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VOLUME 16 ISSUE 3 VERSION 1.0

# Global Journal of Science Frontier Research: B

## Chemistry

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## CHEMISTRY

VOLUME 16 ISSUE 3 (VER. 1.0)

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# Synthesis and Applications of Isocyanate Free Polyurethane Materials

By Mehdi Erfani Jazi, Thualfeqar Al-Mohanna & Fatemeh Aghabozorgi

*University of Kashan*

*Abstract-* The manufacture of conventional polyurethanes include the use of isocyanates, which in turn require using toxic and hazardous phosgene. The safety devices are necessary to prepare these monomers. Therefore, the huge investment is inevitable for this process. Also, these monomers cannot be considered as environmentally friendly chemicals. The increasing global awareness for protection of environment from chemical pollutants has created a necessary demand for environmentally benign products. The reaction of cyclic carbonates (polycarbonates) with amines results in formation of hydroxyurethanes that can be taken into account as a unique reaction. This specific reaction has been investigated over last few years. Most chemists have been strongly attracted by this technique that is due to its potential application to prepare the green, non-toxic, non-sensitive towards moisture isocyanate free polyurethanes.

*Keywords: isocyanate free polyurethane, synthesis, mechanism, application.*

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# Synthesis and Applications of Isocyanate Free Polyurethane Materials

Mehdi Erfani Jazi [α], Thualfeqar Al-Mohanna [σ] & Fatemeh Aghabozorgi [ρ]

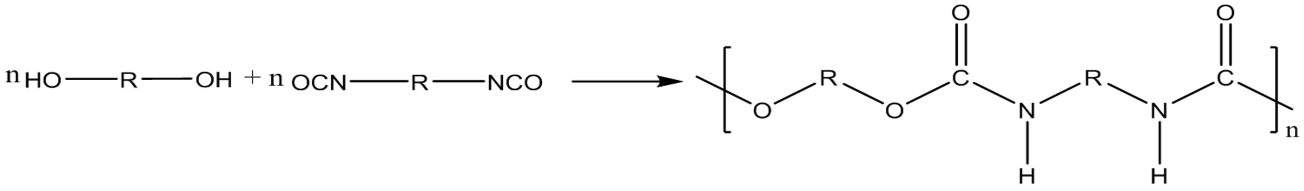
*Abstract-* The manufacture of conventional polyurethanes include the use of isocyanates, which in turn require using toxic and hazardous phosgene. The safety devices are necessary to prepare these monomers. Therefore, the huge investment is inevitable for this process. Also, these monomers cannot be considered as environmentally friendly chemicals. The increasing global awareness for protection of environment from chemical pollutants has created a necessary demand for environmentally benign products. The reaction of cyclic carbonates (polycarbonates) with amines results in formation of hydroxyurethanes that can be taken into account as a unique reaction. This specific reaction has been investigated over last few years. Most chemists have been strongly attracted by this technique that is due to its potential application to prepare the green, non-toxic, non-sensitive towards moisture isocyanate free polyurethanes. This review is focused on the variety of catalysts used to prepare isocyanate free polyurethanes from five membered cyclic polycarbonates. Also, the reaction mechanism and kinetics for their synthesis have been discussed. In this review, the six-membered cyclic carbonates depicted the higher reactivity rather than five-membered cyclic carbonates for production of non-isocyanate polyurethanes. The various functions of isocyanate free polyurethanes in different fields such as coatings, construction and bio-composites have been summarized.

*Keywords: isocyanate free polyurethane, synthesis, mechanism, application.*

## I. INTRODUCTION

The polymer materials based on polyurethane segments have attracted a considerable attention in both academic and industrial fields that is due to the versatile features of polyurethane like its high elasticity, thermal and chemical stability, resistant toward abrasion and other excellent properties. These outstanding properties create polyurethane materials asa suitable candidate which can be used in the coating industry[1]. The worldwide utilization of coatings in the various applications in the industry has been successfully attained. There has been a continuous development on synthesis of polyurethane coatings based on bio-materials to remove the health and environmental hazards. These bio-based polymers should have the high performance capabilities in the coatings industry[1].

