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Sacred Geography Evident from the Theyyam Myths

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Conclusion

The **Ātma bodhodaya sangham Tradition** could reform and elevate the reluctant communities of Kerala spiritually, socially and culturally. This tradition could eliminate, to a great extent, the intrinsic beliefs and practices among them such as superstitious beliefs, unethical religious practices, alcoholism, smoking, sorcery, worship of evil spirits etc. More Philosophical and religious discipline could be inculcated in the society. Spirituality and good conduct could be introduced even among the illiterate people. The philosophical

concepts of AdvaitaVedanta could popularize among common people in simple Malayalam. This tradition still conducts a lot of spiritual activities, in order to attract the common people towards the spiritual path. They propagate the spiritual subjects in a universal manner, which is acceptable to all people irrespective of, creed or religion. They work against the untouchability and for the right to enter the temple and Harijan Welfare. Subananda Ashram had no proper place to worship and to do social services during the earlier period and with the untiring and dedicated supports from obedient disciples.

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SACRED GEOGRAPHY EVIDENT FROM THE THEYYAM MYTHS

Susmitha Ramakrishnan

The religious practices of Kerala especially the cult of Theyyam, popular in modern Kannur and Kasarkode districts, inextricably carry marks of primitive origin. The myths and legends associated with Theyyam are connected with the local beliefs and folklore of the area to which they belong. A study of the surviving primitive religion may provide access to the understanding of the settlement pattern of various communities of the past.

Human beings attach great significance to symbolic expression in their day to day life. Even in situations such as untouchability, caste suppression, poverty and misery, men and women celebrate their life through symbolic expression revealed in myths, folk songs and rituals. All through history, the

myths and symbols have inspired people, and were dreams of paradise or a vision of a Utopia. It is also reflected in their social life and institutions. Here an effort is made to correlate between thottam songs sung at Theyyam performance and the settlement pattern of various communities.

Communities like Vaniya, Thiyya, Pulaya, Mannan, Mavilar all have their own Theyyams. The areas where these Gods were popular directly indicated the settlement patterns of these communities. The thottam songs sung at Theyyam rituals have three sections – *varavilli*, *mumbstanam* and *vachal*. The mumbstanam mentions the movement of each Theyyam and the places where the Theyyam has left indelible marks. These places

directly indicate the areas where each of the communities was popular in the past. In mumbstanam, mention is made of each of the places that particular Theyyam has made its appearance. The Theyyam does not simply pass through the areas, on the other hand it makes its impact felt in each area it passes through. It may be on the request of a devotee or because of the presence of a place of worship that the Theyyam makes a performance at any particular place. There are 17 spots mentioned in the mumbstanam of MuchilotBhagavathi, the patron Goddess of the Vaniya community. Each of these places are the centres of Vaniya community. We can say that these spots marked the cultural spatiality of the Vaniya community. Perumchellur, Karivallur, Trikkarippur, Pariyaram, Kavinisseri, Valapattanam, Kutteri etc. are mentioned in the mumbstanam of MuchilotBhagavathi.¹

Elavillichekon, the Theyyam of Thiyyas mentions places where it makes appearance. And it is not surprising that each of these are places of Thiyya settlement from very early times. Kottakunn, Nambiath, Kakkanamkode, Madathankandi, Chalode are mentioned in the mumbstanam of Elavillichekon.² The mumbstanam of Angakulangara Bhagavathi, patron Goddess of the Mannan community makes mention of Devarkunn, Poovidamkal, Dayaramangalam; and we can make out these as areas where Mannan community was dominant.³ It is when a community emerge dominant in an area, does their Gods get acknowledged, and they get a platform for performance. And the material conditions favourable for the popularity of that God emerge. When we try to make an enquiry regarding the social structure and transactions between various communities in a village we will have to make an enquiry on their commercial contacts also.

By contributing a share of his economic power and personal participation to the festivity, and also by taking part in the communal lunch every person ensures his participation in the community life. Thus socio

religious gatherings at the time of Theyyam performances are occasions for bringing together people of the same community together. In this context, the mumbstanam section of the thottam songs deserve special mention.

When settlement pattern of various villages in Kerala were first made by the colonial masters, only land ownership were taken into consideration. Because they just wanted to get a data of the taxpaying category. There we get details only of the upper land owning class the udayalar.⁴ But along with this class, were numerous functional groups engaged in activities to make the life of the udayalars complete. The Carpenter, blacksmith, gold smith, washer men, persons engaged in agricultural operations were all such classes in the service sector. While the land owning class in various areas may vary, the service classes in all these villages remain the same. Some village may have a Brahmin as the overlord, it may be a Kshatriya or a Nair overlord in another area, but the people in the service sector are constant. Because only if all the people in the service sector are there, will the activities in a village be carried out satisfactorily. The role of a carpenter can be fulfilled only by his presence. The blacksmith, the mason, the washer men were all necessary for the smooth functioning of a village. The role of one functional group cannot be fulfilled by any other group. In most villages we find place names indicating the settlement of these communities. Place names like Asharikkandi, Kollanparambu, Mannanthodi etc. indicate the areas inhabited by these functional groups. These place names in no way reduces the significance of these groups. On the other hand slight changes in place names indicate the indelible presence of these functionaries in each village. At various instances we also find *thara avakashams*, the rights of a community in a thara or desam. The thara avakashams ensured the participation of each service community through a kind of monopoly. It also ensured work security and economic stability of each class.

The geographical area for normal local transactions are Nadus. Political and trade transactions of an area is generally confined to that area itself. That is why even the dialects of an area, differ from another area. The festivities associated with the Theyyam performances are occasions for social and cultural uniqueness and exchange. The Gods and Goddesses portrayed in the Theyyam performances are undoubtedly the religious symbols that the believer carries in his psyche. They are born out of his experience, and have the capacity to indicate many things.

Cultural processes are interesting because they are the medium within which powerful social relationships are played out and possibilities for social betterment are opened up or closed down.⁵ Individual and collective identities are seen as problematic issues, as they are understood as being always created under social pressure. Different questions about culture have focused attention on standardization or convergence. Inequalities in the society have appeared so systemic and entrenched that they have seemed to produce and reproduce themselves almost automatically in the folklore and myths of an area. Economic disparity, caste domination and other forms of coercion, and propaganda becomes an ideological manipulation. The critique of the dominant, aims to secure the representation of the marginalized or the subordinate groups, spaces or themes in various ways.

Ruling ideas of any given society might be displaced by any new ideologies, which reflect changes in political and economic arrangements. However the general interconnections between economic and political conditions, ruling class, power and mass consciousness persists. Philosophy and other intellectual ideas, have to be situated in relation to ruling class interest. Therefore, to explain the rise and fall of philosophies, the power of logic was less adequate than the logic of power.⁶

It can be seen that a multilayered stratified society where custom and tradition, ritual obligations, Jati systems and systems of

purity and pollution had consolidated during the post perumal period. The socio- economic formation of this period was based on ties of dependence among the different social layers, forms of appropriation of labour and over surplus, subjugation of producing classes and political and judicial structures that were designed to ensure these relations. The dominant ideological apparatus was clearly based on the Brahmanic –Sanskritic institutions. However it should not be forgotten that these political and social structures were constituted by patterns of kinship and lineage considered as vestige of tribal society, but acquiring a separate identity in the context of the emerging medieval society.⁷

One of the most striking feature of Theyyam worship is the absence of the Brahmin priest in performing the rituals. In Theyyam performances the priests are indiscriminately from non Brahmanical castes. Generally in kavus offerings are made once or twice in a week and annual festivals are celebrated after harvest, when people are resourceful and at leisure. The different communities which participate in the annual festival offer different objects according to their wealth and influence. The vannan brings the kodikkura (flag), the chaliyar pudiyapudava (new cloth), vettuvayas kayaru (rope), musari bronze objects, panas kuda (umbrella), karuvan sword and knife (valumkattiyam), mukkuvas fish and kumbharan earthen pots. The collective nature of participation and the ceremonial nature of rights of different castes or communities of the locality clearly indicate the remoteness of tradition in the management of the kavus.

A week before the beginning of the annual festival of Theyyam, the velichappad (oracle) or ritual dancer visit each and every house of the village for parayeduppu. The eldest woman of each house welcome him with nirapara and nilavilakku. On the day of the festival Theyyam is performed in front of the temple or in the courtyard of an ancestral house accompanied by drumbeats. Komaram or velichappad or the theyyam performer appears

to be the earthly representative of the God. When the occasion demands, komaram or velchappadu or the Theyyam performer expresses their appreciation of the propitiatory ceremonials, pronounce blessings on their devotees, forecast the future and warn the people of the village about the impending calamities like contagious diseases, crop failure, famine, flood, etc. He also directs them to do some kind of ceremony as a votive offering to avert calamity.

Some formalities associated with the Theyyam are feudal in nature. Just before the commencement of the Theyyam, it is a customary practice to obtain permission from the Karanavar of the local aristocratic family with the handing over of betel leaves and a nominal offering. This is just to show customary allegiance to the land lord. At times customary allegiance is also shown to the Brahmin priest of the most important temple in the vicinity. The sacred fire for lighting the lamp for the festival is also brought from the Brahmanical temple. Thus the hierarchy is strictly observed.⁸

An interesting feature of these performance is the coexistence of archaic legends associated with it, which are sung in the form of ritualized songs like thottam and kalampattu. Most of the legends represented in the thottam songs are almost the same and are connected with the people of the lower castes.

The mode of worship in Kavay is very simple, but certainly archaic. Even today animal sacrifices (of cocks and goats) are performed in some Kavay. In some other Kavay sacrifices are replaced by the *Guruthitharpana*. *Guruthitharpana* is an offering of a red fluid -a mixture of turmeric and lime and it is offered in place of blood to allay the wrath of the deity. Another view of the ritual of *Guruti* is that it has its basis on the tantric cult: a lotus, which is drawn on the ground, and on which the vessel containing guruti (a red fluid made out of mixing turmeric and lime) is kept, is a symbol of female sexual organ.⁹ The most essential feature of fertility is the life-blood. Perhaps the whole ritual guruti also symbolizes the reproductive

functions of mother earth. The red sandalwood paste, red flowers (thetchi, chembarathi etc) used for puja, the importance of red cloth (pattu) and the offer of *guruti*, all signifies the importance given to the aspect of fertility, predominant in the primitive mode of worship.

Inequalities in the society have appeared so entrenched that they have produced and reproduced themselves almost automatically in the folklore and myths of an area. The economic disparities, other forms of cohesion and propaganda are all forms of conscious ideological manipulation. The common experience of being misrepresented often directly fuelled a kind of cultural study that interrogated dominant representations and hegemonic cultural formations. The critique of the dominant however has had a second side: the aim to secure the representation of the marginalized or the subordinated groups, spaces or themes in various ways. The folk songs that prevail among the downtrodden communities, especially at religious ceremonies provide ample scope to assume that the language which once prevailed as a traditionally accepted mode of expression is far from that which is in vogue. But even the folk songs do not fully represent their antique form because they belong to the oral tradition which is liable to change with passing generations.

The life of the common people, two to three thousand years ago, a picture of which is evident from the Sangam literature, was not based on caste distinctions and prejudice. There was a broad division of the population based on the nature of land they occupied. In the ainthinai the Kuravars (Hunters) of the Kurinji (mountain land), the Maravar (Fighting men) of the Palai (Arid land), the Idayas (Sheperds) of the Mullai (Pastures), the Uzhavas (Agriculturists) of the Marutham (wetland) and the Paravas (Fisher men) of the Neytal (Coastal Land) were all from the same race. These people had their primitive Customs and manners which they retained even when new emigrants migrated to their area. Sir William Wilson observes: "Thrust back by the Aryans from the plains that once were

theirs, the aborigines hid themselves in the recesses of the hills like fossil remains found by geologists in the mountain caves, only their specimens are not dry bones, but a living race of mankind." In order to defend themselves from the intruders, they lived in groups and depended mostly on nature for all their needs. Their religion was crude animism. They propitiated spirits for sickness and calamities.

Ancestor worship was also in vogue. We find that the primitive tribes, among whom no distinctions or differentiation prevailed in the beginning, slowly became conscious of their importance and developed a sort of group arrogance. Certain observance of pollution was strictly adhered under the strict discipline of the *moopan* the tribal chieftan in religious and temporal matters.¹⁰ Social relations are manifestations of concrete relations engendered by the economic practice that is realized, reproduced and transformed through a

relatively autonomous process. In economic practice, contradictions exist within and between subsistence strategies of social groups, in spite of the fact that dominance of one or the other in terms of productivity is explicit. In political practice, contradictions exist within and between relations of representations and relations of hegemony expressed in antagonistic interest of those who effectively control the institutions of collective social organization and social groups within the social formation lacking such control. In ideological practice, contradictions exist within and between relations that empower and enable individuals as social subjects and relation of subjection, which restrict individuals to specific roles and capacities.¹¹ In short there was a complex hierarchy of functional groups in Medieval Kerala, whose unity can neither be ignored nor be reduced to a single closed system.

