Prediction Model caters to different stakeholders considering their perspectives; lender will be interested in the accuracy of prediction while the company owner will be interested in knowing the transparency of the model. Total 13 criteria have been short listed for the evaluation; broadly divided as Results, Data and Tools Property[20]. The list of criteria is as follows:

1. Accuracy: prediction classification with minimum error, Type I and II.
2. Result transparency: Tool should be interpretable.

3. Deterministic: Tools must be able to classify the companies.
4. Sample size: The approximate sample size suitable to the tools to function optimally.
5. Data Dispersion: Tool's ability to compute equally or unequally dispersed data.
6. Variable selection: Variable selection method required for optimum results.
7. Multi-collinearity: It checks the sensitivity of the tool to deal with collinearity
8. Variable types: The tools capability to differentiate Quantitative and Qualitative variables.
9. Variable relationship: The tools capability to analyse linear and non-linear relationship.
10. Assumptions imposed by tools: Sample data has to satisfy for a tool to perform optimally.
11. Sample specificity/over-fitting: This is essential when the model is created by using one of the tools and it performs well on the sample but badly on validation of the data.
12. Updatability: Tool should be easy to update in case of any dynamic changes.
13. Integration capability: the ease with which the tool can be integrated with others for making it hybrid.

Approximate 50 research papers on Bankruptcy prediction were reviewed and the analysis of various models resulted in weighing the models on the prescribed variables mentioned above. Accuracy of each model is categorized from low to very high; MDA has the lowest while DT and LR are moderate and ANN has the highest accuracy. Transparency of results is high with LR and DT since LR explicitly shows the variables and its weight in the prediction model and DT diagrammatically shows the weight of variables. ANN, LR and MDA are deterministic while DT is non-deterministic; it means classification of companies is done with former models and not with DT. The quantum of data for prediction has to be generally large in size; it increases the probability of prediction since it considers variety of scenarios. None of the tools work well with small sizes. MDA and ANN have high ability to handle dispersed data while LR has normal but the same is not applicable to DT. The process of suitable variable selection is stepwise in MDA and LR while ANN and DT adopt case based method. Co-linearity amongst the variable is computed best in LR, then MDA followed by ANN and DT. The extreme cases/data where dispersion difference is too high is handled better by LR than MDA, ANN and DT. MDA requires quantitative data only while LR, ANN and DT can use both qualitative as well as quantitative data. MDA requires linear relationship amongst the variables; LR requires Logistic

which means the results are dichotomous, ANN and DT can work on any kind of relationships the user wants to program. Liberty to incorporate assumptions in order to function optimally is well accommodated with MDA, lesser with LR and none with ANN and DT. If the model is developed on sample it should give desirable results on other data also, all the tools have been able to function properly on other data. This is most important of all since the model will be then replicated by the banking industry for lending decisions. The ease in updating the data with additional samples can be done with only ANN while rest does not support this function effectively. For creating hybrid model; ANN and DT can work effectively but not MDA and LR. The decision or the results reflected by some cut-off points or probabilities in MDA, LR and ANN are in binary while DT provides the Decision Rule.

	Important criteria	**Tools**			
		MDA	*LR*	*ANN*	*DT*
1	Accuracy	Low	Mod.	V. High	Mod.
2	Result transparency	Low	High	Low	High
3	Can be Non-deterministic	No	No	No	Yes
4	Ability to use small Samples size	Low	Low	Low	low
5	Data dispersion sensitivity	High	Normal	High	NR
6	Suitable variable selection	SW	SW	Any	Any
7	Multi-collinearity Sensitivity	High	V. High	Low	Low
8	Sensitivity to outlier	Mod.	High	Mod.	Mod.
9	Variable type used	QN	Both	QN (both)	(both)
10	Variable relationship required	Linear	Logistic	Any	Any
11	Other Assumptions to be satisfied	Many	Some	None	None
12	Over-fitting possibility	Yes	Yes	Yes	Yes
13	Updatability	Poor	Poor	OK	Poor
14	Ways to integrate to give hybrid	Few	Few	Many	Many
15	Output Mode	Cut-off	Binary	Binary	DR

NR: Not Reported SW: Stepwise V.: Very Mod: moderate QN: Quantitative QL: Qualitative DR: Decision rules.

Table 1 : Evaluation of Bankruptcy Prediction Models-Multivariate Discriminant Analysis (MDA), Logistic Regression (LR), Artificial Neural Network (ANN) and Decision Tree (DT) Adapted version[20]

The combination of all the four would overcome the weakness of each other; based on various factors evaluated Accuracy and Transparency are most diverse and critical from the view point of the end user, hence model selection must stress upon these factors.

Debate and Comparison of Bankruptcy Prediction Models

The following discussion is based on using various techniques to find better method in various countries and industries. Z-Score method has been very popular across the world, to test the accuracy of model, parameters of Z-Score were used Artificial Neural Network techniques resulted in better accuracy than MDA; ANN resulted 90% and MDA with 85% accuracy rate for US companies[21]. Similarly, an attempt to find the bankruptcy risk for Greek banks used a hybrid method of Rough Sets to predict the risk of insolvency used many financial ratios and qualitative data like years of experience of the bank managers, errors of management, firm's market position, and special competitive advantage claimed to be functioning well with Greek Banks[22]. In a comparative study of various bankruptcy prediction models for Korean companies, viz., Case Based Reasoning, MDA and ANN, 51 financial ratios across 6 industries were used resulting in accuracy ranging between 81 and 83% in all the methods; ANN with 82.98%, MDA at 82.43% and Case Based Reasoning at 81.88%[23]. A study on model comparison of 1139 banks in all the regions of the USA used ANN, Logit and MDA for 3 years prior to the bankruptcy resulting in ANN with better accuracy and lesser cost in comparison to other methods[24]. Various branches of computer programming based methods became famous amongst the financial fraternity and grabbed the attention of Computer Science, Financial and Banking sectors. Support Vector Machine method was used for 1160 bankrupt and non-bankrupt Korean companies each with 10 financial ratios as the variables. The method of optimizing was used to discover where SVM has the highest level of accuracies and better generalization performance than BPN as the training set size was getting smaller sets. Overall accuracy was more than 73% at the optimum level[25]. As discussed above, prediction models, in a study covering all non-finance industry UK firms fully listed on the London Stock Exchange (LSE) at any time during

the period 1985-2001 with a sample size of 2,006 firms, a total of 15,384 firm years, and 103 failures, used prominent models, viz., Z-Score, Hillegeist Models and Bharat Schumway Model. Z-Score had the best result with 89% accuracy followed by Bharat Schumway with 87% and Hillegeist with 84%[26]. For bankruptcy prediction with respect to Turkish Banks, a sample of 65 failed banks and 130 non failed entities was selected with 20 variables including that of CAMEL analysis, capital adequacy, asset quality, management quality, earnings, liquidity and sensitivity to market risk.

The study used 2 methods to predict the failure: Neural Network and Multivariate Statistical methods; in the case of neural networks, four different architectures namely multi-layer perceptron, competitive learning, self-organizing map and learning vector quantization are employed while multivariate statistical methods; multivariate discriminant analysis, cluster analysis and logistic regression analysis tested. Learning vector quantization (LVQ) resulted in a phenomenal result of 100% accuracy followed by Multi-Layer Perceptron with 95% and Support Vector Machines (SVM) with 91% accuracy[27].