The utilization of polyurethane compounds which are based on isocyanate chemistry(Scheme 1) has been considerably enhanced in comparison to other polymer materials. The polyurethane materials have distinguished properties but they suffer from some serious issues[2]. The isocyanate based-materials are toxic because they have been synthesized from toxic starting material called phosgene which jeopardizes both environment and human' life[3].Also, polyurethane based-isocyanate materials are sensitive towards moisture and when they are exposed to the environment, an irreversible reaction between isocyanate and water would occur, producing the urea and carbon dioxide which results a useless product (Scheme 2)[2b, 4]. The other negative aspect of conventional polyurethanes is an intrinsic weakness in the hydrolytic bonds of molecules which cause them to be degraded gradually in the environmental conditions. Therefore, the chemical resistance of polyurethane polymers is poor in the environment and it can create a grave challenge for their use in the long period of time[4].



*Scheme 1 :* Reaction between diols and isocyanates to form linear polyurethanes

$$R—NCO + H_2O \longrightarrow R—NH—COOH \longrightarrow RNH_2 + CO_2$$

*Scheme 2 :* Hydrolysis of isocyanate in the environment

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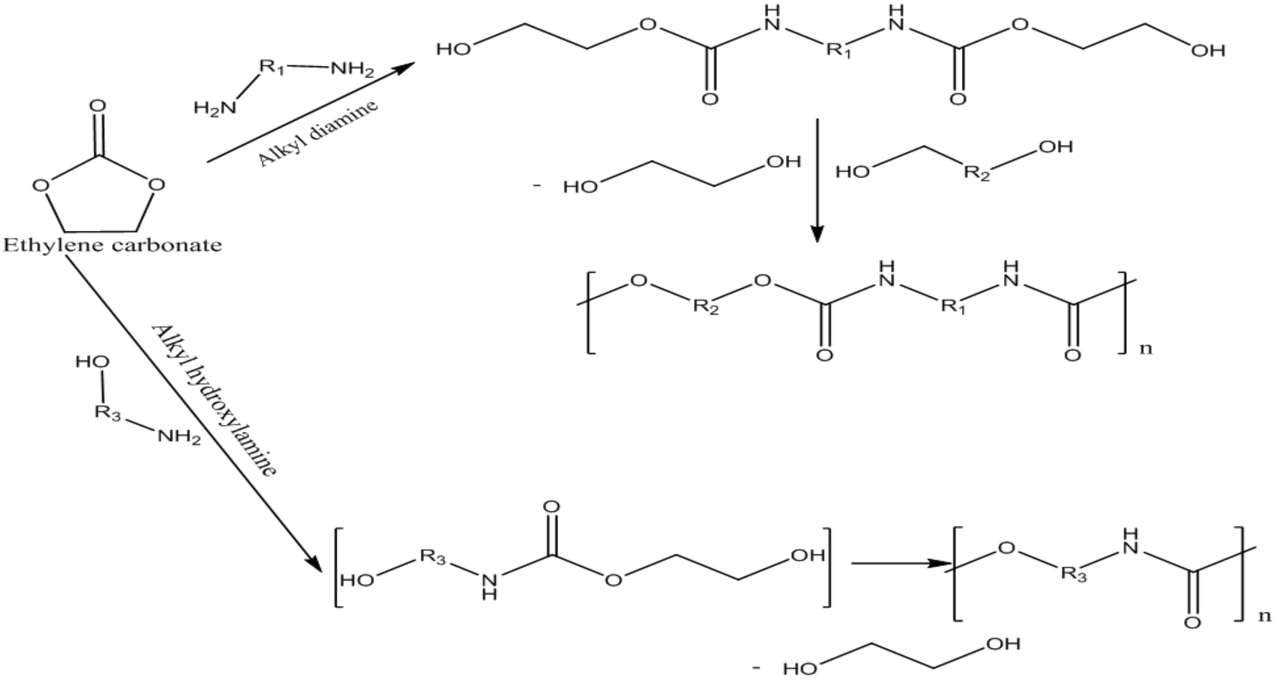
*a) Isocyante free polyurethanes*