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AN ACCOUNT OF NARRATIVE RENDITIONS BY BAINDLAS

Theegala Sreenivas & Thallapally Manohar

An attempt to probe the origins of the name *Baindla*, and the reason for their occupation as singers reveals that the name originated from name of *Bhavani* or Goddess *Shakti*. Those worshipping the Goddess are known as *Bhavaneeyulu*, which over time got corrupted to the name *Baindla*. According to *Andhra Bhasha Nighantuvu* (Telugu Language Dictionary) the term *Bavaneedu* means

Kshudrasanghaprasamsi (those who live by praising people of lower castes). Even the pure Telugu glossary (*Atcha Tenugu Padakosam*) conveys the same sense – *Kshudrasanghaprasamsi* – one of the communities that lives by praising people of lower castes. References to *Sabdaratnakaram* and *Sree Suryanarayana andhra Bhasha Nighantuvu* reveal the meaning of the term



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Locating the dislocated : An Analysis of the Migrant Labour Influx and its Repercussions in Kozhikode

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political and even religious (Aerthayil, M. 2008). During the British regime a number of opportunities for intermingling of tribals and non tribals were created as a result the tribal social fabric is also slowly tearing a part due to infiltration of non tribal values in to their societies. (Behra, T.K. 1999).

The plantation economy had a huge impact on tribal groups who had freely used the forest and hills that were now being converted to in ordered productive landscape. Labour recruitment for the plantation, the disciplining of the worker and the interference of missionaries forced them to migrate in to interior forest (kavita Philip, 2003). Thus the ecological equilibrium is making a serious impact on the life of kattunayakas.

Here I would like to use the term *inward movement* to denote the movement of tribe especially Kattunayakas to the interior forest to resist the non tribal interventions. It is a

movement from the outskirts of hill and forest to the interior part. Thus inward movement is a resistance method followed by Kattunayakas to protect their cultural identity.

Thus developments in means and relations of production transform a society both in positive and negative. Emergence of new plantation economy creates new social order and change in Wayanad. The capitalist mode of agriculture in the form of plantation in tea and coffee led to the spread of monetization to the tribal communities. From comparative isolation and dependence on exchange and barter, the tribal communities were brought in to the vortex of monetization in their relations with non tribes. But the capital penetration to the peripheral areas of Wayanad for agricultural and plantation had disturbed the kattunayakas. So as a part of resistance and reaction to it they moved to interior forest to protect their customs, traditions and their culture.

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LOCATING THE DISLOCATED : AN ANALYSIS OF THE MIGRANT LABOUR INFLUX AND ITS REPERCUSSIONS IN KOZHIKODE

Priyadarsini. P

Migration is a vital component of the poor people's struggle for survival. The major function of migration is to act as safety-valve in poor areas. It is clear that migration is the response to the uneven distribution of

opportunities over space. The socio-economic impacts of migration are very important to the source area from they come and the destination area where they work for a good number of years. Since the macro databases like the census

and NSSO (National Sample Survey Office) data fail to adequately capture the flow of seasonal /circulatory migration, they become an invisible and floating population in the country.

Due to chronic poverty a large number of India's rural youth migrated to urban areas of Kerala in the last few decades. Kozhikode in Malabar has been attracting many a migrant since 1990 and they have been working mainly in construction firms, hotels, shops etc. The influx of migrant labour has a lot of repercussions in the socio-economic fabric of the society. Out of the total of 1210.2 million population in India, the size of rural population is 833.1 million.¹ A good number of them are forced to migrate to urban areas and are facing the challenges due to migration. Migration has brought about rapid transformations in the structure of the labour market and consequently of the employment².

The impacts of out migration certainly helps the migrants and their families to survive poverty and their remittances are of great help to save them from the web of debts and loans. Evidence reveals that with rising incomes, migrant remittances can encourage investment in human capital formation particularly increased expenditure on health, and also to some extent education of their children. Migrants bring back to the source areas a variety of skills, innovations and knowledge known as 'social remittances', including change in tastes, perceptions and attitudes (for example, non-acceptance of poor employment conditions, low wages and semi-feudal labour relationships and improved knowledge and awareness about workers' rights). To a certain extent migration helps the labourers to escape caste divisions and restrictive social norms and to work with dignity and freedom at the destination.

The statistics show how outmigration of males is many times higher than women. This leaves women the responsibility of taking care of the households. Many migrants talked about the psychological and material insecurity in the absence of men folk from their homes. But a positive impact of the male outmigration is how women emerge as decision makers and interact

more with outside society to tackle the daily problems of life. Marriage is one major reason which forces a woman to migrate to a new surrounding with her husband. Many women migrants are seen in Kozhikode who after marriage migrated along with their husbands. Many of them take up jobs to support their husbands. The women thus get empowered and thus are able to support their family in a better way. Some of them bring their children along and this forces the children to be school dropouts in their home state. These are the few positive impacts of migration but it has a bitter grey side too.

A lot of changes are visible in the society of Kozhikode with the influx of migrant labour to the society. Their presence has certainly helped the construction business to overcome the dearth of unskilled labour when the youth of the locality sought white collar jobs. The industry has flourished and the number of high rise buildings is on the rise ever than before. They are also willing to do all the filthy and dirty tasks which the educated natives of Kozhikode refuse to do. Since they are un-unionized, their power to bargain in the labour market is almost nil and so their presence in the society reduces the cost of labour on the whole. The absence of trade unions to demand for their better working conditions and the lack of political representatives to speak for their cause force them to take up long hours of working and also hazardous jobs. The migrant labourers due to their ignorance and vulnerability work in very unsafe circumstances without any safety measures or protective gears.³ In construction sites they climb up heights without any safety belts and helmets. These are work which the local labourers refuse to do taking into account the risks involved. Many cases are reported in Kozhikode where the migrants fall from such heights and thus meet with accidents which are very fatal and result in death. The laws of the state ensures protection and compensation to the family members of the deceased but the private owners take advantage of the situation and give nothing. The dead body is sent to the home state and the family ends up with neither

insurance nor compensation. Such a shocking incident which shook the consciousness of mankind happened on 24th November 2015, when two migrant workers opened a manhole to check the water level in the 12ft sewer near Jaya auditorium, Kozhikode. Fire force officials said that the security measures were not taken while cleaning the drainage. Due to shortage of oxygen and presence of poisonous gases in the drainage one should not enter the manhole as soon as it is opened. The witnesses said that they did not even check whether there was poisonous gases. However due to lack of safety arrangements, Narasimhan fainted after inhaling the toxic gas that emanated from the manhole and fell into the sewer. Bhaskar Rao jumped into the sewer to save Narasimhan but both were trapped and died of asphyxiation.⁴ The contractors who got them on duty failed to provide safety gears for the workers. We can see that due to their difficulties and lack of awareness the migrants are forced to do such risky and filthy jobs which no one in the locality dare to do. As a result they meet with a number of mishaps and accidents. Such exploitation takes place when Interstate Workmen's Act of 1979 clearly states about the rights and benefits that a migrant can avail. We can see how the law becomes toothless when the exploited are ignorant and are not conscious of their rights.

Another major problem faced by the migrants is the severe discrimination that the north Indian migrants face from the local population. Though they work very hard day and night and to a great extent trustworthy the local society that speaks high about cultural acculturation and show lenience toward Marxist-communism keep them at bay and are insensitive to most of their problems. Still treated as strangers though an indispensable part of the society, the migrant population faces severe isolation. They face a lot of exploitation from the intermediaries through which they get the jobs. Most of them are forced to share a good amount of their earnings with these men. As the migrants are not organized and lack education their chances of getting exploited are very high. From

the house owners to shopkeepers and policemen treat them in a very insulting matter.

The local people who generally known for their good health and hygiene standards fail to be sensitive to the health issues faced by the migrants. They make shift tents and single room apartments in which the migrants are crammed barely have the basic amenities. In the absence of toilets and bath rooms, they use public toilets or defecate in the open which becomes a major issue. As a result they are prone to get infected by a number of diseases.⁵ Reports show that most of the patients who get affected with malaria and filariasis are migrants. It is mainly due to the unhygienic set up where they are put up. Another common disease which is seen among the migrants is skin disease. This is also due to lack of water availability and hygiene in the places they stay. Poor quality of water attributes to a good number of diseases and epidemics amongst the urban poor⁶

In Kerala though health care is really affordable and almost free to poor people but they can avail it only by producing their ration cards. Migrants whose entry to the city itself is unregistered cannot avail these medical facilities. Hence they are forced to go to private hospitals that are expensive. Only recently the Government of Kerala has taken initiative to give free health check up and medical care to the migrant population.⁷ It was very lately that a separate counter was set up exclusively for them taking into consideration the spread of many alarming diseases among them. The consultation timings in the government hospitals make the migrants difficult to adjust their day's work and meet the doctor. Since the migrants are given daily wages when take leave due to health reasons they do lose on a day's wages. Hence there is the tendency for self treatment with painkillers and antibiotics. Off lately the government is creating health awareness amongst migrants with the help of *Asha* workers who distribute pamphlets to spread awareness and medicines to prevent contagious diseases. As they are away from their families and since they do not have any way for entertainment the

migrants fall prey to lose sex life which result in an increase in a number of them suffering from sexually transmitted diseases and AIDS. Medical studies find migration as a major cause in spreading AIDS. AIDs control Society is also active nowadays in conducting awareness classes for the migrants towards safe sex by using condoms. Certain NGO's have Migrant labour Security Schemes which organize cleanliness drives amongst migrants.⁸

The local population of Kozhikode has a lot of grievances against the indiscriminate use of natural resources by the migrants including land and water bodies. *Mampuzha*, a famous river and supplier of pure drinking water is now filled with filth and non biodegradable plastic waste. The allegation for the present situation of the river is mainly on the callous approach of the migrants.

They lack environmental consciousness and thus damage the concept of sustainable use of nature and ecology. A livelihood is commonly regarded as sustainable when it can cope with and recover from the stress and shocks and maintains or enhances its capabilities and assets both now and in the future, while not undermining the natural resource base.⁹ Sustainable livelihoods bind people to their communities and to their land. Not only do they have a positive impact on health, fertility reduction, migration and other demographic behavior, but they also permit a far more effective use of resources for the benefit of all¹⁰ Migrants lack environmental consciousness and thus damage the concept of sustainable use of nature and ecology. Common man has to be entrusted the responsibility of what is happening to the environment, especially in developing countries where people's ignorance is often sustained for easy rule by the political parties.¹¹

The authorities had not taken any measures to register the entry of migrants to the city. So the local people do not have any idea about their whereabouts. As they are not registered the migrants cant avail the facilities and Government schemes for the poor.¹² Along with people who were in dire need of jobs to

escape from poverty back in their home state, migration also resulted in the movement of people with criminal and anti-social background to Kozhikode. The crime rate in the city is on the rise and the alleged involvement of migrants in rapes, thefts drug trafficking and murders make them anti-social elements of the society. A number of cases have been registered by the local police against the migrants.

We can see that unemployment that leads to migration also results in personal and financial pathology and carries with it a range of stressors (psychological, social and economic).¹³ The pressure of the host culture and the parent culture cause the creation of a sandwich culture coexisting with the host culture. Also there is worry of an unwelcome reaction by the natives against the arriving cultures demanding an equal treatment

Migration of labourers has severely added to the overuse of natural resources and congestion in Kozhikode. Migration to the cities adds to their population thereby significantly increasing the demand for land and housing. But even if sufficient accommodation is available at reasonable prices, it may be argued that the rural poor migrating to the cities mostly end up in slums¹⁴. This is very true in the case of Kozhikode district.

Another major impact is the presence of the children of the migrants accompanying their parents and brothers. The problem of child labour is interrelated to the inadequate wages of the parents. Chronic poverty and also the illiteracy of the parents force many children to take up hard and tough jobs. Diseases and other contingencies may need extra money and the employment of children is resorted to as an easily accessible method to bring in that money¹⁵ The presence of child labour in the urban sector restaurants small industries, paper sellers, Shoe shine boys, rag pickers¹⁶ Though not much of child migrant labour is reported in Kozhikode it is seen that the informal sector like the kiln factories and quarries have children employed. The local authorities have not done anything worth to provide good education to the children of the migrants.