In yet another attempt to find the better technique for bankruptcy prediction, 32 bankrupt and 45 non-bankrupt companies in England comprised the sample. Variables selected are ratios regarding Management Inefficiency, Capital Structure, Insolvency, Adverse Economic conditions and Income Volatility for the Logit model and the quadratic interval logit model, Multi Layered Perceptron and Radial basis Function Network resulted in the accuracy ranging from 91.5% to 77.05% where the best method is Radial Basis Function Network[28]. Considering the Decision Tree models for bankruptcy predictions, 200 US companies with 142 non-bankrupt and 58 bankrupt companies were selected to fit in Recursive Partitioning Analysis (RPA), Multivariate Discriminant Analysis and CART. RPA and CART has provided best results of accuracy as compared to other methods[29]. In an exhaustive study on Neural Network techniques for bankruptcy prediction, more than 200 researches on bankruptcy prediction were analyzed since 1964. It was found that the most predominant techniques are discriminant analysis, logistic regression and multi-layer perceptron neural network. The research data consisted of 260 bankrupt and healthy French companies respectively. The idea was to shortlist the variable to be

used for the bankruptcy prediction model; 41 variables in total were considered the important variables. NN is the best of all with an accuracy of 92.32% while MDA with 84% and Logistic Regression with 89%[30]. For 887 bankrupt companies in the US from 1980-2006, compared Altman, Ohlson, Zmijewiski, Shumway, and Hillegeist models resulted as Ohlson being the best followed by Zmijewski, Hillegeist, Shumway and lastly Altman. In a new proposed model, most of the variables from the above mentioned model were used comprehensively provided best results with accuracy of 89%[31].

A total of 562 bankrupt Slovenian companies were studied on 64 financial variables by using the Decision Tree technique, CART. For estimation, 75% of the variables were used and the remaining for the test. The accuracy rate stood at 94.6%[32]. In Iranian companies, logistic regression model provided 88.8% accuracy[33]. A study on bankruptcy models for UK companies used 18589 company-years and selected 12 variables covering accounting, market and macro economy. Three methods were tested upon; NN, Altman's Z Score and Logistic Regression. NN had the maximum accuracy of 84.7%, Altman's with only 65% and Logistic Regression with 84%[34].

A study on bankruptcy prediction involving Russian companies were worked upon for Bankruptcy prediction on the data size of 3505 company years Bankrupt and 3104 Non Bankrupt company year. It used 98 unique ratios across various parameters including Cash Flow, Liquidity, Profitability, Turnover, Balance Structure, indicators from previously constructed models and Russian Legislations to compute by using LR, MDA, ANN and Classification and Regression Tree (CRT). A unique method of combining various models was decided on the basis of significance, intersection and CRT+LR. The basis of intersection by using ANN provided best results with an accuracy of 88.8% while MDA, CRT and LR resulted in accuracies of 74.5%, 86.7% and 87.8% respectively[35]. In an extension to the study on bankruptcy prediction models by Phillippe Jardin, further focuses on retail, construction and service sectors in France from 2005-2010 with 50 financial ratios. The failure prediction 1, 2 and 3 years prior to default computed by using a new failure based model to compute LR, Cox model, MDA and ANN techniques. Accuracy rate was ranging from 75 to 85 % across the period. Failure based model

provided best results in predicting accuracy 3 years before the default for all the years for all the techniques. However, average accuracy rate for all the methods was 80%[36]. A study on 250 companies, including 107 bankrupt ones, for which data were obtained from a Korean bank with 107 Bankrupt companies, used 6 major heads of financial ratios to decide how MDA, SVM and LR methods can predict accurately. With 94.55% accuracy, SVM was the best and MDA at around 93% and LR with 92% predictions[37]. For the bankrupt companies in Pakistan, a sample pool of 422 bankrupt companies used Altman's Z-score, Ohlson's O-score, Zmijewski Model, Shumway Model and Blums model resulted in overall accuracy of 66%, 68%, 70%, 73% and 42.8% respectively[38].

For India, 1460 listed companies were taken as sample to test Altman's, Zmijemski's, Springate's and IN05 models. It was further computed using Decision Tree model where the accuracy rate was a meager 54.6% and ANN was just 43%[39]. Prior to this, from 2002-2016 a research study focusing on Wilful Default used total 558 sample companies with equal number of bankrupt and non-bankrupt, 279 in each category used logistic regression and resulted in overall 87.5% accuracy[40]. In the quest to develop a bankruptcy model for Cyprus based companies, 318 companies out of which 73 were bankrupt used financial ratios of the non-financial listed companies with the help of Logistic Regression resulted in 91.2% accuracy in the results[41].

On the basis of the preceding literature review, bankruptcy prediction models have been summarized on the basis of the country, variables used and accuracy rate of various techniques in Table 2.

Year	Author	Variables	Country	Method/Accuracy										
				LR	**DT**	**MDA**	**ANN**	**Z Score**	**CBR**	**SVM**	**Schumway**	**Heillegiest**	**Ohlson**	**Zmijewski**
1966	Beaver	Financial Ratio-30	US			87								
1968	Altman	Financial Ratio -5	US			95								
1972	Deakin	Financial Ratio -14	US			90								
1972	Edmister	Financial Ratio -7	US			93								
1974	Blum	Financial Ratio -12	US			93-95								
1980	Ohlson, James	Financial Ratio -10, Macroeconomic-1	US		96.3									
1988	Zavgren,	Financial	US	98										

	Freidman	Ratio -7												
1994	Rick L. Wilson and Ramesh Sharda	Altman-5 Variables	US			85	90							
1995	R. Slowinski and C. Zopounidis		Greece											
1997	Hongkyu Jot And Ingoo Han Hoonyoung Lee		Korea			82.43	82.98		81.88					
1997	Harlan L. Etheridge1 and Ram S. Sriram		USA				Be-tter							
2001	Shumway	Financial Ratio -5	US	95										
2005	Kyung-Shik Shin*, Taik Soo Lee1 , Hyun-jung Kim2	10 financial ratios	Korea							73				
2006	Vineet Agarwala and Richard Tafflerb*		UK					89			87	84		

2009	Melek Acar Boyacioglua Yakup Karab Ömer Kaan Baykanc	CAMEL Analysis Variables	Turkey				100			91				
2010	Fang-MeiTsenga Yi-ChungHub	Financial, macro economic	UK	77.05			91.5							
2010	Adrian Gepp, Kuldeep Kumar, Sukanto Bhattacharya		USA											
2010	Philippe du Jardin	Financial Ratio -41	France	89		84	92.32							
2010	Wu, Gaunt, & Gray	Models-Altman, Ohlson Zmijewski, Shumway, Hillegiest	US	89				28			73.96	75.24	79.7	78.54
2012	Arjana Brezigar-	Financial	US		94.6-									