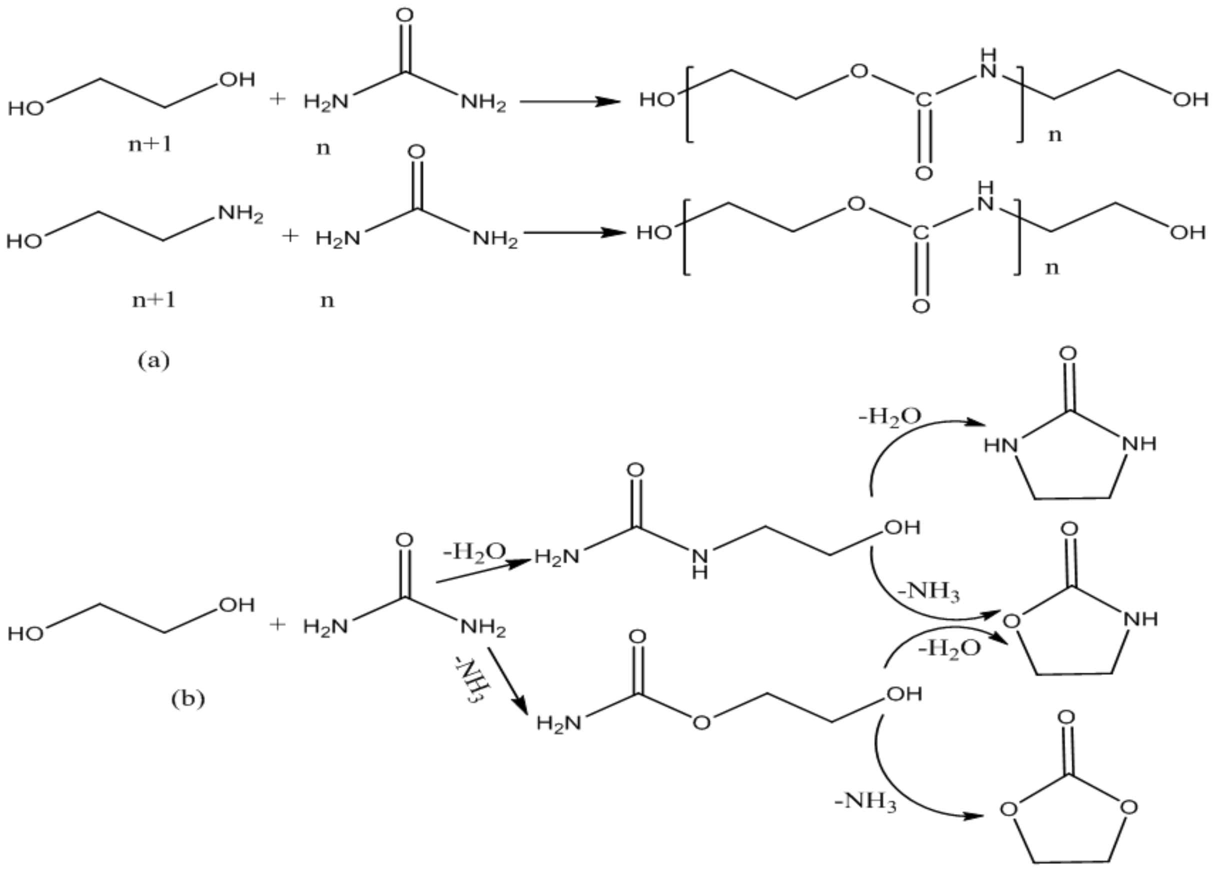
The first use of ethylene carbonate and amines for synthesis and preparation of polymeric polyurethanes has been reported by Dyer and Scott [5]. The ethylene carbonate and primary diamines react with each other to form bis(2-hydroxyethyl carbonate) with release of ethylene glycol as a byproduct under vacuum conditions at 150°C. The catalyst used for this reaction was zinc borate or barium oxide (scheme 3). Also, the preparation of substituted polyurethanes has been achieved by reaction between amino alcohols such as 1,10 aminodecanol or 4-aminomethylbenzyl alcohol and ethylene carbonates through formation of intermediate compounds. In addition, the bis(2-hydroxyethyl carbamate) can be obtained via the transurethanization reaction of ethylene carbonate and 1,4-diaminobutane or 1,6-diaminohexane a long with formation of 1,6-hexanediol or 1,10-decanediol as side products. This reaction is accelerated in presence of tin catalyst [6]. The polyurethane characterization shows both urethanes and urea groups in those products[7].