Interstate workmen regulations of employment and conditions of services Act (ISMW Act), 1979 states equality of payment to the domestic migrant labourers and also the regulations that contractors who appoint labourers have to follow. It clearly says about the responsibility of the contractor in providing accommodation to the labourers with good sanitation facilities. It also says how the contractor should issue a passbook to every labourer working under him and has to deposit a small amount in his or her name.¹⁷ Due to the floating nature of the migrant population most of the contractors refuse to get the migrants registered under them as they are not willing to take up the responsibility all the activities of the migrant always. Minimum Wages act 1948 of the Ministry of Labour, Govt of India ensures fixed minimum wages to all the labourers including those in the highly informal sector.¹⁸ The Unorganized Sector Workers Security Act, Ministry of Labour, Govt of India, 2008 has clauses on old age protection, health and maternity benefits.¹⁹ The Equal Remuneration Act 1983 Ministry of Labour, Govt. of India also speaks loud about the rights and working conditions of all the labourers.²⁰ The Emigration Act 1983 of Ministry of Labour, Govt. of India says that no person can function as recruiting agent without a valid certificate.²¹ The Contract Labour (Regulations and Abolition) Act 1970 Ministry of Labour, Govt of India has clauses to prevent the exploitation of contract labourers.²² Report of the National Commission on Rural Labour 1991 and the Report of the Study Group on Migrant labour in 1991 all have numerous recommendations on how to improve the condition of the migrants and also to integrate them to the mainstream society. But due to lack of support from the civil society and the overstretched nature of all the above regulations this seems to be impossible. Moreover subcontracting and segmentation of labour are common features in the labour market of Kozhikode which supply the employers with a regular and cheap supply of labour. The builders and contractors do not want the migrants to form unions and they expressed their concern as to

what would happen if the north Indian migrants formed their trade unions.²³ ISMW Act insists that each district should maintain Inter-State Migrant Register registers to keep a track of the number of migrants who are working on contract in various firms. The registration is done in the name of the principal employer of the firm who entrusts the jobs to contractors who have to get the license as per the Contract Labour Act and Interstate Migrant Workmen's Act. A security deposit of Rs 2000 has to be remitted in the name of every migrant by the contractor

Though the rules are strict, it comes with a lot of loopholes. The contractors register only less than half of the migrant labourers required. This shows their unwillingness to take risks on behalf of the migrants and their hesitation to pay Rs 2000 as security deposit for every migrant worker. So the figure shown by the register is far from being accurate. As firms employing more than 5 migrant labourers need to get registered many who are working in shops and offices don't come within the ambit of these laws. Kerala Government has allotted Rs 50 lakhs for migrant welfare measures in the state budget of 2016 as per (2230-01-103-91) plan.²⁴

The District Labour office, Kozhikode conducts a lot of awareness classes and free medical camps every year with the support of Panchayat members and ward councillors.²⁵ Professional counselors are involved in such camps to chalk out ways to reduce the criminal tendencies among the migrants. As the migrants lose a day's job by attending these camps, many hesitate from participating in such drives and initiatives.²⁶

Migration to Kozhikode has drastically affected the villages in North India, the source destinations from where they have migrated. Villagers are deprived of their most productive and dynamic manpower because most of the migrants are young men and women who aspire for more secure and higher income and better life in the cities. They go to live in the cities through most of their working life and return to their villages only at the end²⁷. Women in the absence of their men folk experience a lot of stress and

agony due to this separation. Some women accompany their husbands who migrate to Kozhikode. Women are placed under different types of responsibilities in the cities where life revolves around the clock. Working hours and other form of discipline replace the informality of rural living. Commuting to work, late working hours, absence of sufficient female workers and distance to work place – all these make them easy prey to the anti social elements .

Case study of migrant labourers

Nitai Biswas- (age-35) who migrated from Orissa was a tailor before he moved to Kozhikode. He has been working in the construction industry for the past six years. Currently he does centering and plastering work with building construction contractors and earns Rs 540/ per day. He said that after all his expenses he has been able to send Rs 20,000 to his family in Orissa. His plan is to earn as much as possible while he is in Kerala and then join his family. Though he finds the working conditions adjustable he doesn't plan to settle in the district.²⁸

Sujith – (age -21) who belongs to Jharkand worked as a security Guard in his state. He had completed his Higher Secondary Education but it was the poverty in his family that didn't allow him to pursue higher education. It was his uncle who had earlier migrated to Kozhikode who brought Sujith to the city. He said though Jharkand has plenty of coal mines the wages there are very less and engaging in agriculture also didn't generate profit. In Kozhikode after all his expenses he has been able to send Rs. 13,000 / - to his mother. He sends the money through State Bank of India and keeps in touch with his family with the smart mobile phone he owns.²⁹

Rakesh Biswas (age -21) came from Malkangiri district in Orissa. He has been in Kozhikode for the past five months. He was pursuing under graduation course in Economics but poverty forced him to discontinue his studies. He is basically an artist who presently is doing centering work in building construction. During his free time he does painting work and earn

some money. He said that while in Orissa people get Rs 200/- as daily wages for masonry they were paid Rs 500-/- in Kozhikode.³⁰

Naresh Rai (age- 24) who came to Kozhikode from Uttardinajpur in West Bengal has been working in Kozhikode for the past six months. He said that socialism and communism for more than fifty decades in West Bengal brought prosperity to the common people there. He mentioned of the stark disparity between the rich and poor in his state. It was his friends who migrated to Kerala last year who said about the better wages in Kerala. He has three elder sisters at home and he had to find ways to get them married off.³¹

Ratan Kumar Rai (age -26) migrated from Orissa. He owns a gift shop that is run by his father when he is away. He loves travelling and is very keen in doing adventurous activities. He collects money for his travel by doing extra work like masonry and painting. He has done such work in cities like Hyderabad and Chennai. But personally he likes cities in Kerala. He said that the cities in Kerala are much more tidy and the people cordial and warm while compared to other states. His aim is to collect money as much as possible while in Kerala and then go on an all India tour. He said that helmets and safety measures are taken by the contractor under whom he worked. But he also had certain grievances like the non availability of hot water during cold season and also filtered water to drink.³³

From the case study conducted it is clear that the migrants now in Kozhikode are mainly from West Bengal, Jharkhand, Chhattisgarh and Orissa. It is mainly due to unemployment, poverty and less wages in these states which made the people move out of their home states. They are all young people who are struggling to find ways to feed and take care of their families who belong to the age group between twenty and thirty eight. Most of them earn between Rs 15000/- and Rs 30,000 /- per month. As they stay in a shed provided by the contractors many are able to save an amount which otherwise should have been given as rent.

Some acted as agents who recruited youth from their villages and brought them to Calicut. They were hesitant to share any grievances against the contractors and local people as they didn't want to create any hostility to them. Majority didn't bring their families home and felt isolated from the main stream society. They didn't make deliberate attempts to befriend the local people but at the same time had fear and respect for them. Though to many Kerala is their Gulf, None of them had plans of settling permanently in Kozhikode but to leave for their state after saving a good amount here.

Some measures can be taken by the authorities for improving the conditions of the migrants. When the state establishes an industrial estate or a wholesale market, the housing of the labourers should form part of planning within the urban infrastructure. This step can prevent overcrowding and growth of slums in the city. Another step is to have a proper record of migrants and their whereabouts. We should have enough information about the migrants: their identity in terms of employment, residence, places from which they have migrated, reasons for migration, local contacts, age, sex, skills etc. This will help assess the state of unemployment among migrants with specific categories of skills, the direction of migrant inflow, the demands made on housing, transport, communications and social welfare. A welfare state has to operate on these lines assuming all these responsibilities.³³

The increased attractiveness in rural areas will alleviate or discourage the rural to urban migration by increasing activities right in the rural areas through community development projects. Besides the economic development, the most significant aspect of checking rural to urban migration is to inculcate in rural young the pride and enthusiasm for rural customs, beliefs, values, attitudes, and general culture which educated urban youth tend to shun. It can be done through national rural youth mobilization programmes inducing the young to be responsive, adaptive, and accommodative of rural environment and contingencies³⁴

Though one basically agrees with the concepts of deregulations, privatization and liberalization of the economy, their extreme forms are not likely to work in the interest of the economy or in the interest of the poor. Selectivity and graduality both are desirable. There is a need for a fresh look at the structural adjustment package in the context of the interests of the total economy as well as the welfare of the poor.³⁵ Planning in India doesn't incorporate the requirements and demands of the poor. This is because in India the nexus of Dada, Lala, Neta and Babu have played havoc with the lives of the hungry.³⁶ The cities need the poor as automations to keep the show going but are increasingly intolerant to their existence as human beings³⁷ The city migrants eventually earn more and eat more and better and whether they continue to live with their kith and kin or not, they certainly miss their rural fraternity and wear a cross of the clinging sense of ennui on their bosom (same) Vienna Declaration of 1993 says that the vulnerable group of migrant workers should be protected from the discrimination and the states must create suitable conditions for their education and public health³⁸ Free Market Economy must not end up creating islands of prosperity surrounded by sea of destitution.³⁹ Migration which is ensued by dislocation of millions is going to be graver even more in the coming days. It so becomes the need of the hour to safeguard their interest and make them a part of the mainstream society.

The statistics proves that the migrant labour influx to Kerala is going to be higher in the coming years. The city of Kozhikode which took pride in being courteous and humane to the strangers is not so now in the recent times. Urgent measures should be adopted to accept the migrants into the mainstream society. The responsibility of it vests on the shoulders of the local authorities of the district. Labour cells can be set up in the district for this purpose. Public private partnerships can be sought to tackle this problem. However the most important aspect is to change the mindset of the local population. The society should take care not to stereotype them as rapists, thieves and criminals because

certain major crimes and rapes had their involvement. Calicut, the medieval city that was the epitome of honesty, compassion and

humanity can retain its name in the future only if the people of the city are courteous and humane to all.

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Development of Passive Film and Enhancement of Corrosion Protection of Mild Steel Exposed in Hydrochloric Acid due to the Adsorption of Water Dispersed 4-[(*E*)-(3,4-Dihydroxybenzylidene)amino]-6-Methyl-3-Mercapto-1,2,4-Triazin-5(*4H*)-one(DHMMT)

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Abstract Corrosion inhibition activity of 4-[(*E*)-(3,4-Dihydroxybenzylidene)amino]-6-methyl-3-mercapto-1,2,4-triazin-5(*4H*)-one (DHMMT), a triazine-based Schiff base, for the corrosion of mild steel in HCl has been investigated by weight loss and electrochemical methods. Effect of inhibitor concentration, immersion time, acid concentration and temperature on inhibition efficiency has been studied. It is shown that inhibition efficiency increased with increase in inhibitor concentration and decreased with increase in acid concentration, immersion time and temperature. Polarization studies show that DHMMT act as mixed type inhibitor and adsorption of DHMMT on mild steel obeys Langmuir adsorption isotherm. The presence of protective film on mild steel surface is further confirmed by surface morphological studies.

Keywords Mild steel · Acid corrosion · Organic inhibitors

1 Introduction

Mild steel is one of the most widely used materials in industrial sectors due to its structural and mechanical strength. Hydrochloric acid and sulphuric acid are commonly used mineral acids for pickling as well as removal of rust and scales in industries [1–4]. These acid solutions are

very corrosive in nature, attack the mild steel surface and initiate vigorous corrosion [5]. Due to this adverse impact of acid solutions on metal surface, nowadays almost all industries are suffering from a huge and incredible amount of economic loss [6]. Therefore, corrosion control is an urgent problem and primary interest to protect metallic corrosion in solution phase. Among various corrosion inhibition techniques, use of inhibitors is widely accepted because of high efficiency availability and economic feasibility [7–12]. Generally inhibitors are adsorbed on the metal surface to form a protective barrier and interact with anodic or/and cathodic reaction sites. A large variety of inhibitors have been studied in various corrosive media and on several metal surfaces. Compounds containing heteroatoms like nitrogen, sulphur, phosphorous and oxygen along with aromatic rings, multiple bonds or delocalized π -electrons are often found to be good inhibitors [13–18].

The Schiff's bases are important class of compounds characterized by the presence of $-C=N-$ group. They are easily obtained from cost-effective substrates, and most of them are harmless to environment. Due to the improved flexibility and diverse structural features, a wide range of Schiff's bases have been synthesized and utilized for extensive applications in medicinal, agricultural, pharmaceuticals and material science fields [19–23]. The excellent corrosion inhibition efficiencies offered by different Schiff's bases compared to the building aldehydes and amines are not fully explored. The presence of electron cloud on aromatic ring and sp^2 hybridized heteroatoms in the molecule enhances the corrosion inhibition activity. The presence of sulphur, oxygen, nitrogen and aromatic ring in the molecule motivated to synthesize, 4-[(*E*)-(3,4-Dihydroxybenzylidene)amino]-6-methyl-3-mercapto-1,2,4-triazin-5(*4H*)-one (DHMMT). It shows corrosion inhibition efficiency up to 99% for mild steel in 0.5 N HCl

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solutions. The change in efficiency with time, temperature and acid concentration is less compared to other Schiff bases.

2 Experimental

2.1 Materials

Mild steel samples of composition (atom %): C (0.2%), Mn (1%), P (0.03%), S (0.02%) and Fe (98.75%) were used for the present studies. For electrochemical measurements, mild steel coupons of 1 cm² area were exposed in each test. Before the measurements are taken, the samples were polished using different grades of emery papers, degreased by washing with ethanol, acetone and then washed with distilled water.

2.2 Inhibitor

The inhibitor, DHMMT, is prepared by condensing 4-amino-3-mercapto-6-methyl-1, 2, 4-triazine-4*H*-5-one with 3, 4-dihydroxy benzaldehyde in ethanol. The former compound is synthesized in the laboratory by reacting pyruvic acid and thiocarbohydrazide [24]. The purified and recrystallized sample is characterized by physico-chemical methods. Structure of the molecule is given in Fig. 1. The compound is soluble in water at room temperature, and the concentration range of inhibitor used is from 50 to 200 ppm.

2.3 Electrolyte Medium

The electrolyte medium for the study was prepared by diluting analytical grade 35% HCl (E. Merk) with double distilled water.

2.4 Weight Loss Method

The weight loss method is very important in monitoring inhibition efficiency because of its simple usage and

reliability. Effect of time, inhibitor concentration and acid concentrations on inhibition efficiency have been investigated by weight loss measurements. Experiments were carried out in 250-ml beaker containing test solution at 300 K under total immersion condition. After exposure, the specimens were washed initially under running tap water, to remove loosely adhering corrosion products then cleaned with 15% HCl followed by acetone. From the weight loss in each measurement, the corrosion rate was calculated in milligram per centimetre square per hour (mg/cm² h). Experiments repeated minimum four times to ascertain consistency. Whenever the variations are more than 1%, the data were confirmed by further repetition. The corrosion rate (C.R), surface coverage (θ) and inhibition efficiency, η (%) were calculated using the relation [25–28]:

$$\text{C.R} = \frac{W}{A.t} \quad (1)$$

where W is the weight loss (mg), A is the surface area (cm²), and t is the time (h).

$$\theta = \frac{W_0 - W}{W_0} \quad (2)$$

$$\eta(\%) = \frac{W_0 - W}{W_0} \times 100 \quad (3)$$

where W_0 and W are the weight losses in uninhibited and inhibited solutions, respectively.