	Masten, Igor Masten	Ratio -64			CART									
2012	Akbar Pourreza Soltan Ahmadi, Behzad Soleimani, Seyed Hesam Vaghfi and Mohammad Baradar Salimi	Financial ratios	Iran	88.8										
2012	Gaeremynck & Willekens	Financial Ratio -7	Belgium	90										
2013	Bagher Asgarnezhad Nouri1 , Milad Soltani2	Financial Ratio	Cyprus	91.2										
2013	Mario Hernandez Tinoco, Nick Wilson	Financial Ratio, market and macro economy-12	UK	84			84.7	65						
2013	Elena Fedorova,	Financial	Russia	87.8	86.7	74.5	88.8							

	Evgenii Gilenko, Sergey Dovzhenko	Ratio -98												
2014	Philippe du Jardin	Financial Ratio -50	France	80.5		80.15	80.9							
2015	Lawrence, Pongsatat, & Lawerence	Financial Ratio- Macroeconomics	Thailand										<90	
2017	Hafiz A. Alakaa , Lukumon O. Oyedele, Hakeem A. Owolabi , Vikas Kumar, Saheed O. Ajayi, Olugbenga O. Akinadef, Muhammad Bilal	NA												
2017	Vicente García, Ana I. Marqués,	6 Category of Financial	Korea	92		93				94.5				

	J. Salvador Sánchez, Humberto J. Ochoa-Domínguez	Ratio												
2018	Karthik, Lakshmi; Subramanyam, M.; Shrivastava, Arvind; Joshi, A. R.	Financial Ratio -9	India	87.5										
2019	Ashraf, Felix, & Serrasqueiro	Models-Altman, Zmijewski, Ohlson, Shumway, Blum	Pakistan					66			73		68	70

Table 2: Review of Bankruptcy Prediction Models based on Accuracy rate (%)

Research Gaps

After an extensive survey of literature, few areas are identified which requires attention, there has been limited research in the field of Wilful Default in India. New models focusing on Wilful Default, that is, deliberately going bankrupt by unfair means can be constructed that can suit the condition of Indian conditions.

Conclusion

Bankruptcy Prediction Models across the world studied and found to be very dynamic in nature. Multiple factors are considered in selecting models and its applicability. The techniques like accounting ratio, econometric techniques, Expert systems, hybrid systems and Artificial Intelligence have been used so far for different countries like the US, UK, Spain, Belgium, France, Greece, Korea, India, etc. by using 50 different bankruptcy models across 15 countries were studied and following points were observed.

1. Notably, major 4 techniques are widely used; Logistic Regression since it brings out dichotomous results whether the company will default or not, Multivariate Discriminant Analysis which includes all major affecting variables and provides a binary answer, Decision Tree provides a pictorial presentation of the weight of variables and Artificial Neural Network which has been predominantly used in many cases with best results compared to others.
2. Variables used are mostly Financial Ratios of the companies and few were macro economic variables to factor in the impact of business cycle (Boyacioglu, Kara, & Bayken, 2009) (Feng, Shaonan, Chihoon, & Ling, 2019) (Ohlson, 1980).
3. Initially LR was used while later in 1960 MDA became more popular and few prominent models like Altman's Z Score Model, Ohlson's O Score Model, Zavgren Model, Zmisjewski Model, etc. were constructed. After 1990, ANN technique was widely used with various versions and models like Support Vector Machines, Rough Sets, Case Based Reasoning, Decision Tree and Genetic Algorithm.

4. The tools are evaluated mainly on the basis of transparency in the process and most importantly; accuracy of the models. LR and MDA have the maximum transparency of the process as compared to other like ANN, DT, SVM, etc. However, in terms of accuracy; ANN and related techniques provides the best results as compared to LR and MDA.
5. Results of various bankruptcy models can be categorized in terms of accuracy. When one wants to deal with the systemic problem; accuracy of the models is of vital importance. Based on the survey of literature it concludes the ANN has an average accuracy rate of almost 90% ranging from 80 to 100% in different set ups followed by LR with around 87% and MDA with 86% average accuracy rates.
6. There is ample literature available based on existing models like Altman, Ohlson, Zmijewski, Schumway, Heillgeist, etc. which have been incorporated to test the accuracy of these models in various conditions like time period, country and the sample size. Testing has been done for US, UK, Iran, India, Thailand and Pakistan results in accuracy ranging from 60% to 80%.

Future Direction

As identified in the Research gap, it will be a good forward path to consider these models in Indian condition and construct a new model after considering the evaluation of Bankruptcy Prediction Models with special reference to Wilful Default.

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Optimization of Weld Bead Geometry for Flux Bounded Tungsten Inert Gas Welding of 316L Stainless Steel

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Abstract

Tungsten Inert Gas (TIG) welding process is used to weld variety of materials, however due to its less penetration and low productivity, Activated TIG (A-TIG) welding process has been introduced. A-TIG welding process overcomes demerits of TIG welding process but high amount of slag formation is being observed on weld bead surface as molten flux get mixed with base metal. Flux Bounded Tungsten Inert Gas (FB-TIG) is variant of A-TIG welding process which gives high penetration and also conquers the demerits of A-TIG welding process. To achieve constant welding speed and arc length during autogeneous welding experimental set up is developed. This paper presents the effect of activated oxide fluxes such as Al_2O_3, ZnO and TiO_2 on weld bead geometry of SS316L plate. The maximum penetration is reported with TiO_2 flux. Box-Behken design matrix is used to design the experiments and influence of process variables such as welding current, welding speed, arc length on weld bead geometry of SS 316L plate. The process variables are optimized the by Multi-Objective Optimization on the basis of Ratio Analysis (MOORA) as this method proved to be a robust domination over other multi-objective optimization. Maximum weld penetration depth of 5.56 mm has been achieved with desired weld bead quality with optimized process parameters.

Keywords

A-TIG, FB-TIG welding, Flux, MOORA

Introduction

Austenitic stainless steels are widely used in heat exchangers, aircraft engine parts and furnace parts due to its excellent properties like high corrosion resistance, high strength and ductility[1]. It contains minimum 10.5 % chromium with addition of other elements such as C, Mo, Ni, Cu, Ti, W, N, Mn[2,4]. From total volume 50% stainless steel products is made from austenitic group of stainless steels[1]. TIG is popular process among all welding processes to weld verity of materials. However due to less penetration in single pass and edge preparation reduce the productivity[5]. A-TIG welding process successfully increased the weld penetration more than 300% compared to TIG welding[6,7]. In A-TIG welding flux applied at the weld area which offers the high resistance to arc and becomes conductive only at high temperature. As fraction of the arc energy is used to melt and vaporize the flux, the process effectiveness decreases[8]. Also activated TIG weld bead contain the high amount of slag which is affect the welds quality[9].

These short comings of A-TIG process can be overcome by novel approach of FB-TIG proposed by Sire and Marya[10]. In FB-TIG welding process flux is applied on either side of weld centerline leaving the narrow space of metal as shown in figure1[8]. In case of FB-TIG welding arc directly comes in contact with base metal due to this FB-TIG welding eliminate the adverse effect of A-TIG welding.