*Scheme 3 :* Synthesis of polyhydroxyurethane materials from cyclic carbonates

Another strategy for synthesis of the polyurethanes compounds is reaction between urea and ethyl alcohol. This method is called transesterification reaction because it is similar to the mechanism of transesterification of alcohol with carboxylic acid. The diol organic compounds containing urethane and biureate linkages have been prepared and synthesized based on this strategy[8]. The polyurethane prepolymermaterials contain isocyanate functional groups which are used as the chain extenders that can form urethane bonds in the backbone structure. Basically the diol organic materials obtained from transesterification of urea and ethyl alcohol are employed as the curing agents in the conventional method of polyurethanesynthesis[8a, 9].

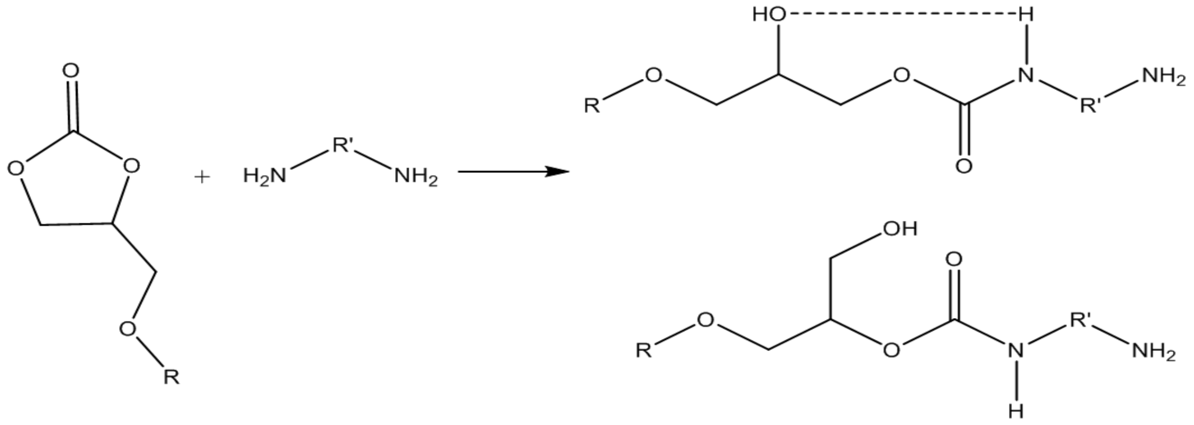
Furthermore, several efforts had been performed to synthesize diols organic compounds using urea and monoethanolamine(or urea and ethylene glycol) which can produce the highly viscous diol organic materials. These materials can be used as the cross linking materials which have a capability to react with diisocyantes and melamine formaldehyde in order to produce the rigid and flexible coatings (Scheme 4a)[10]. Consequently, the production of coatings which have similar properties to urethane materials either without any utilization of diisosyanates or a limited use of diisocyanateshas remarkably reduced the consumption of toxic diisocyanates. Nevertheless, these reactions can produce the undesirable byproducts such as ethylene glycol, carbamates and etc (Scheme 4b) [6, 11].