2.5 Electrochemical Studies

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) experiments were performed using Gill AC computer-controlled electrochemical workstation (ACM, UK model no: 1475). Conventional three-electrode cell consisting of saturated calomel electrode, platinum auxiliary electrode and mild steel as working electrode was used. Electrochemical tests were carried out with various concentrations of DHMMT ranging from 50 to 200 ppm at different temperatures. Prior to experiments, working electrode was immersed in test solution for 1 h to establish a steady-state open circuit potential (E_{ocp}). Potentiodynamic polarization measurements were taken in the potential range from –250 to +250 mV with a sweep rate of 60 mV/min. Inhibition efficiency can be calculated from corrosion current density using Eq. (4) [29–31].

$$\eta(\%) = \frac{i_{\text{corr}} - i_{\text{corr}^*}}{i_{\text{corr}}} \times 100 \quad (4)$$

where i_{corr} and i_{corr^*} represent corrosion current density values without and with inhibitor, respectively. Similar experimental procedure is used for EIS studies with a frequency range of 0.1–10,000 Hz using 10 mV peak-to-

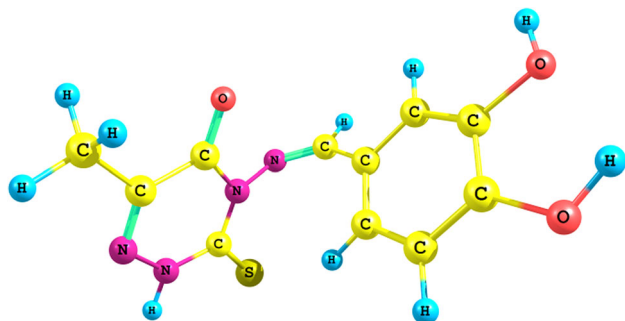


Fig. 1 Optimized geometry of the inhibitor DHMMT

peak excitation. Inhibition efficiency is calculated by the relation,

$$\eta(\%) = \frac{R_{ct*} - R_{ct}}{R_{ct*}} \times 100 \quad (5)$$

where R_{ct} and R_{ct*} are the charge transfer resistance in the absence and presence of inhibitor, respectively.

2.6 Surface Morphological Studies

Surface morphology of mild steel was carried out using stereomicroscope and scanning electron microscopy (SEM) technique. Images of bare mild steel and mild steel immersed in 0.5 N HCl solution for 3 h without and with inhibitor were obtained from LeicaM80 stereomicroscope. To confirm the results, surface analysis was carried out by scanning electron microscope model SU6600 (Serial No: HI-2102-0003) with an accelerating voltage of 12.0 kV and a magnification of 800 SE. Samples were attached on the top of an aluminium stopper by means of carbon conductive adhesive tape

3 Results and Discussions

3.1 Effect of Inhibitor and Acid Concentration

Cleaned and pre-weighed mild steel samples were suspended in 0.5, 1, 1.5 N HCl for 24 h without and with different concentrations of DHMMT. Table 1 represents the parameters derived from weight loss experiments, and a graphical representation of the effect of acid and inhibitor concentration on efficiency is shown in Fig. 2. From the values listed in Table 1, it can be seen that increase in concentration of DHMMT leads to an increase in surface coverage which ultimately resulted in an increase in inhibition efficiency for all the studied concentrations of acid. But inhibition efficiency decreased with increase in acid concentration. Even though efficiency decreased with acid concentration, DHMMT exhibit 99% efficiency in 0.5 N HCl and 95% in 1.5 N HCl at 303 K. These results suggest that the synthesized inhibitor acts as an efficient inhibitor in all the concentration ranges of acid.

3.2 Effect of Immersion Time

The immersion time is another important parameter in assessing the stability of inhibitive property of a compound, and therefore, it is necessary to evaluate the inhibition efficiency for a long time interval. In the present study, the effect of immersion time (24, 48, 72 and 96 h) on corrosion inhibition efficiency of DHMMT in 0.5 N HCl has been investigated by weight loss method. The

parameters derived from the experiment in the absence and presence of DHMMT in 0.5 N HCl at various time intervals are listed in Tables 1 and 2. Graphical representation of effect of time and inhibitor concentration on efficiency is shown in Fig. 3. As listed in table, inhibition efficiency decreased with increase in time interval, but careful examination of results showed that at higher concentrations of inhibitor, the decrease in inhibition efficiency with time is insignificant and it is almost comparable.

3.3 Electrochemical Studies

Potentiodynamic polarization curves for mild steel in 0.5 N HCl without and with DHMMT at different temperatures are given in Fig. 4, and corresponding electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic and cathodic Tafel slopes (β_a and β_c) and inhibition efficiency, η (%) are listed in Table 3. From polarization curves, it is clear that introduction of DHMMT to corrosive medium significantly decreased corrosion current density compared to acid solution without inhibitor. The change in values of i_{corr} in the presence of inhibitor is attributed to the protection of mild steel surface by the inhibitor [32, 33]. Also in the presence of inhibitor, the corrosion potential (E_{corr}) shifted towards more negative direction, but shift is lower than 85 mV thereby suggesting that DHMMT act as a mixed type inhibitor with predominantly inhibiting cathodic reaction [34, 35]. The results obtained from electrochemical impedance spectroscopy (EIS) are not different from that obtained from polarization studies. Nyquist plots for the corrosion of mild steel in 0.5 N HCl at various concentrations of DHMMT at different temperatures are given in Fig. 5. The appearance of Nyquist plots in the absence and presence of inhibitor showed a single slightly depressed semicircle, indicating non-ideal capacitive behaviour of solid/liquid interface [36]. It is clear from the figure that the diameter of semicircle significantly increased after the addition of the inhibitor into corrosive solution. The electrochemical parameters such as charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}), corrosion current density (i_{corr}) and inhibition efficiency, η (%) determined from EIS data are given in Table 4. The increased value of R_{ct} in the presence of inhibitor indicates the formation of protective film on mild steel surface. Also with increase in concentration of inhibitor, the value of R_{ct} is increased, which reveals a better surface coverage and percentage inhibition efficiency at higher concentrations of DHMMT [37]. The double layer between solution and charged metal surface is considered as an electrical capacitor. The adsorption of inhibitor on mild steel surface decreases its electrical capacity by displacing water molecules and other ions adsorbed on surface. In the present study, it is also

Table 1 Weight loss parameters for the corrosion of mild steel in different concentrations of HCl in the absence and presence of DHMMT

Acid Conc. (N)	C_{inh} (ppm)	Weight loss (mg)	C. R (mg/cm ² .h)	Surf. Cov. (θ)	η (%)
0.5	Blank	788.40	8.69		
	50	77.10	0.85	0.90	90.22
	100	38.30	0.42	0.95	95.14
	150	27.30	0.30	0.96	96.53
	200	10.20	0.11	0.99	98.70
1.0	Blank	1007.50	11.10		
	50	99.80	1.10	0.90	90.09
	100	60.00	66.13	0.94	94.04
	150	48.80	0.54	0.95	95.15
	200	41.60	0.46	0.96	95.87
1.5	Blank	1269.5	13.99		
	50	139.30	1.54	0.89	89.02
	100	73.80	0.81	0.94	94.18
	150	56.40	0.62	0.96	95.55
	200	56.10	0.62	0.96	95.58

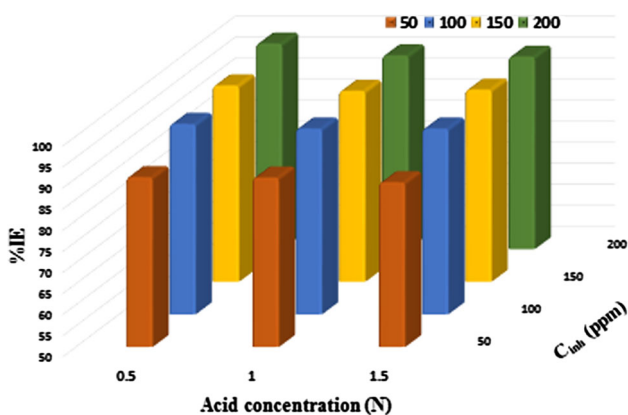


Fig. 2 Variation in the inhibition efficiency of DHMMT for mild steel by the effect acid and inhibitor concentration

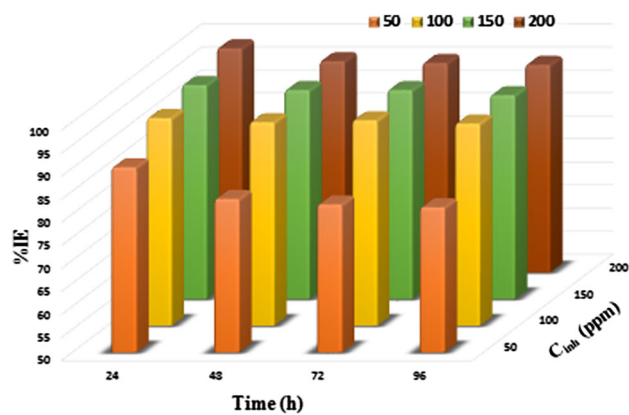


Fig. 3 Graphical representation of variation of inhibition efficiency by the effect of immersion time at 303 K

Table 2 Weight loss parameters for mild steel corrosion in 0.5 N HCl in the absence and presence of DHMMT at different immersion time intervals

Time (h)	C_{inh} (ppm)	Weight loss (mg)	C. R (mg/cm ² h)	Surf. Cov. (θ)	η (%)
48	Blank	901.30	4.97		
	50	149.70	0.83	0.83	83.39
	100	52.30	0.28	0.94	94.19
	150	41.90	0.23	0.95	95.35
	200	37.30	0.20	0.96	95.86
72	Blank	1095.00	3.93		
	50	196.10	0.70	0.82	82.09
	100	59.70	0.21	0.95	94.54
	150	50.40	0.18	0.95	95.39
	200	49.60	0.18	0.95	95.47
96	Blank	1177.20	3.17		
	50	217.40	0.59	0.82	81.53
	100	71.80	0.19	0.94	93.90
	150	66.60	0.18	0.94	94.34
	200	57.20	0.15	0.95	95.14

Fig. 4 Potentiodynamic polarization curves for mild steel in 0.5 N HCl in the presence of various concentrations of DHMMT **a** 303 K **b** 308 K **c** 313 K and **d** 318 K

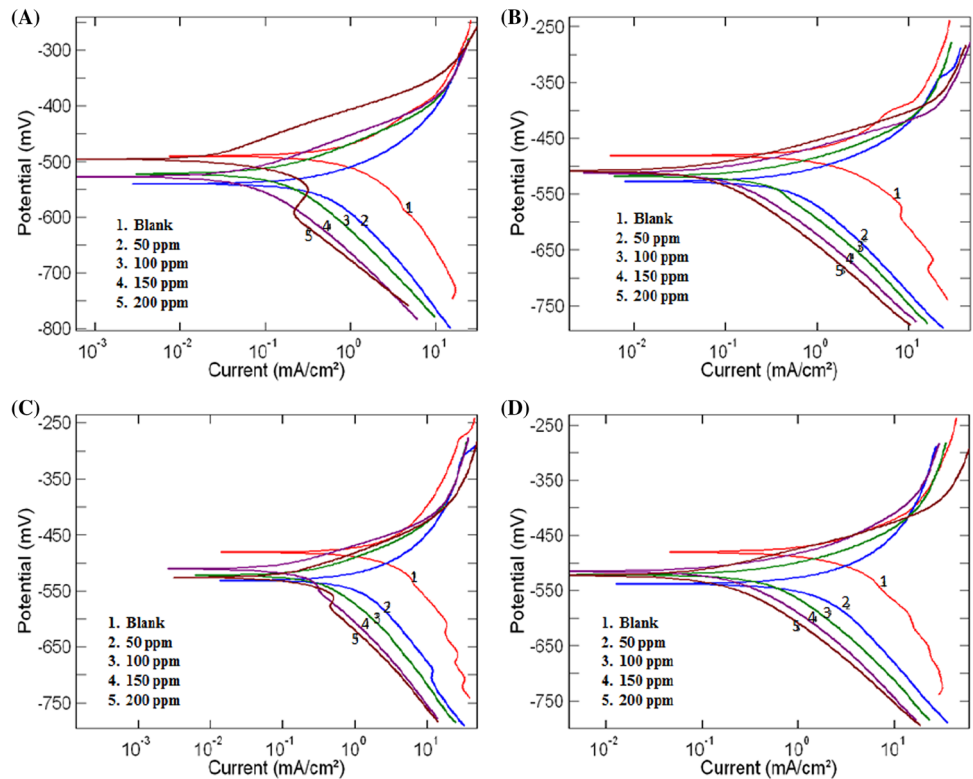


Table 3 Potentiodynamic polarization parameters for mild steel in 0.5 N HCl in the absence and presence of various concentrations of DHMMT at different temperatures

Temp. (K)	C_{inh} (ppm)	E_{corr} (mV)	β_a (mV)	β_c (mV)	i_{corr} (mA/cm ²)	C.R (mils/yr)	η (%)
303	0	-490	155	227	1.83	835.86	
	50	-520	69	142	0.18	83.91	90.16
	100	-525	64	129	0.08	40.43	95.62
	150	-524	66	101	0.05	23.21	97.26
	200	-528	60	60	0.01	7.99	99.45
308	0	-480	161	185	2.65	1210.40	
	50	-525	72	168	0.64	291.37	75.84
	100	-516	56	123	0.27	124.15	89.81
	150	-509	51	140	0.15	69.88	94.33
	200	-506	53	137	0.10	45.42	96.22
313	0	-481	189	178	3.58	1633.10	
	50	-533	100	176	1.52	695.20	57.54
	100	-524	72	132	0.49	222.90	86.31
	150	-510	52	140	0.23	105.12	93.57
	200	-524	51	117	0.15	70.21	95.81
318	0	-480	138	213	4.11	1876.20	
	50	-538	119	207	1.99	911.79	51.58
	100	-517	64	164	0.67	306.49	83.69
	150	-514	59	147	0.33	150.99	91.97
	200	-521	54	121	0.19	88.32	95.37

observed that the double layer capacitance (C_{dl}) is decreased by the addition of inhibitor to corrosive medium when compared to blank which confirms the formation of a protective film on metal surface [38].