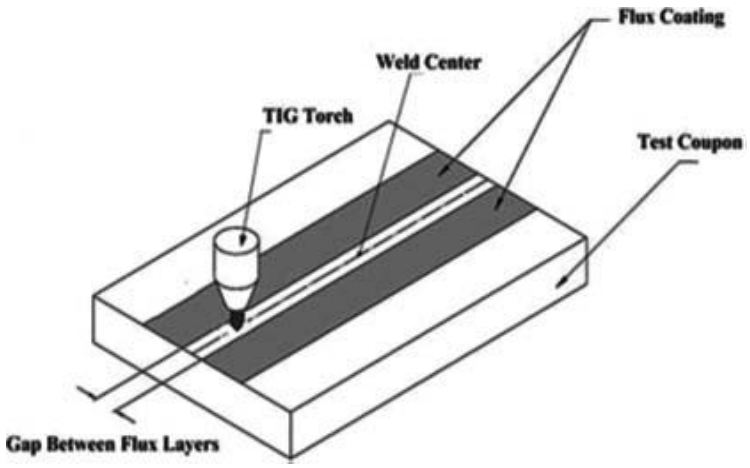


Figure 1: A schematic diagram of flux bounded TIG welding[8]

Mechanisms of improved penetration in A-TIG welding have been proposed are also applicable to FB-TIG welding. The first mechanism identified by Heiple (1982) is Gibbs Merangoni effect[11]. In merangoni effect the direction of fluid flow depends on surface tension

gradient of weld pool, due to surface active elements (flux) surface tension gradient become negative to positive with temperature gradient and create the deeper penetration[12]. In case of FB-TIG welding by reducing the flux gap concentration of surface active elements increases in weld pool and thereby create the inward flow in weld pool[13]. Second mechanism is arc constriction, discovered by Howse and Lucas in 2000[14]. In this phenomena vaporized flux capture the electron from outer region of arc, forms the arc more constrict and there by create the inward flow in weld pool[15,16]. The third prime mechanism is insulating effect which only observed in FB-TIG welding[13]. In FB –TIG welding oxide flux coating on either side of the weld centerline act as insulating barrier so during the welding electron choose the least resistive path and forms the arc more constrict[13]. Due to insulating effect improvement in penetration is observed by Vilarinho et al. in FB-TIG welding[17]. Increase in the flux gap, penetration capability is decreases reported by Ding et al.[18] and Ruckert et al.[8]. FB-TIG welding on AISI 304L is performed, reveals that SiO_2 flux effect weld penetration more compare to TiO_2 and Cr_2O_3[19]. Mechanical properties were observed in A-TIG and FB-TIG welding in aluminum and alloy steel[20,21]. However efficient investigation on weld bead morphology is not presented in published literature.

Experimental Investigation

Austenitic stainless steel 316L was used for experimental study whose chemical composition is listed in Table 1. The 6 mm thick plates cut to 100 mm length 40 mm width for butt welding. To study the effect of variables in FB-TIG welding, it is required to achieve the different welding speed and arc length during the autogeneous welding. To achieve the desired result welding fixture has been developed as shown in figure 2.

316L	Cr	Ni	C	Si	Mn	P	S	Mo	Fe
	24.11	20.7	0.046	0.44	1.47	0.016	0.01	0.07	Max Balance

Table 1: Chemical composition of 316l L stainless steel plate

To examine the influence of oxide flux such as Titanium Dioxide (TiO_2), Zinc Oxide (ZnO) and aluminum oxide (Al_2O_3) on 316L mixed with acetone to obtain the paint like consistency. Before welding plates are machined on milling machine to remove the air gap between butt joint. Plate surface is cleaned with acetone in order to eliminate the surface

impurities. Before welding uniform thickness 0.15 mm flux is spread with paint brush on either side of weld line by keeping the 4 mm gap on surface as shown in figure 3.

Figure 2: Welding Fixture

Figure 3: Application of flux before welding

Operating welding parameters are given in table 2 to perform the autogeneous TIG and FB-TIG welding. To examine the influence of flux, welding current, speed and arc length are kept 140 Amps, 135 mm/min and 2 mm respectively, these process variables are selected from literature survey. Flux gap varies between 2 to 7 mm. In present study flux gap is kept 2 mm as Venkatesan et al.[19] has reported that increase in flux gap weld penetration start to reduce.

Arc length	2mm
Shielding gas flow rate	12 l/min
Shielding gas	Argon,
Vertex angle of electrode	45^0
Welding electrode	Thoriated Tungsten (EWTh-2) diameter (d) 2.5 mm
Conical length of electrode	3 mm
Torch angle	90^0
Nozzle diameter	8 mm
Flux width	12 mm
Flux gap	2 mm

Table 2: Autogeneous Welding parameters for TIG and FB-TIG welding

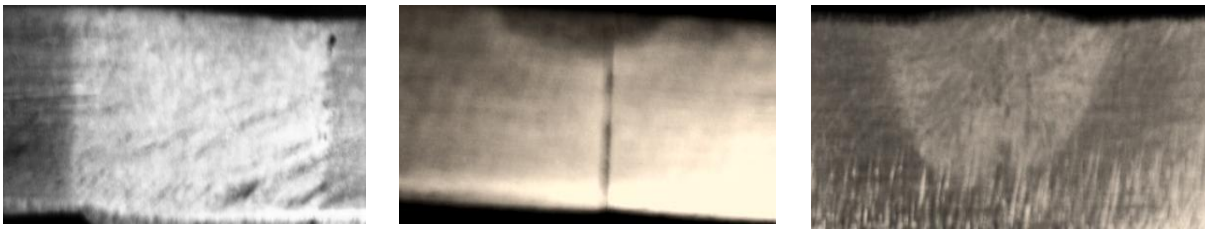
After welding process, the cross section of weldment was polished and etched in 100ml of hydrochloric acid with 5gm of copper sulphate mixture. Weld bead macrostructures is observed. Higher depth to width ratio was observed with FB-TIG process compare to

conventional TIG welding process. The result indicated that maximum penetration was achieved in TiO_2 flux as shown in figure.4. Therefore, in the present study TiO_2 flux was used for further experiments.

TIG Weld FB –TIG with ZnO FB-TIG with Al_2O_3 FB-TIG with TiO_2

Figure 4: Weld profile of the TIG and FB-TIG weld beads formed with and without ZnO, Al_2O_3 and TiO_2 oxide flux.

Three factorial three level Box-Behnken design (BBD) approach is adopted to acquire the correlation between the variables (welding current, welding speed, arc length) and responses (bead width and penetration). The variables level was coded as -1 (low), 0 (central point) and 1 (high) as shown in table 3. Trial experiments were performed to identify the range of process variables. At high welding current and minimum welding current condition weld pool become wider as shown in figure 5(a). With low welding current and high welding speed very low penetration was observed as shown in figure 5(b). It was observed that optimum penetration to bead width was achieved with average value of welding current and speed as shown in figure 5(c).



(a) (b) (c)

Welding current : 250 A, Welding speed 80 mm/min

Welding current : 120 A, Welding speed 200 mm/min

Welding current : 150 A, Welding speed 140 mm/min

Figure 5 : Weld profile with TiO_2 flux and at different welding parameters

From the above results working range of process variables were identified as shown in table3.

Variables	Factor Levels		
	-1	0	1
Welding current (Ampere)	120	150	180
Welding speed (mm/min)	120	140	160
Arc length (mm)	1	2	3

Table 3: Welding variables and levels for FB-TIG welding

In the present study experiments were conducted based on BBD technique and analyzed the depth of penetration and bead width, results shown in table 4.

Trial	**Input Parameters**			**Responses**		
	Welding Speed (mm/min)	**Arc length (mm)**	**Current (Ampere)**	**Penetration (P)(mm)**	**HAZ width (W) (mm)**	**Aspect ratio (P/W)**
1	120	1	150	4.22	5.82	0.72
2	160	1	150	3.93	6.43	0.61
3	120	3	150	4.61	6.52	0.70
4	160	3	150	3.42	6.11	0.55
5	120	2	120	3.54	5.86	0.60
6	160	2	120	2.24	6.32	0.35
7	120	2	180	3.87	6.29	0.61
8	160	2	180	3.65	6.30	0.57
9	140	1	120	2.43	5.13	0.47
10	140	3	120	2.17	4.92	0.44
11	140	1	180	3.64	7.22	0.50
12	140	3	180	3.48	6.85	0.51
13	140	2	150	5.56	6.22	0.89

Table 4: Box Behken design matrix and results

FB-TIG weld metal microstructure observed under 20x magnification. The weld profile is measured in terms of D/w ratio which is more desirable if it near to unity. Maximum D/w ratio was reported with experiment 13 (welding current 150 amps, arc length 2 mm, welding speed 140 mm/min),as shown in table 4.

Optimization of process variables

In current study multi objective optimization is carried out by MOORA method as this method prove to be a robust domination over other methods[22].The MOORA method response matrix presenting the performance of different alternative solution with respect to all objectives [23-25].

$$X = \begin{bmatrix} X_1(1) & X_1(2)... & X_1(n) \\ X_2(1) & X_2(2)... & X_2(n) \\ X_m(1) & X_m(2)... & X_m(n) \end{bmatrix} \qquad \text{-------(1)}$$

where m is the number of alternatives, and n is the number of objectives.

The ratio system which is part of MOORA is used in this study. In this method each performance of an alternative on an objective is compared to a denominator which is a representative for all the alternatives linking to that objective [24]. This ratio can be articulated as below:

$$X_{ij}{}^{a} = X_{ij} / \sqrt{\sum_{i=1}^{m} X_{ij}{}^{2}} \qquad \text{---------(2)}$$

where X_{ij} is a dimensionless number, belongs to the interval [0,1] representing the normalized performance of i[th] alternative on j[th] objective [24].

In multi-objective optimization, the case with maximization these normalized performances are added for favorable attributes and with minimization case it is subtracted for unfavorable attributes. The optimization problem converts:

$$Y_i = \sum_{j=1}^{g} X_{ij}{}^{a} - \sum_{j=g+1}^{a} X_{ij}{}^{a} \qquad \text{---------(3)}$$

where g is the number of attributes to be maximized, a is the number of attributes to be minimized, and Y_i is the normalized assessment value of i[th] alternative with respect to all objectives[24]. In some cases, its often observed that some attributes are more important than the others. In order to give more importance to that attribute, it is multiplied with its

corresponding constant[25]. The modified question 3 becomes as follows:

$$Y_i = \sum_{j=1}^{g} W_j \times X_{ij}{}^{a} - \sum_{j=g+1}^{n} W_j \times X_{ij}{}^{a} \qquad \text{--------(4)}$$

where W_j is the weight of j[th] attribute, which can be determined by Analytic Hierarchy Process (AHP) or entropy method. An ordinal ranking of Yi shows the final preference. Thus, the best alternative has the maximum Yi value, while the worst alternative has the minimum Yi value.

In FB-TIG welding to optimize weld penetration, bead width and aspect ratio MOORA method is implemented. Weightage of various responses are 0.45,0.10 and 0.45 for penetration, bead width and aspect ratio respectively. The normalized performance values of each attributes were obtained using equation 2, shown in table 5. Based on these score and acquired weightage of each response, normalized assessment value of each attributes are calculated using equations 4. The outcome of the MOORA method, provides ranking of each attributes based on the normalized assessment value as shown in table 5.

Trial No.	Penetration (mm)	Bead width (mm)	Aspect ratio	$\bar{Y}$	Rank
1	0.2720	0.2429	0.2900	0.2286	3
2	0.2533	0.2683	0.2457	0.1977	4
3	0.2971	0.2721	0.2820	0.2334	2
4	0.2204	0.2550	0.2215	0.1734	8
5	0.2281	0.2445	0.2417	0.1870	6
6	0.1444	0.2637	0.1410	0.1020	13
7	0.2494	0.2625	0.2457	0.1966	5
8	0.2352	0.2629	0.2296	0.1829	7
9	0.1566	0.2141	0.1893	0.1343	11
10	0.1399	0.2053	0.1772	0.1222	12
11	0.2346	0.3013	0.2014	0.1661	9
12	0.2243	0.2859	0.2054	0.1648	10
13	0.3583	0.2596	0.3585	0.2966	1

Table 5: Normalized decision-making matrix and results of multi-objective analysis

Rank of table 5 will help to identify the optimal values of process variables.

Conclusion

Present study reveals that FB-TIG welding with TiO_2 flux provide the higher penetration compare to other two oxide fluxes (ZnO, Al_2O_3) on 316L stainless steel plate. Higher penetration is reported in FB-TIG welding by overcoming the limitation of A-TIG welding which make the process more attractive. Optimized FB-TIG welding process parameters obtained are welding current 150 amperes, welding speed of 140 mm/min and arc length 2 mm, for 6 mm thick SS 316L plate by MOORA method. These combinations of process parameter obtained penetration 5.56 mm, bead width 6.22mm with maximum aspect ratio 0.89.

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Hydrophobic Ionic Liquid/Sugar Surfactant (PLANTACARE® K- 55)/Water Microemulsions: Phase Studies and Effect of Co-surfactant

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Abstract

Microemulsions have become more important because it is easier to tune the structure and the size of domains. They are unique and versatile media for various types of chemical reactions including nanoparticle preparation, organic synthesis, bio-organic synthesis, and so on. In the present study, hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate was used to replace conventional hydrocarbon solvent and industrial grade sugar based lauryl glucoside (and) cocamidopropyl betaine surfactant was used instead of a conventional non-ionic surfactant (alkyl polyoxyethylene ether class); while formulating an ionic liquid / sugar surfactant/ water ternary microemulsion system respectively. Moreover, effect of alkanol of higher chain length (dodecanol) as co-surfactant on the phase behaviour of ternary microemulsion system was also investigated. The ability of industrial grade sugar-based surfactant PLANTACARE® K- 55 which is a lauryl glucoside (and) cocamidopropyl betaine to solubilize both water and hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate phases, i.e. $\overline{\mathbf{X}}$or $\overline{\boldsymbol{\gamma}}$ was evaluated. The addition of long chain length alkanol (co-surfactant) leads to decrease in the $\overline{\mathbf{X}}$-point and simultaneously increases the efficiency of the industrial grade sugar-based surfactant.

Keywords

Microemulsion, hydrophobic Ionic Liquid, Lauryl Glucoside (and) Cocamidopropyl Betaine surfactant, Co-surfactant.