3.4 Effect of Temperature

Study of temperature effect on inhibition efficiency has been carried out at four different temperatures both by

Fig. 5 Nyquist plots for corrosion of mild steel in 0.5 N HCl at various concentrations of DHMMT **a** 303 K **b** 308 K **c** 313 K and **d** 318 K

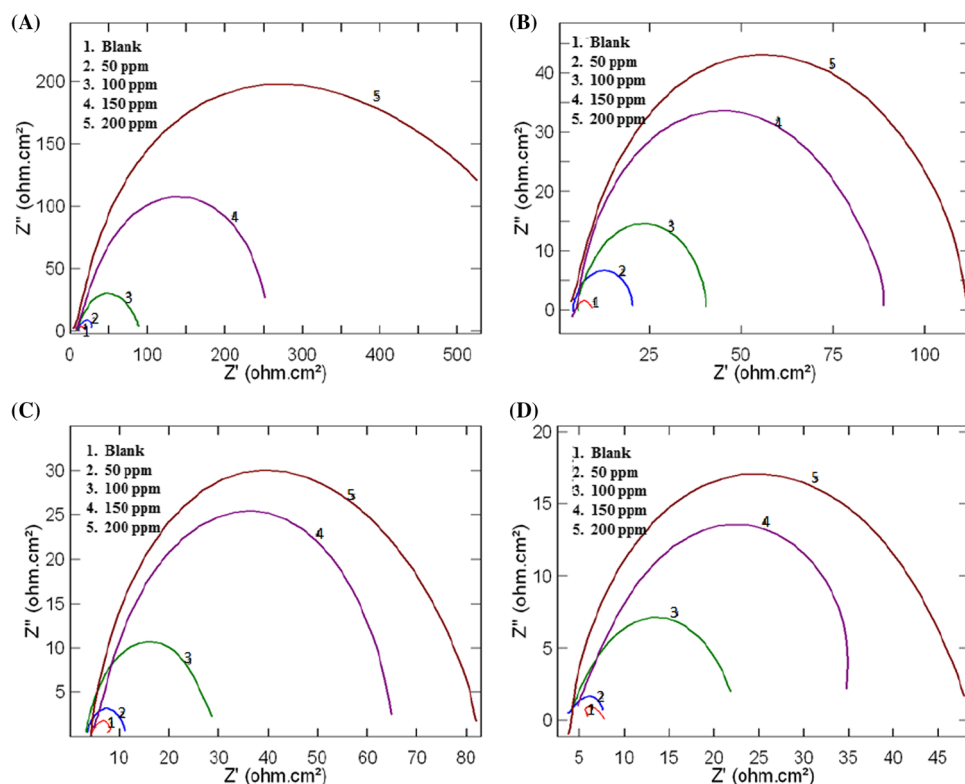


Table 4 Electrochemical impedance parameters for mild steel corrosion in 0.5 N HCl in the absence and presence of DHMMT at different temperatures

Temp. (K)	C_{inh} (ppm)	R_{ct} (Ohm cm^2)	C_{dl} ($\times 10^{-4}F$)	i_{corr} (mV/ cm^2)	C.R (mils/year)	η (%)
303	0	7.59	2.90	3.44	1567.00	
	50	78.06	0.88	0.33	152.50	90.27
	100	203.80	0.39	0.13	58.41	96.27
	150	271.40	0.36	0.10	43.86	97.20
	200	579.00	0.93	0.05	20.56	98.68
308	0	4.07	11.79	6.41	2923	
	50	17.45	2.84	1.49	682.10	76.67
	100	37.72	1.72	0.69	315.60	89.20
	150	84.94	0.88	0.31	140.10	95.24
	200	111.20	0.68	0.23	107.00	96.33
313	0	3.74	9.79	6.98	3184.00	
	50	8.75	5.20	2.98	1361.00	57.25
	100	26.77	2.09	0.97	444.70	86.02
	150	65.77	1.20	0.39	181.00	94.31
	200	82.58	1.20	0.32	144.10	95.47
318	0	2.29	29.21	11.38	5193.00	
	50	4.93	8.80	5.29	2413.00	53.54
	100	17.86	1.52	1.46	666.50	87.17
	150	35.44	1.21	0.74	335.90	93.53
	200	46.38	1.10	0.56	256.70	95.06

polarization and EIS studies. A graphical representation of results obtained is shown in Fig. 6. It is clear from the figure that calculated inhibition efficiency values are not

drastically affected by temperature as it shows 95% efficiency even at 318 K. The results showed that with rise in temperature, the values of i_{corr} increased both in inhibitor-

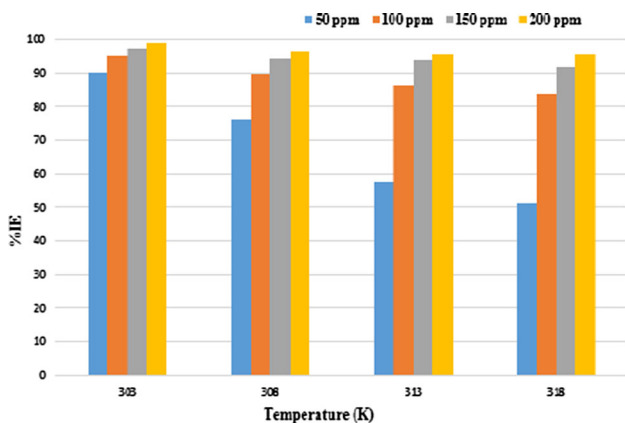


Fig. 6 Graphical representation of temperature effect on inhibition efficiency of DHMMT for corrosion of mild steel in 0.5 N HCl solution

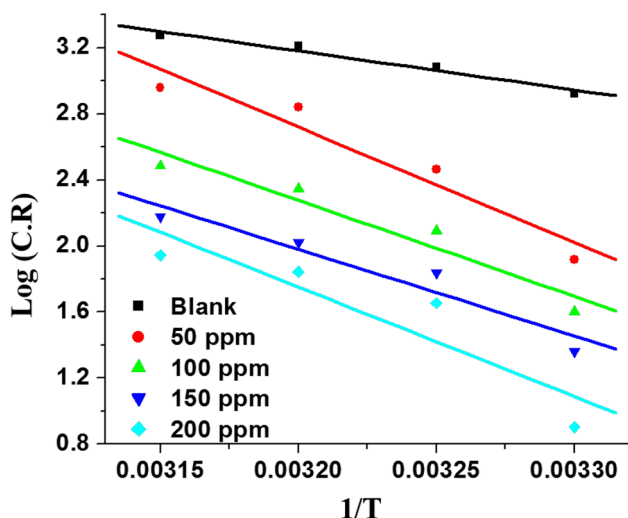


Fig. 7 Arrhenius plot of log (C.R) versus (1/T) for mild steel corrosion in 0.5 N HCl solution in the absence and presence of DHMMT

free and DHMMT added test solutions. The relation between temperature and corrosion rate is generally interpreted with Arrhenius equation,

$$\log(C.R) = \log A - \frac{E_a}{2.303RT} \tag{6}$$

where E_a is the activation energy value, A is pre-exponential factor, R is universal gas constant, and t is absolute temperature. For this purpose, i_{corr} values determined from polarization studies were utilized. From the slope of Arrhenius plot (Fig. 7), the activation energy values can be calculated and are listed in Table 5. From the table, it is revealed that the values of E_a in the presence of inhibitor are greater than that for uninhibited solution which indicates the formation of a high energy barrier against the

Table 5 Values of activation parameters for mild steel in 0.5 N HCl in the absence and presence of DHMMT

C_{inh} (ppm)	E_a (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
Blank	43.69	41.12	-53.38
50	128.9	126.29	209.89
100	106.99	104.47	131.70
150	96.75	94.18	93.14
200	123.06	120.6	173.09

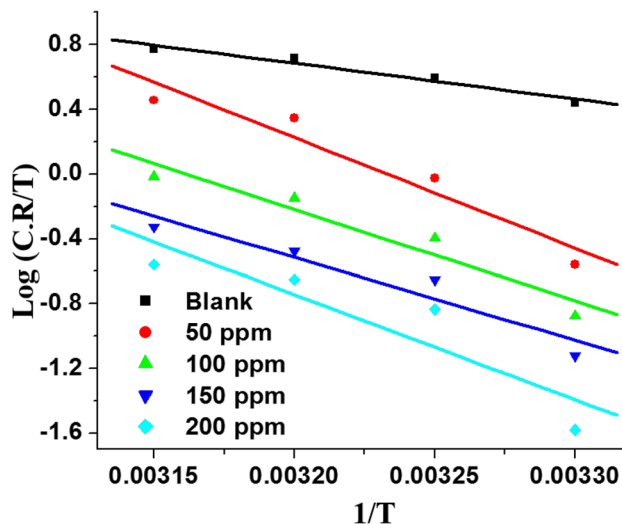


Fig. 8 Plot of log (C.R/T) against (1/T) for mild steel in 0.5 N HCl solution in the absence and presence of DHMMT

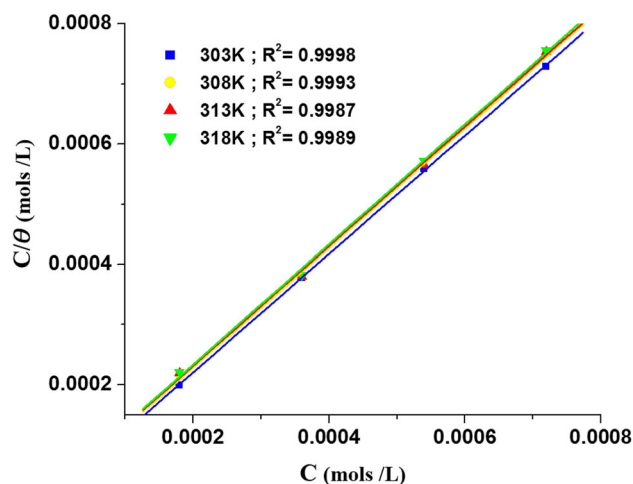


Fig. 9 Langmuir adsorption isotherm for mild steel corrosion in 0.5 N HCl solution containing different concentrations of DHMMT

corrosion process in the presence of inhibitor. The high energy barrier is formed by adsorbed layer of inhibitor molecules which then prevents mild steel surface from acid

Table 6 Values of equilibrium constant (K) and standard free energy change (ΔG) for mild steel in 0.5 N HCl in the presence of DHMMT

Temp. (K)	K (kmol ⁻¹)	ΔG (kJ/mol)
303	41.93	-36.93
308	31.89	-36.84
313	30.77	-37.35
318	29.41	-37.82

corrosion [39, 40]. For elucidating further details about the interaction of inhibitor on metal surface, thermodynamic parameters were employed. Experimental corrosion rate values in the absence and presence of inhibitor (polarization data) were used in the transition state equation to determine the enthalpy of activation (ΔH) and entropy of activation (ΔS) for the corrosion process. The transition state equation can be expressed as,