Introduction

Microemulsions are macroscopically isotropic, homogeneous, thermodynamically stable solutions consisting of at least three constituents, namely a polar phase (generally water), a non-polar phase (generally oil), and a surfactant (sometimes a surfactant in combination with a surfactant are used). A surfactant or surface-active agent is a molecule that consists of a water soluble (hydrophilic or polar) part and an oil-soluble (hydrophobic or non-polar) part. The hydrophilic part is called the head group and the hydrophobic part is called the tail group. The two different hydrophilic and hydrophobic parts make the surfactant surface active in the sense that it adsorbs or accumulates at interfaces between polar and non-polar media, so that the head group is solvated in the polar medium and the tail group in the non-polar medium. Examples of such interfaces are those between water and air or between water and oil. On a microscopic level in a microemulsion, the surfactant molecules form an interfacial film separating the non-polar and polar domains. This interfacial layer forms different microstructures ranging from droplets of oil dispersed in a continuous water phase (o/w-microemulsion) over a bicontinuous phase to water droplets dispersed in the continuous oil phase (w/o-microemulsion). The isotropic mixture of the three components usually forms nanoscale aggregates such as oil swollen micelles and water swollen reverse micelles when the immiscible liquids are oil and water. Such mixtures of water, oil, and surfactant show a rich variety of microstructures within the single-phase called as microemulsion and sometimes it exhibits rich variety of liquid crystalline or lamellar phases, in addition to many different kinds of multiple phase domains.[1]

Room temperature ionic liquids (RTILs) are liquid at room temperature that consist solely of ions. Cations and anions of RTILs are generally organic and inorganic in nature, respectively. In RTILs, the coulombic interactions between ions are substantial compared to dipolar or multipolar interaction in Volatile Organic Compounds (VOCs). The most important and unique feature of RTILs is their nonvolatile nature, owing to which; they do not contribute VOCs in the global atmosphere. Hence, RTILs are preferred for formulation of microemulsions rather than VOCs or conventional hydrocarbon solvents.[2] RTILs have been successfully used to replace organic solvents in a microemulsion system because of their beneficial properties, viz. low vapor pressure, low volatility, high thermal stability, broad liquids temperature range 96–300 °C, excellent conductivity and the ability to dissolve a wide variety of organic and inorganic materials.[3] In general, the polar phase is water, and the non-

polar phase is an organic solvent (very often *n*-alkanes are used) in a microemulsion system.[3,4] The studies on microemulsion systems wherein equal amounts of water and a hydrophobic Ionic Liquid are solubilized in presence of conventional non-ionic alkyl polyglycol ether (C_iE_j) surfactants to formulate a microemulsion are already reported in literature.[5] However, a thorough investigation on preparation and phase behavior studies of microemulsion systems involving ionic liquid/s, water and industrial grade sugar based lauryl glucoside (and) cocamidopropyl betaine surfactant is lacking.

We have formulated microemulsion formulations, wherein, hydrophobicionic liquidis used as a non-polar phase to replace oil (organic solvent). The microemulsion is stabilized by an industrial grade lauryl glucoside (and) cocamidopropyl betaine surfactant. The intent of the present work is to determine the conditions under which the surfactant solubilizes the maximum amounts of ionic liquid and water, i.e. to study phase behavior in order to achieve the reduction in surfactant concentration required to solubilize the two immiscible solvents (water and hydrophobic ionic liquid) by replacing the alkyl polyglycolether (C_iE_j) surfactants with a "green alternative", viz. lauryl glucoside (and) cocamidopropyl betaine surfactant in a ternary system and formulating microemulsion systems that are stable over a wide temperature range.[6] The conventional nonionic surfactants of the alkyl polyglycol ether (C_iE_j) type exhibit several phenomenon that are temperature dependent and are not ideal for formulating microemulsions that are stable over a wide temperature range. [6, 7, 8] On the contrary, the properties of sugar surfactants are not temperature sensitive. Hence, a microemulsion formulated using a hydrophobic ionic liquid and water stabilized a sugar surfactant can aid in extending the conventional thermal stability range from room temperature to 150 ºC. Ionic liquid microemulsions have been reported to be temperature-independent, offering a possibility of droplet-shaped microstructure in a large temperature range, thus making these systems suitable for broad range of applications.[9] The formulation of a less toxic, biodegradable microemulsion is of enormous importance and such a microemulsion can be formulated by use of a zwitterionic alkyl polyglucoside and cocamidopropyl betaine surfactant. Moreover, the water-in-bmimPF_6 microemulsions can dissolve compounds such as $Ni(NO_3)_2$, $CoCl_2$, $K_3Fe(CN)_6$ and methyl orange and hence they can be utilized for the solubilization of these compounds.[10] The ionic liquid [Bmim][PF_6]has been reported to serve as a directing or vectoring agent for the formation of silica microrods with nanosized pores using water/TX-100/[Bmim][PF_6] microemulsions.[1] Hence ionic liquid microemulsion

systems are capable of dissolving the above compounds can be explored for applications in different fields, viz. preparation of nanomaterials and chemical reactions.[1,11,12]

Material and Methods

The industrial grade sugar-based surfactant, Lauryl Glucoside (and) Cocamidopropyl Betaine (PLANTACARE® K-55) was received as a gift sample from BASF, Germany. The alcohol, dodecanol ($C_{12}H_{26}O$, purity 99%) and the Ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim] [PF_6] ($C_8H_{15}F_6N_2P$, purity ≥97.0%) were procured from Sigma Aldrich, USA. All chemicals were used as received.

Phase Studies of Microemulsions

Phase behavior measurements are a vital aspect during an investigation and formulation of a microemulsion system. A rapid method for quantifying the efficiency of a microemulsion system is to determine the $\overline{X}$-point by recording a $T - \gamma$ section of an ionic liquid/ (water + ionic liquid) volume fraction ϕ = 0.5. Such an approach aids determination of the optimal state $\overline{X}$ by extrapolation of the phase boundaries from $\underline{2}$ to 1 (turbid to clear) and 1 to $\overline{2}$ (clear to turbid), which makes the exact determination of the three-phase region dispensable. Hence, the phase behavior of self-assembling ternary mixtures of water, hydrophobic ionic liquid and surfactant as well as quaternary mixtures of water, hydrophobic ionic liquid, surfactant and alkanol as co-surfactant has been studied as a function of temperature and composition at a 1:1 water to Hydrophobic IL (Oil) ratio, i.e. polar/apolar 1:1, while changing the surfactant concentration. Microemulsion was formulated by weighing in known amounts of water, hydrophobic ionic liquid, and surfactant in test tubes. The sealed test tubes were then placed in a transparent water bath. The number of phases (1∅, 2∅, or 3∅) were determined by visual inspection of phase boundaries at temperatures ranging from 30 to 60 °C.[4, 5]

The sample compositions of the ternary mixtures are defined as the mass fraction of IL in the solvent (water- to- oil) mixture.

$$\alpha = \frac{m_{[\mathrm{Bmim}][\mathrm{PF_6}]}}{m_{[\mathrm{Bmim}][\mathrm{PF_6}]} + m_{[\mathrm{H_2O}]}} \quad (1)$$

and as mass fraction of surfactant in the total mixture

$$\gamma = \frac{m_{surfactant}}{m_{[\mathrm{Bmim}][\mathrm{PF_6}]} + m_{[\mathrm{H_2O}]} + m_{surfactant}} \quad (2)$$

The phase boundaries exhibit a characteristic "fish" shaped outline as illustrated in Figure 1. The phase boundaries of T and γ results in the formation of fish shaped body, which ultimately aids in determination of the phase inversion point, i.e. $\bar{T}$ and $\bar{\gamma}$ which is also known as fish tail point $\bar{X}$. $\bar{\gamma}$ or $\bar{X}$ represents the minimum surfactant concentration required to solubilize whole amount of two immiscible (water and oil) solvents. [4, 5]

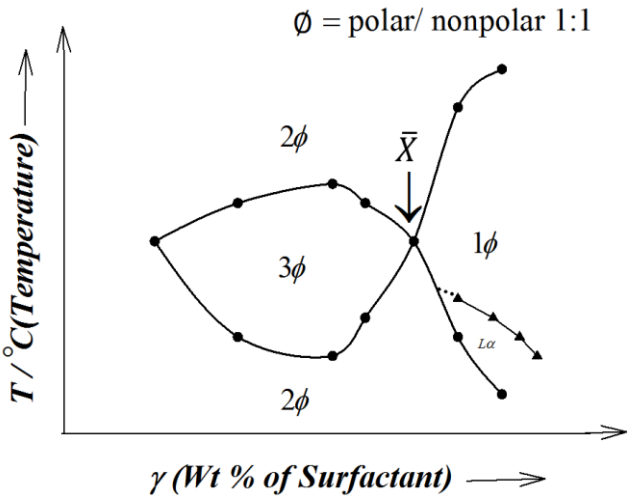

Figure 1: Schematic Fish-shaped phase diagram obtained by taking a vertical section through the phase prism, consisting of equal masses of polar (water) and non polar (Ionic Liquid) solvent, depicting single phase (1∅), two phase (2∅) and three phase (3∅) regions. 'γ' is the mass fraction of surfactant in the total mixture.

Results and Discussion

Phase behavior studies with industrial grade sugar-based surfactant.

In the present work, we have attempted to formulate a microemulsion system using water, hydrophobic ionic liquid, i.e. 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6] and industrial grade sugar-based surfactant PLANTACARE® K- 55, i.e. lauryl glucoside (and) cocamidopropyl betaine. Herein, we wanted to replace organic solvent i.e. an oil phase, so hydrophobic ionic liquid i.e. 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6] was used as oil phase in formulation of the microemulsion system.[13] In a recent study, the microemulsion system formulated using conventional nonionic surfactant Triton X-100 (TX-100), water and hydrophobic ionic liquid (e.g.,1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6] was compared with the microemulsion system formulated

using nonionic sugar based industrial grade surfactant PLANTACARE 810–UP (UP-810). Upon comparison of the absolute $\overline{\mathbf{X}}$values, it was observed that, when a conventional nonionic surfactant Triton X-100 is used, the $\overline{\mathbf{X}}$ value, i.e., the surfactant required to solubilize oil and water is high.[14] Similar observation of lower efficiency of a conventional nonionic surfactant during formulation of a ionic liquid microemulsion has been reported by Anjum et al.[5] We anticipate enhancement in efficiency while using an industrial grade zwitterionic alkyl polyglycoside and cocamodipropyl betaine surfactant to formulate a water/sugar surfactant/ hydrophobic ionic liquid microemulsion.

The typical fish shaped phase diagram obtained for the system, PLANTACARE® K- 55/ 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6]/water is illustrated in Figure 2.

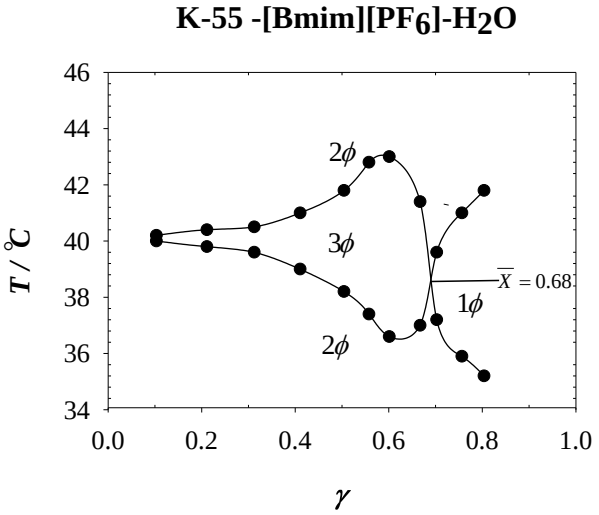

Figure 2: Schematic Fish-shaped phase diagram obtained for equal masses of water and IL [Bmim][PF_6] using industrial grade sugar-based surfactant PLANTACARE® K- 55 (K-55).

The corresponding characteristic parameters *($\emptyset$,γ_0, T_0,* $\overline{\gamma}$or$\overline{X}$, $\overline{T}$ *, $\Delta\gamma$, ΔT)* of the fish shaped phase diagrams of a microemulsion system formulated are presented in Table 1.The coordinates of the so-called fish head (lowest surfactant concentration at which a third middle phase appears) are γ_0 and T_0, whereas those of the fish tail (lowest surfactant concentration at which one phase is formed) are $\overline{\gamma}$ and $\overline{T}$, respectively.

Microemulsion System	$\emptyset$	γ_0	T_0/℃	$\bar{\gamma}$	$\bar{T}$/℃	$\Delta\gamma$	ΔT/℃
K-55/ [Bmim][PF_6]/ H_2O	0.5	0.09	40.0	0.68	38.3	0.59	10.6

Table 1: Characteristic values for the Phase Behavior of Water/ PLANTACARE® K-55(K-55)/1-butyl-3-methylimidazolium hexafluorophosphate microemulsion system.

It is evident that for microemulsion system formulated using 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim] [PF_6] instead of organic solvent as oil, the $\bar{X}$, which is the minimum surfactant concentration required to solubilize two immiscible solvents obtained is 0.68. Although microemulsion could be formulated, the efficiency of the surfactant in dissolving both water and oil, $\bar{X}$,value is quite high. It means that 68% of sugar surfactant is required to solubilize two immiscible solvents, oil and water to formulate a microemulsion system.

Here, at T= $\bar{T}$ temperature and a very low surfactant concentration ($\gamma<\gamma_0$), the oil and the water phase are at theintermediate temperatures. Hence, the surfactant will have high solubility in both water phase as well as oil phase which will give rise to a surfactant-rich middle phase in equilibrium with excess of oil and water.[7, 8] With further increase in temperature, the middle phase also starts to increase until entire amount of water and oil gets solubilized in this phase giving rise to $\bar{X}$ point which is found to be 0.68.