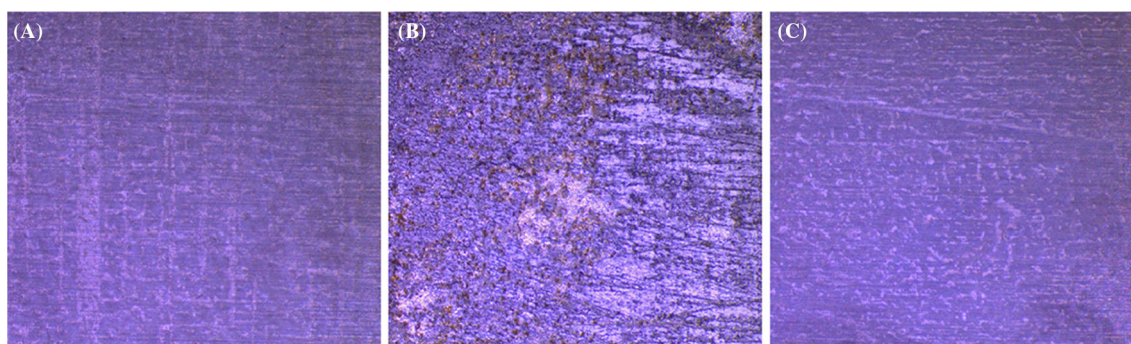
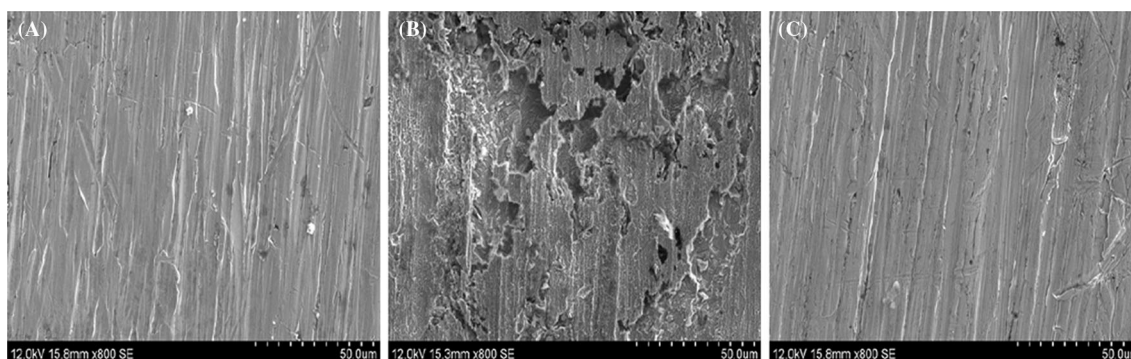
$$\text{C.R} = \frac{RT}{Nh} e^{\frac{\Delta S}{R}} e^{\frac{-\Delta H}{RT}} \quad (7)$$

where C.R is the corrosion rate, N is the Avogadro number, h is Plank's constant, R is molar gas constant, and T is absolute temperature. A plot of $\log(\text{C.R}/T)$ against $(1/T)$

was drawn (Fig. 8), and the values of ΔH and ΔS calculated from the slope ($-\Delta H/2.303R$) and intercept ($\log(R/Nh) + \Delta S/2.303R$) of the plot are listed in Table 5. The positive value of ΔH as listed in Table 5 specifies endothermic nature of mild steel dissolution process in 0.5 N HCl solution. Also increase in the value of ΔH in the presence of inhibitor when compared to blank indicates that mild steel dissolution is difficult in the presence of inhibitor [41]. The increased value of ΔS in the presence of inhibitor suggests increased disorder in the system due to adsorption of inhibitor on mild steel surface [42].

3.5 Adsorption Isotherm

Adsorption isotherm provides information on the interaction of organic compounds on metal surface. The surface coverage ($\theta = \eta (\%)/100$) at different concentrations of DHMMT in 0.5 N HCl was evaluated using data obtained from EIS studies and fitted for various adsorption isotherms. The validity of Langmuir adsorption isotherm was confirmed on the basis of linearity of C/θ versus C plot (Fig. 9) with very high correlation coefficient (>0.99). According to Langmuir adsorption isotherm, θ is related to concentration of inhibitor (C) as [43],

**Fig. 10** Stereomicroscopic images of **a** bare mild steel, **b** mild steel in 0.5 N HCl and **c** mild steel in 0.5 N HCl in the presence of DHMMT**Fig. 11** SEM images of **a** bare mild steel, **b** mild steel in 0.5 N HCl and **c** mild steel in 0.5 N HCl in the presence of DHMMT

$$\frac{\theta}{1-\theta} = KC \quad (8)$$

where K is the equilibrium constant, which is calculated from the reciprocal of the intercept of adsorption isotherm (Table 6). The higher values of K even at higher temperatures indicate that the adsorbed molecules could not be easily removed by solvent molecules from mild steel surface. The standard free energy of adsorption (ΔG) was calculated from the value of K by the relation,

$$\Delta G = -2.303RT \log(55.5K) \quad (9)$$

The value 55.5 represents the molar concentration of water in solution. The negative values of ΔG in Table 6 indicate spontaneity of adsorption process. It is established that the adsorption process is considered as chemisorption when the value of ΔG is around or less than -20 kJ/mol and it is considered as physisorption when value is around or higher than -40 kJ/mol. In fact, there is no strict boundary between physisorption and chemisorption. In the present investigation, the adsorption of DHMMT on mild steel involves mainly a chemical adsorption accompanied by physical adsorption since ΔG values range between -36 and -38 kJ/mol [44].

3.6 Surface Morphological Studies

The interaction of metals with corrosive environment particularly with regard to accumulation of corrosion products can be explained by surface morphological studies. Surface morphological images of mild steel samples obtained from stereomicroscopic technique and scanning electron microscopy (SEM) are shown in Figs. 10a–c and 11a–c, respectively. The rude surface of mild steel in uninhibited solution (Figs. 10b and 11b) shows that the sample is seriously damaged by aggressive medium. However in the presence of inhibitor (Figs. 10c and 11c), the surface has remarkably improved with respect to that in uninhibited solution indicating a considerable reduction in the corrosion rate. This improvement in surface morphology in the presence of inhibitor is due to the formation of protective film on surface which reduces the attack of acid on mild steel surface.

4 Conclusions

The inhibition performance of synthesized inhibitor DHMMT for mild steel corrosion in hydrochloric acid was evaluated, and following conclusions are obtained from the study,

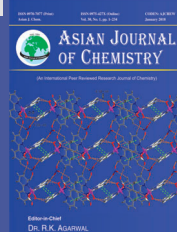
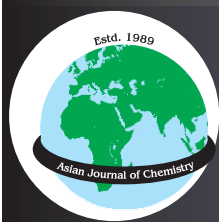
- DHMMT is an excellent inhibitor for mild steel corrosion in HCl solution.

- Inhibition efficiency increased with increase in inhibitor concentration but decreased with increase in immersion time, acid concentration and temperature.
- DHMMT was found to behave as a mixed type inhibitor.
- Adsorption process of DHMMT on mild steel surface obeys Langmuir adsorption isotherm.
- Values of thermodynamic parameters indicate endothermic nature of corrosion process.

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Reactions of Huisgen Zwitterions with Diphenyl Cyclopropanone: A Novel Strategy for the Synthesis of Oxazinone Derivatives

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A facile and novel route for the synthesis of diphenyl oxazinones in good yield was developed using diphenyl cyclopropanone and dialkyl azodicarboxylate with triphenyl phosphine as catalyst at room temperature and are well characterized using spectroscopic studies.

Keywords: Oxazinones, Diphenyl cyclopropanone, Dialkyl azodicarboxylate.

INTRODUCTION

In synthetic organic chemistry carbon hetero-atom and carbon carbon bond forming reactions are of prior importance. Generally polar and pericyclic reaction strategies are used for this which utilize reactive intermediates like carbanions, enols, radicals, carbenes, zwitterions, *etc.* Although potentially very useful, zwitterions have received less attention from this perspective. The present work is concerned with the use of a less well-known reactive intermediate *viz.*, zwitterion. Neutral nucleophiles like triphenyl phosphine, nucleophilic carbenes, and isocyanides can form zwitterionic intermediates with azodicarboxylates and activated acetylenes [1-4].

Although, phosphine-azoester zwitterion generally known as the Huisgen zwitterion [5], has been known in the literature for almost five decades, barring its use as nucleophilic trigger in the Mitsunobu reaction [6-8]. The chemistry of these powerful reactive intermediates remained largely unexplored. In recent years, our research group has explored the synthetic potential of these zwitterionic intermediates with a view to synthesize a variety of heterocycles [1,2] and uncovered the interesting reactivity patterns of the zwitterions generated from triphenyl phosphine and dialkyl azodicarboxylate. In continuation these studies, presently, we investigated the reactions of Huisgen zwitterions derived from triphenylphosphine-azodicarboxylate with diphenyl cyclopropanones leading to the formation of oxazinones. Cyclopropanones are an important class of compounds because of their application in a wide range of reactions such as decarbonylation, addition, oxidation, substitution reactions, *etc.* Further, the variety of reactions for such a simple

system as cyclopropanone has also led to the incorporation of phosphine azoester into the cyclopropanone system.

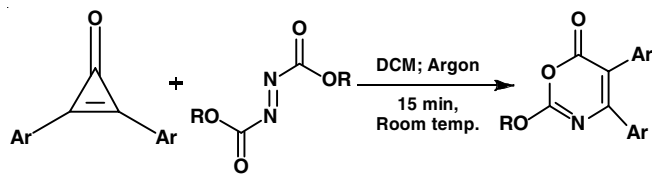
EXPERIMENTAL

¹H NMR spectra are recorded at 300 and 500 MHz, respectively and ¹³C spectrum at 125 MHz using Bruker Avance DPX-500 MHz NMR Spectrometer. Chemical shift values (δ) are reported with respect to TMS (¹H) and CDCl₃ (¹³C) as internal standards while coupling constant values (*J*) are reported in hertz (Hz). IR spectra are recorded with Bomem MB Series FT-IR spectrophotometer. Mass spectra are recorded with FAB/LRMS and EI/HRMS using JEOL mass spectrometer. Diethyl azodicarboxylate, diisopropyl azodicarboxylate and dibenzyl azodicarboxylate are purchased from Lancaster Chemical Co. and are used as such. Triphenylphosphine is purchased from Merck. Organic solvents are distilled before use. Thin layer chromatography is done using glass plates with silica gel coating having calcium sulfate as binder material. Column chromatography is performed with silica gel (100-200 mesh) using hexane-ethyl acetate mixture for elution.

Diphenyl cyclopropanone was prepared by employing known procedures [9]. 3,3'-Dinitrodiphenyl cyclopropanone and 3,3'-dibromodiphenyl cyclopropanone were obtained from diphenylcyclopropanone by aromatic electrophilic substitution reactions [10,11]. 4,4'-Dichlorodiphenyl cyclopropanones are prepared starting from their corresponding *para* substituted phenyl acetic acids [12].

General procedure for the synthesis of 2-alkoxy-4,5-diaryl-6H-1,3-oxazin-6-one: These were obtained from the reaction of the corresponding diaryl cyclopropanone (0.25 mmol) with

dialkyl azodicarboxylate (4 mmol) in dichloromethane (DCM) in the presence of triphenylphosphine (4 mmol) at room temperature for 15 min under argon atmosphere (**Scheme-I**). The product was isolated from the mixture with the help of column chromatography using hexane and ethyl acetate (95:5) as eluent. The reaction was found general for a number of diphenyl cyclopropenones prepared from dibenzyl ketones as shown in Table-1.



Scheme-I

TABLE-1
REACTIONS OF DIARYL CYCLOPROPENONES
WITH DIALKYL AZODICARBOXYLATES

Compound	Ar group	R group	Yield (%)
1	Phenyl	Isopropyl	63
2	Phenyl	Ethyl	68
3	Phenyl	Benzyl	65
4	<i>m</i> -Nitro phenyl	Isopropyl	56
5	<i>m</i> -Nitro phenyl	Ethyl	65
6	<i>p</i> -Chloro phenyl	Isopropyl	85
7	<i>p</i> -Chloro phenyl	Ethyl	75
8	<i>p</i> -Chloro phenyl	Benzyl	50
9	<i>m</i> -Bromo phenyl	Ethyl	75
10	<i>m</i> -Bromo phenyl	Isopropyl	70

Spectral data

2-Isopropoxy-4,5-diphenyl-6H-1,3-oxazin-6-one (1): White solid; IR (KBr, ν_{\max} , cm^{-1}): 1746, 1607, 1096 and 1295; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.17-7.27 (m, 10H), 5.37-5.39 (m, 1H, $J = 6$ Hz), 1.47-1.48 (d, 6H, $J = 6.5$ Hz); $^{13}\text{C NMR}$ (75.47 MHz, CDCl_3): δ 161.2, 160.3, 157.1, 136.5, 133.0, 130.8, 128.3, 127.8, 113, 74.7, 21.6 ppm. LRMS (+FAB) m/z calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_3$ (M+H) $^+$: 308.12; Found: 308.58.

2-Ethoxy-4,5-diphenyl-6H-1,3-oxazin-6-one (2): White solid; IR (KBr, ν_{\max} , cm^{-1}): 1754, 1614, 1319 and 1096; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.18-7.33 (m, 10H), 4.56-4.57 (q, 2H, $J = 7$ Hz), 1.47-1.5 (t, 3H, $J = 6.5$ Hz); $^{13}\text{C NMR}$ (75.47 MHz, CDCl_3): δ 161.11, 160.1, 157.5, 136.4, 132.9, 130.8, 130, 128.3, 127.9, 127.8, 66.3, 14.1 ppm. LRMS (+FAB) m/z calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_3$ (M+H) $^+$: 294.11; Found: 294.50.

2-(Benzyloxy)-4,5-diphenyl-6H-1,3-oxazin-6-one (3): White solid; IR (KBr, ν_{\max} , cm^{-1}): 1752, 1612, 1305 and 1115; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.17-7.47 (m, 15H), 5.51 (s, 2H); $^{13}\text{C NMR}$ (75.47 MHz, CDCl_3): δ 160.9, 160.0, 157.5, 136.3, 134.3, 132.8, 130.8, 130, 129.9, 129, 127.9, 113.5, 71.5 ppm. LRMS (+FAB) m/z calcd for $\text{C}_{23}\text{H}_{17}\text{NO}_3$ (M+H) $^+$: 356.12; Found: 356.67.

2-Isopropoxy-4,5-bis(4-chlorophenyl)-6H-1,3-oxazin-6-one (4): White solid; IR (KBr, ν_{\max} , cm^{-1}): 1759, 1608, 1091 and 1309; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.91-7.11 (m, 8H), 5.4-5.25 (m, 1H, $J = 6.3$ Hz), 1.46-1.450 (d, 6H, $J = 6.3$ Hz); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 160.3, 159.8, 157.3, 136.4, 134.6, 134.1, 1.32.1, 128.9, 128.3, 112, 21.59 ppm. LRMS (+FAB) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{NO}_3\text{Cl}_2$ (M+H) $^+$: 376.04; Found: 376.34.

2-Ethoxy-4,5-bis(4-chlorophenyl)-6H-1,3-oxazin-6-one (5): White solid; IR (KBr, ν_{\max} , cm^{-1}): 1753, 1611, 1311 and 1091; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.11-7.31 (m, 8H), 4.53-4.60 (q, 2H, $J = 7.5$ Hz), 1.47-1.5 (t, 3H, $J = 7.5$ Hz); $^{13}\text{C NMR}$ (75.47 MHz, CDCl_3): δ 159.7, 157.7, 136.5, 134.5, 134.2, 132.1, 131.2, 128.9, 128.4, 112.3, 66.6, 14.1 ppm. LRMS (+FAB) m/z calcd for $\text{C}_{18}\text{H}_{13}\text{NO}_3\text{Cl}_2$ (M+H) $^+$: 362.03; Found: 362.38.

2-(Benzyloxy)-4,5-bis(4-chlorophenyl)-6H-1,3-oxazin-6-one (6): White solid; IR (KBr, ν_{\max} , cm^{-1}): 1741 and 1611; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.41-7.10 (m, 13H), 5.50 (s, 2H); $^{13}\text{C NMR}$ (75.47 MHz, CDCl_3): δ 161.0, 160.1, 157.4, 136.3, 134.3, 132.8, 130.8, 130, 129.9, 129, 128.5, 127.9, 113.5, 71.5 ppm. LRMS (+FAB) m/z calcd for $\text{C}_{23}\text{H}_{15}\text{NO}_3\text{Cl}_2$ (M+H) $^+$: 425.28; Found: 425.69.

2-Isopropoxy-4,5-bis(3-nitrophenyl)-6H-1,3-oxazin-6-one (7): White solid; IR (KBr, ν_{\max} , cm^{-1}): 1759, 1609, 1096 and 1295; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.8-7.2 (m, 10H), 5.18-5.14 (m, 1H), 1.35 (d, 6H, $J = 6.5$ Hz); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 162, 150, 148, 147.9, 136, 129.7, 125, 120, 72.4, 21.6, 21.5 ppm. LRMS (+FAB) m/z calcd for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_5$ (M+H) $^+$: 397.09; Found: 397.5.

2-Ethoxy-4,5-bis(3-nitrophenyl)-6H-1,3-oxazin-6-one (8): White solid; IR (KBr, ν_{\max} , cm^{-1}): 1761, 1614, 1311 and 1091; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.64-7.15 (m, 8H), 4.2-4.02 (q, 2H, $J = 7$ Hz), 1.27-1.22 (t, 3H, $J = 7$ Hz); $^{13}\text{C NMR}$ (75.47 MHz, CDCl_3): δ 162.2, 133.1, 132.8, 132.3, 132.1, 129.8, 128.7, 128.6, 123.3, 61.2, 61.1, 14.7 ppm. LRMS (+FAB) m/z calcd for $\text{C}_{18}\text{H}_{13}\text{N}_3\text{O}_5$ (M+H) $^+$: 383.08; Found: 383.51.

2-(Isopropoxy)-4,5-bis(3-bromophenyl)-6H-1,3-oxazin-6-one (9): White solid; IR (KBr, ν_{\max} , cm^{-1}): 1759 and 1609; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.92-7.18 (m, 8H), 5.180-5.091 (m, 1H), 1.35 (d, 6H, $J = 6.5$ Hz); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 162.4, 150, 139, 131, 130, 125, 124.6, 120.6, 64, 23 ppm. LRMS (+FAB) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{NO}_3\text{Br}_2$ (M+H) $^+$: 462.94; Found: 462.85.

2-Ethoxy-4,5-bis(3-bromophenyl)-6H-1,3-oxazin-6-one (10): White solid; IR (KBr, ν_{\max} , cm^{-1}): 1759, 1609 and 1611; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.8-7.2 (m, 8H), 5.180-5.14 (m, 1H, $J = 6$ Hz), 1.35 (d, 6H, $J = 6.5$ Hz); $^{13}\text{C NMR}$ (75.47 MHz, CDCl_3): δ 162.4, 149, 139, 131, 125, 123, 120, 55.16 ppm. LRMS (+FAB) m/z calcd for $\text{C}_{18}\text{H}_{13}\text{NO}_3\text{Br}_2$ (M+H) $^+$: 448.93; Found: 448.34.

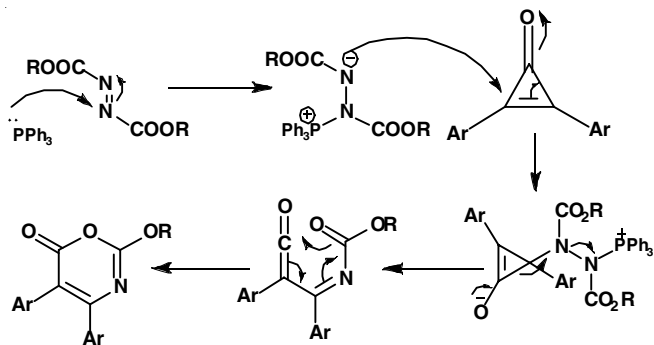
RESULTS AND DISCUSSION

Despite their potential utility, zwitterions are rarely used in synthetic organic chemistry when compared with other reactive intermediates. However, we have employed the utility of Huisgen zwitterion for the synthesis of various oxazinones (**1-10**).

The mechanism of the reaction is explained by the nucleophilic attack of Huisgen zwitterion on cyclopropenone followed by internal cyclization to yield corresponding oxazinone (**Scheme-II**).

Conclusion

We have unravelled a facile and novel route for the synthesis of oxazinones and successfully employed it for a series of diaryl cyclopropenones with various dialkyl azodicarboxylates. It is

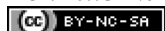


Scheme-II

noteworthy that the reactivity of cyclopropenones, the ambident electrophiles, towards Huisgen zwitterions is explored for the first time. It may also be mentioned that oxazinones are important compounds since many of them are reported to possess antimicrobial and antifungal activities [13,14].

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In vitro conservation and propagation of the endemic species of “floating hearts” (*Nymphoides krishnakesara* Joseph and Sivar. - Menyanthaceae) as a conservation strategy

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ABSTRACT

Nymphoides krishnakesara Joseph and Sivar. (Menyanthaceae), an endangered aquatic angiosperm, endemic to Kerala, was multiplied and propagated through *in vitro* culture. It is a rare species with very restricted distribution occurring in a single location. It is an annual herb, grows in shallow temporary pools on laterite. The nodal explants when cultured in Murashige and Skoog (MS) medium attained bud break in 20 days. Maximum multiple shoot proliferation observed in 1.0 mg/L benzyl amino purine (80 shoots/explant). Shoots developed *in vitro* were rooted in MS medium with both indole 3-butyric acid (IBA) (1.0 mg/L) and naphthalene acetic acid (mg/L). Roots developed in IBA are found to be more favorable based on the histological studies. The rooted plantlets were then transferred to the field after hardening and they flowered after 2 months. Total time taken from explants to flowering is 10 months. This work standardizes an easy protocol for mass production of plantlets, and thus enhances conservation of this endemic and rare aquatic plant. The hardened plants were successfully reintroduced and recorded 100% survival.

1. INTRODUCTION

India is rich in its aquatic flora, of which majority comprises from South India. Among the aquatic plant diversity *Nymphoides* Seg. is an interesting genus of about 20 spp. [1], widely distributed in the tropical and temperate regions of both the Old World and the New World. *Nymphoides krishnakesara*, an endemic emergent herb found in shallow waters of seasonal ponds of lateritic hills, is an interesting dioecious plant [2]. *N. krishnakesara* was originally reported from Madayipara, a midland lateritic hill in Kannur District, Kerala, South India [2]. Habitat of the species is threatened due to environmental modifications and urbanization. Its occurrence in a single location made this plant endemic to Northern Kerala and also included in the IUCN Red list of threatened species version 2011 [3]. The plant being dioecious and unavailability of male and female plants in the same location restricts the natural propagation through seeds. In traditional folklore medicine, the flowers and roots of this plant are used as a febrifuge [4].

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The genus can be easily distinguished from the similar looking water lilies (*Nymphaea* spp.) by its petiole-like uniphyllous sympodial branches bearing a cluster of flowers at the nodal region. Only few works were undertaken on the micropropagation of *Nymphoides* spp. The genus *Nymphoides* is a less exploited one. A protocol for rapid shoot organogenesis from petiole explants of the ornamental aquatic plant *Nymphoides indica* L. [5] and indirect regeneration of *Nymphoides cristatum* floral buds [6,7] are some works on the genus. The application of tissue culture as a tool for the conservation of rare and endangered plants has gained huge trust in the recent decades. The present study was undertaken to formulate a standard protocol for micropropagation of the endangered and endemic species *N. krishnakesara* Joseph and Sivar. and its introduction to the field, thereby helping habitat restoration.

2. MATERIALS AND METHODS

2.1. Bud Break and Proliferation

A healthy growing plant in the Aquagene (Aquatic Plant Conservatory of Malabar Botanical Garden and Institute for Plant Sciences) introduced from the original locality is used as the explant source. Nodal cuttings from fresh sprouts (3rd and 4th leaf) were used as explants [Figure 1a]. The leaves were collected, washed in running water for 25 min and the nodal region was separated and treated with Tween 20 (2–3 drops in 1 L distilled water) for 15 min followed by washing with double distilled

water 3–5 times. Surface sterilization of explants was done with 0.1% (w/v) HgCl_2 for 2–3 min and washed thrice with sterile double distilled water before inoculation inside the laminar air flow chamber. The nodal segments were trimmed into two equal vertical halves of about 1 cm long aseptically and used directly as the explant. The surface sterilized explants were inoculated in Murashige and Skoog (MS) basal medium [8] and MS medium with combinations of auxins (indole 3-butyric acid [IBA]*, naphthalene acetic acid [NAA]**) and cytokinins (benzyl aminopurine [BAP]***) were tried for shoot or root induction. Once shoot formation was noticed, they were subcultured in the rooting medium with auxin after the formation of roots and they were transferred to basal MS medium containing low concentration (4.5 mg/L) of agar. After 2–3 weeks, the fully developed plants were transferred to pots with sterile clay and kept in the greenhouse for hardening.

The media used were fortified with 3% sucrose and the pH adjusted to 5.8, before the addition of agar and followed by autoclaving at 121°C for 20 min. The cultures were maintained at $25 \pm 1^\circ\text{C}$ with 70% relative humidity and a photoperiod of 12/12 h $35\text{--}40 \mu\text{mol m}^{-2} \text{s}^{-1}$ irradiance provided by cool white fluorescent tubes.

2.2. Anatomical Studies

The roots developed *in vitro* were investigated anatomically. Hand sections of root formed in medium supplemented with 0.5 mg/L IBA and 0.5 mg/L NAA were taken, stained with 1% safranin and observed under microscope and photographed.

3. RESULTS AND DISCUSSION

3.1. Establishment of Explants and Bud Initiation

The nodal segments inoculated on basal MS medium showed bud break after 20 days. After the bud break, direct regeneration of a single shoot was noticed on the 30th day of inoculation in MS medium without any PGR [Figure 1b]. Once the regeneration is noticed, they were transferred to the multiplication medium. Different concentrations (0.25–1.0 mg/L) [Figures 2 and 3] of cytokinins (BAP) were tried for shoot proliferation. Highest shooting percentage (90%) with maximum shoot proliferation (80 shoots/explant) is attained in medium supplemented with 1.0 mg/L BAP [Figure 1c]. 0.25 and 0.5 mg/L BAP gives 20 and 50 shoots/explant and 60% and 80% of shooting response, respectively. Initially, the concentration of agar used was 6.5 g/L in which the *in vitro* shoot development showed stunted growth with brittle leaves [Figure 1d]. A combination of BAP and IBA both 0.5 mg/L showed rhizogenesis after 10 days along with multiple shoots where the shooting percentage noticed was the same as that of 0.5 mg/L fortified medium.

3.2. Effect of Auxin in the Development of Roots

The *in vitro* regenerated shoots were excised and transferred to rooting medium with different concentrations (0.5 and 1.0 mg/L) [Table 1] of auxins (IBA and NAA). Both IBA and NAA were found to be effective in rhizogenesis. *In vitro* developed shoots when subcultured in a medium with 0.5 mg/L NAA showed rhizogenesis after 5 days of inoculation [Figure 1e] with an average of 14 roots while that of media fortified with 0.5 mg/L of IBA produced roots after 1 week [Figure 1f] with an average of five roots. The average number of roots were high in NAA and the number showed a considerable increase when the concentration of NAA was raised to 1 mg/L. There was no callus formation at the base, and hence, the rhizogenesis is direct. Highest rooting percentage was noticed in medium fortified with 1.0 mg/L NAA with an average of 24 roots.