At low temperatures, the lower phase (2$\emptyset$) is water-rich phase and the upper phase (2$\emptyset$) is oil (IL)-excess phase where the surfactant will form oil-swollen micelles also called as microemulsion droplets. Upon addition of surfactant to this binary mixture, the surfactant gets solubilized in both the phases. Later on, with further addition of the surfactant, the concentration of the surfactant increases to surfactant mass fraction i.e. $\gamma=\gamma_0$, and it can be observed that at the fish head, both oil and water phases are being saturated. With further addition of the surfactant, the third phase which is the middle phase (3$\emptyset$) appears.[11, 12]

When the temperature is increased, the surfactant tends to get solubilized until the three-phase region (3$\emptyset$) ($\gamma<\bar{\gamma}$) is observed. Further addition of the surfactant, now decreases the interfacial tension between the phases which results into formation of one-phase region (1$\emptyset$) ($\gamma>\bar{\gamma}$) as shown in Figure 2.At higher temperatures, ionic liquid (oil) is a superior solvent for the surfactant, and IL-swollen reverse micelles form in an oil continuous phase, in equilibrium with a lower phase of excess IL.

Phase behavior of sugar surfactant in presence of Co-surfactant (Dodecanol):

To verify the effect of co-surfactant on the phase behavior and microstructure of microemulsion systems, a microemulsion involving dodecanol, i.e. PLANTACARE®K-55/1-butyl-3-methylimidazoliumhexafluorophosphate [Bmim] [PF_6]/Dodecanol/water was formulated as illustrated in Figure 3. The ratio of surfactant to co-surfactant (dodecanol) was 1:1.

The sample compositions of the quaternary mixtures are defined as the mass fraction of a surfactant in the total mixture,

$$\gamma = \frac{m_{surfactant}}{m_{[\mathrm{Bmim}][\mathrm{PF_6}]} + m_{[\mathrm{H_2O}]} + m_{surfactant} + m_{co-surfactant}} \quad (3)$$

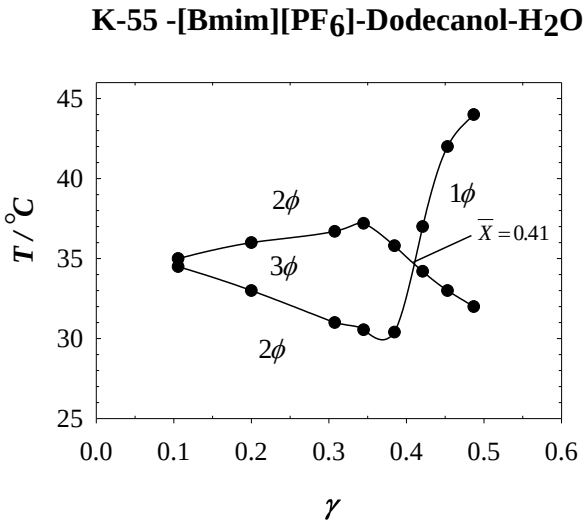

Figure 3: Schematic Fish-shaped phase diagram obtained for equal masses of water and Ionic Liquid [Bmim][PF_6]in presence of co-surfactant (Dodecanol) using sugar based non-ionic surfactant PLANTACARE® K- 55 (K-55).

It is reported that the efficiency of the ionic liquid microemulsion system did not improve by addition of octanol as a co-surfactant and the efficiency is too low for technical applications.[13] However, it is evident from Figure 3 for a microemulsion formulated by us that, the $\overline{X}$ or $\bar{\gamma}$ which is the minimum surfactant concentration required to solubilize two immiscible solvents (IL as oil and water) obtained is 0.41 when co-surfactant is used along with the surfactant. It can be inferred that the $\overline{X}$ or $\bar{\gamma}$is reduced 0.68 to 0.41 in presence of co-surfactant, implying

that the concentration of industrial grade sugar surfactant required to solubilize two immiscible solvents i.e.oil and water, to formulate a microemulsion system has been reduced from 68% to 41%. The co-surfactant, dodecanol is itself surface active, orients itself at the hydrophobic ionic liquid/water interface and also influences the surfactant solubility. The addition of co-surfactant leads to a decrease in the interfacial tension and subsequently reduces the amount of surfactant required to solubilize two immiscible solvents, oil and water.[11, 12]

The characteristic parameters *($\emptyset$,γ_0, T_0, $\overline{\gamma}$, $\overline{T}$, $\Delta\gamma$, ΔT)* of the fish shaped phase diagrams of a microemulsion system formed are presented in Table 2. The coordinates of the fish head (lowest surfactant concentration at which a third middle phase appears) are γ_0 and T_0, whereas those of the fish tail (lowest surfactant concentration at which one phase is formed) are $\overline{\gamma}$ and $\overline{T}$, respectively.

Microemulsion System	$\emptyset$	$\boldsymbol{\gamma_0}$	$\boldsymbol{T_0}$/℃	$\overline{\boldsymbol{\gamma}}$	$\overline{\boldsymbol{T}}$/℃	$\Delta\boldsymbol{\gamma}$	$\Delta\boldsymbol{T}$/℃
K-55/ [Bmim][PF_6]/ Dodecanol/ H_2O	0.5	0.1	34.6	0.41	34.7	0.31	6.4

Table 2: Characteristic values for the Phase Behavior of Water/ PLANTACARE® K- 55 (K-55)/IL/Dodecanol microemulsion system.

In the present system, it has been observed that in presence of the co-surfactant, the solubility of the surfactant used, i.e. PLANTACARE® K- 55 which is lauryl glucoside (and) cocamidopropyl betaine, increases and it decreases the interfacial tension of the middle phase region and results into formation of one phase region at $\bar{X}$ (which is the minimum surfactant concentration required to solubilize two immiscible solvents, oil and water) 0.41. Thus the surfactant efficiency increases on addition of co-surfactant.

Thus compiling the data for both the system, i.e.1) PLANTACARE® K- 55/ 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6]/ water, and 2) PLANTACARE® K- 55/ 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6]/dodecanol/water, it can be concluded that on addition of the higher chain length co-surfactant, i.e. dodecanol (alkanol), the surfactant efficiency increases as the $\overline{X}$which is the minimum surfactant concentration required to solubilize two immiscible solvents decreases.

Conclusions

The phase behaviour and the surfactant efficiency of microemulsion system consisting of water, the hydrophobic ionic liquid [Bmim][PF_6] and industrial grade sugar-based surfactant PLANTACARE®K-55 which is a lauryl glucoside (and) cocamidopropyl betaine, were studied as a function of temperature and surfactant mass concentration. A microemulsion was successfully formulated wherein, the conventional organic solvent was replaced with the hydrophobic ionic liquid [Bmim] [PF_6].

The effect of alkanol (dodecanol) as a co-surfactant on the phase behavior of water/1-butyl-3-methylimidazolium hexafluorophosphate/PLANTACARE®K-55 was investigated. Substantial reduction in surfactant concentration required to solubilize the two immiscible solvents was achieved upon addition of long chain co-surfactant to the ternary microemulsion system; water/1-butyl-3-methylimidazolium hexafluorophosphate/PLANTACARE®K-55.

The formulation of ionic liquid microemulsion system enables to overcome the limitations of ionic liquids alone to dissolve various types of compounds and thus can be used for several industrial applications. It is evident from our studies that ionic liquids play a role not only as a polar phase but it can also be used as a replacement of an organic solvent. The sugar-based surfactant used in the present work plays a role as a greener alternative while formulating a microemulsion. The microemulsion system formulated can be explored for use in various applications, viz. solubilization of an otherwise water insoluble dye and as a template for preparation of nanomaterials and chemical reactions.

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