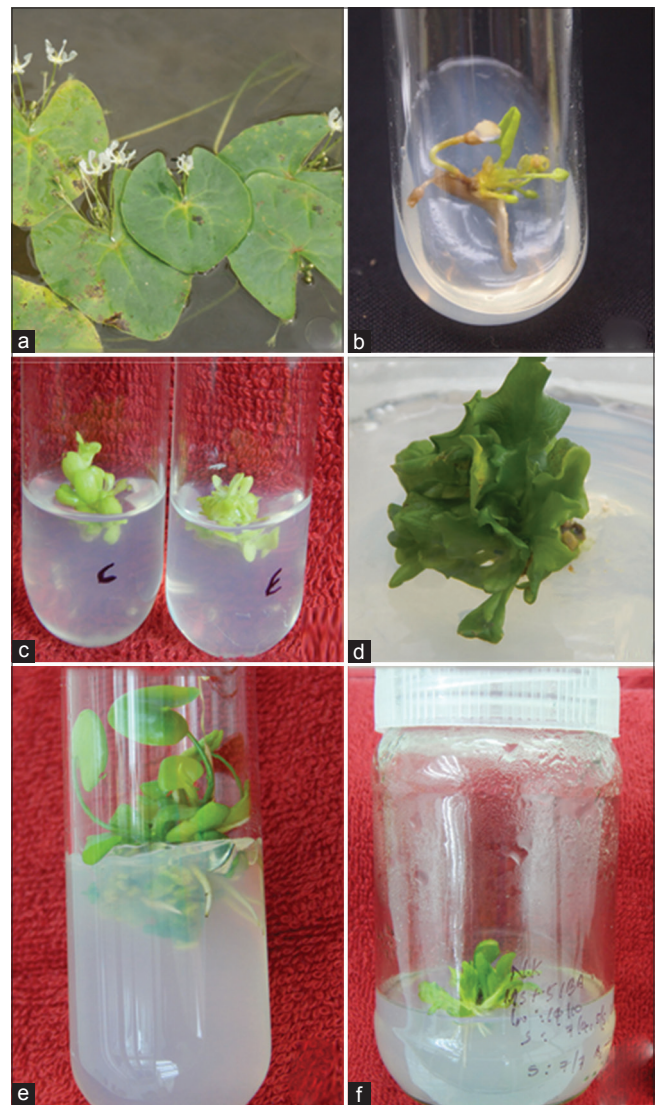


Figure 1: (a) Habit, (b) direct organogenesis, (c) multiple shoot formation in 1mg/L benzyl amino purine, (d) short and brittle leaves in 6.5 mg/L Agar, (e) induction of roots in 0.5 mg/L Naphthalene acetic acid. (f) induction of roots in 0.5 mg/L Indole 3- butyric acid.

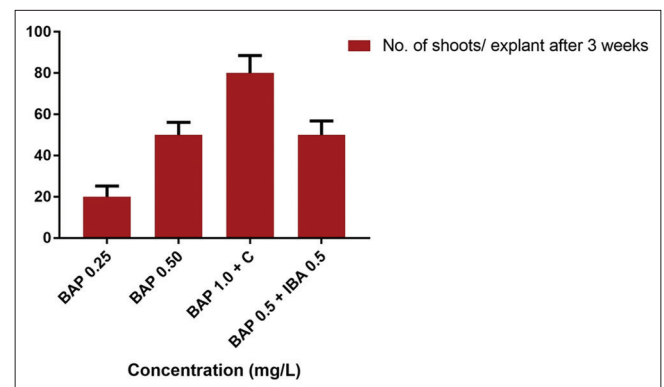


Figure 2: The number of shoots in different concentration of benzyl aminopurine.

Table 1: Effect of different concentration of auxins promoted rooting of the plant.

Hormone	Concentration	Root induction (%)	Rooting in number of days	Number of roots
IBA	0.5	80	7	5
	1.0	80	7	10
NAA	0.5	70	5	14
	1.0	80	7	24

IBA: Indole 3-butyric acid, NAA: Naphthalene acetic acid.

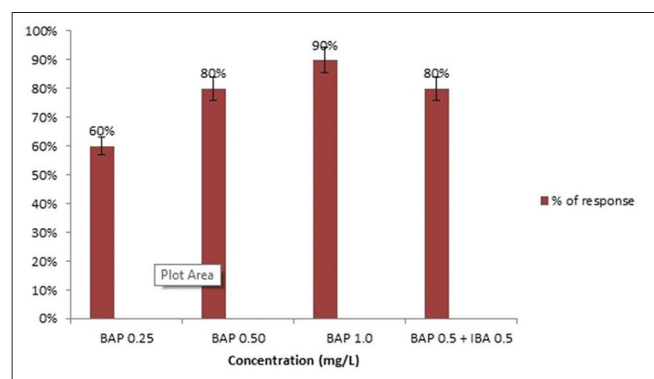


Figure 3: Percentage response of shoot formation in different concentration of benzyl aminopurine.

The roots formed in NAA were soft, spongy, and numerous while the roots formed in IBA were strong with lateral roots. Once the roots were formed, they were transferred to medium with low concentration of agar (4.5 g/L) for the better absorption and root development [Figure 4a and b]. In this concentration of agar, the normal leaf with long petiole, which helps the lamina to float on the water surface, was developed. Among the plants developed *in vitro*, those developed roots in medium containing IBA showed better establishment under field conditions.

3.3. Acclimatization of Plantlets Developed *In Vitro*

For the hardening process, the individual plantlets were separated from the medium and cleaned with sterile water to get rid of the excess agar [Figure 4d]. The plants were first transferred to sterilized tap water and kept in culture conditions [Figure 4c]. After 2 weeks, they were planted in cups with sterile clay with 1 cm deep water and kept in the greenhouse [Figure 4e].

The plants developed *in vitro* flowered within 2 months of introduction to the field [Figure 4f]. Of these, the plants rooted in medium with IBA showed better development in the field conditions, and initially, these were smaller in size than the normal ones.

3.4. Histological Studies

In histology, the root developed in NAA has more number of aerenchyma (air spaces) in the cortical region than that of the roots developed in the medium with IBA [Figure 4h and i]. The C.S. of the control root also showed a lesser number of aerenchyma [Figure 4g] indicating that lesser number of aerenchyma favored better establishment of roots in field conditions.

4. DISCUSSION

The aquatic systems in Kerala currently face a serious threat of extinction due to rapid urbanization and industrialization. Developmental initiatives by filling wetlands have seriously affected

the rich aquatic biodiversity of Kerala which include several endemic and endangered species, many of which are reported from transient pools developed on the laterite hills of midland region during the rainy seasons but become dry during the summer season. *N. krishnakesara* is reported from such a unique habitat which survives the summer drought through dormant shoots and regenerates during next monsoon with vigor. Since the plant is a dioecious one, seeds develop only when both the male and female plant exists in the same region. This taxon is highly endemic and reported from only one locality in the Northern Kerala.

Only few works were undertaken on the micropropagation of aquatic plants. Of these, major works were on the micropropagation of medicinal plants such as *Bacopa monnieri* [9,10] and *Acorus calamus* [11,12]. For *in vitro* clonal propagation, the common explants used are the nodal segments. In the present study also, the explant selected was the nodal region, from where direct organogenesis is achieved, similar result was obtained in *N. indica* [5] also, while floral buds of *N. cristatum* produced friable callus from which organogenesis was achieved [6,7]. In this study, even though growth regulator-free MS medium was able to induce bud break and shoot formation, the number of shoots formed from single explant was found to be less in number. BAP was the single cytokinin used for the multiple shoot formation. Several reports point out the capacity of BAP for bud proliferation and multiple shoot formation in many plants such as *B. monnieri* [12] and *Avicennia marina* [13]. Averages of 80 shoots were obtained from 2-week-old cultures in medium with 1.0 mg/L BAP while 60 shoots were obtained from per piece in 50 days of culture in *Passiflora caerulea* L. [14].

Two auxins (IBA and NAA) were tried for the root induction, both showed favorable results. It is reported earlier that the auxins at lower concentration facilitate better root formation [15]. Even though the time taken for rhizogenesis in MS medium with NAA was less and produced more roots, the roots produced in IBA were strong both in morphological and anatomical studies. Similarly, the increase in the rooting percentage and the better rooting in the medium containing IBA were reported in *Alnus glutinosa* [16]. Earlier reports indicate that NAA also induces callus tissue; hence, establishment of plants in the field is hindered by the interfering callus tissue [17,18].

The institute has undertaken several studies on different aspects of the aquatic vegetation of South India with a view to develop a comprehensive conservation protocol for aquatic and wetland plants of the country. The study also involves micropropagation of aquatic plants of rare, endangered, and threatened category through *in vitro* cloning. The present study facilitates an easy protocol for the production of rooted multiple shoots up to 80 from a single explant in basal MS medium supplemented with 1.0 mg/L BAP. It is therefore established that the most reliable way for rapid clonal propagation of *N. krishnakesara* is through direct organogenesis.

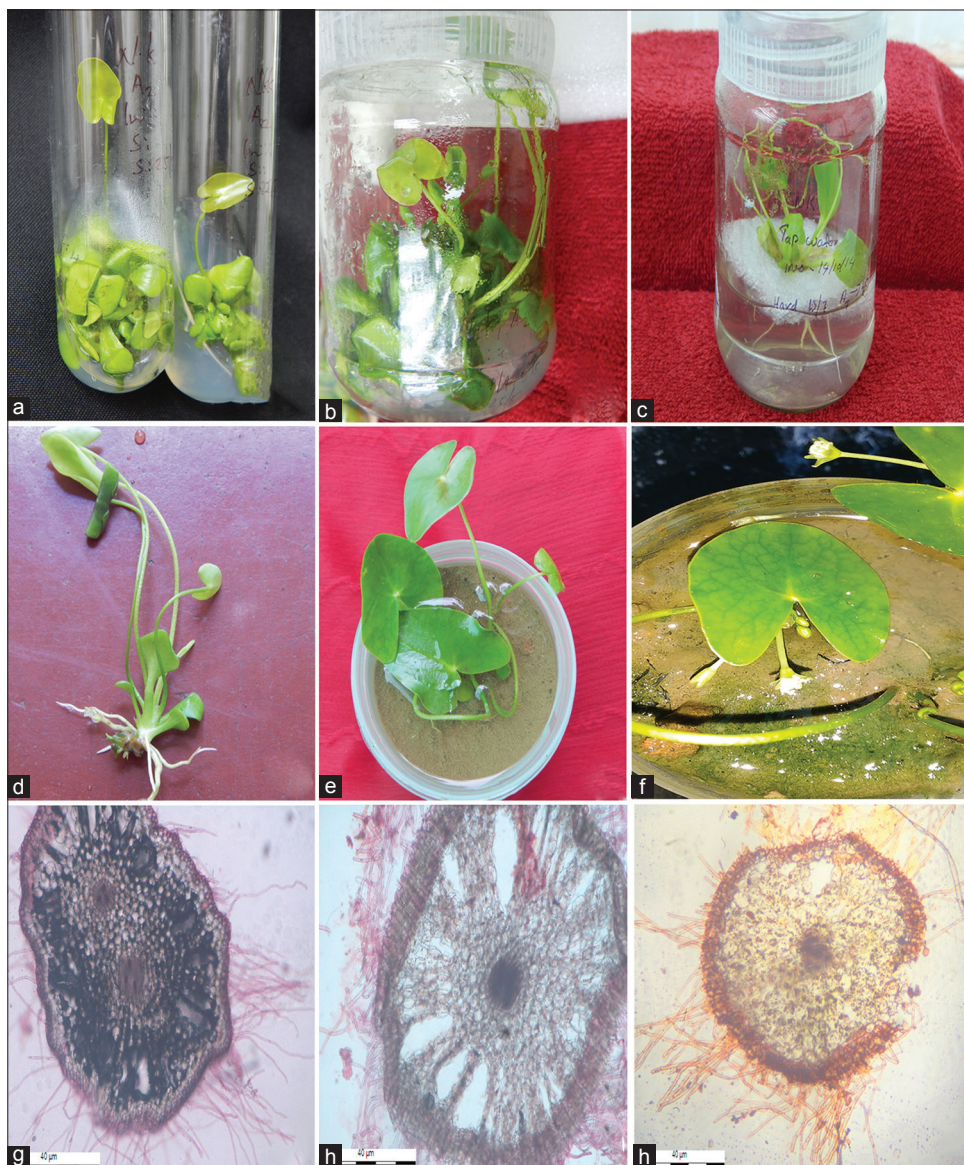


Figure 4: (a and b) Normal leaves in 4.5 mg/L agar, (c) hardening in tap water, (d) plantlet before planting, (e) plant in greenhouse for hardening, (f) flowering in field, (g) C. S. of control root, (h) C. S. of root in Naphthalene acetic acid and (i) C. S. of root in Indole 3- butyric acid showing lesser number of air chambers.

5. CONCLUSION

In the present situation, there is a great need for the conservation of aquatic plants since the rapid urbanization has led to the loss of our valuable aquatic and wetland habitats. In this context, the present study suggesting a simple protocol for micropropagation of rare and endemic aquatic plants owes its importance. This study is the first attempt on the micropropagation and the successful field establishment of the endemic plant *N. krishnakesara* Joseph and Sivar.

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