*Scheme 4 (a) :* Preparation of polyhydroxyurethanes from ethylene glycol or ethanolamine with urea. (b) Formation of side products from reaction of ethylene glycol and urea.

The traditional production of hydroxyurethane is the reaction between cyclic carbonate and amine that can be seen as the best alternative method to produce non-isocyanate polyurethane materials [12]. Particularly, the hydroxyurethane materials are formed through the reaction of five or six membered cyclic carbonates with the materials containing-amine functional groups. The products of this reaction show two isomers which contain both urethane and hydroxyl groups. The main feature of poly(hyroxyurethane) compoundsis presence of hydroxyl groups which have a considerable capability to form intramolecular hydrogen bonds with urethane functions in the backbone structure of polymer (Scheme 5) [2a, 13].

Consequently, the formation of hydrogen bonds between alcohol and urethane functional groups decreases the susceptibility of polyurethanes towards moistureabsorption and deterioration by abrasion that leads to the remarkable enhancement in chemical and thermal stability of polyhydroxyurethanes[13-14].



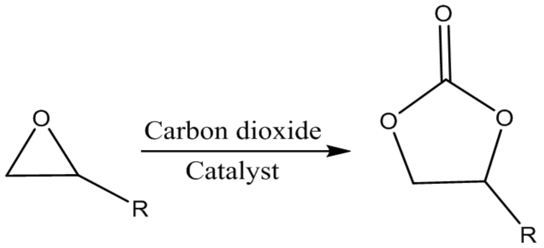
*Scheme 5 :* Reaction of diamine with substituted cyclic carbonate and formation intermolecular hydrogen bonds

Therefore, the thermal properties of polymers are influenced by hydroxyl functional groups. The compounds with intramolecular hydrogen bonds display the excellent chemical resistance towards the similar compounds without such intramolecular hydrogen bonds [15]. Furthermore, the process of the isocyanate-free polyurethane synthesis is not sensitive to the moisture and thus the coating application of isocyanate-free polyurethane is much better than that of conventional polyurethane compounds [7].

Moreover, there are strict environmental regulations and therefore the application of more environmentally benign procedures to prepare non-hazardous polymer compounds is unavoidable. There has been a limited research for the exploration of new strategies such as utilization of cyclic carbonates materials containing amine functional groups to prepare the high value added polymers. Thus, the utilization of cyclic carbonates, which are produced from the incorporation of carbon dioxide into epoxides, should be considered as an environmental advantage because the carbon dioxide consumption leads to a reduction in the amount of greenhouse gases[16].The basic preparation and synthesis of isocyanate-free polyurethane compounds is based on the reaction of cyclic carbonates with amines or polyamines[17].

## II. The Synthesis of Cyclic Carbonates

Basically the cyclic carbonates are starting materials for synthesis of isocyanate-free polyurethanes and there is a variety of methods for preparation of cyclic carbonates. In particular, the main and cost effective method is the incorporation of carbon dioxide into the epoxy rings because the epoxy compounds are easily reacted with carbon dioxide in presence of catalyst at a high temperature to produce cyclic carbonate materials (Scheme 6). Therefore, the cyclic carbonate can be used as a precursor to react with the various amine functional groups to produce different types of linear or crosslinked-isocyanate-free polyurethane networks[18]. For example, the oxirane (ethylene oxide) can react with carbon dioxide which is not a flammable and hazardous reagent in order to form cyclic carbonate [19].



*Scheme 6 :* Cycloaddition reaction of substituted epoxide with $CO_2$ in presence of catalyst

## III. Reaction of Amines or Polyamines with Cyclic Carbonates

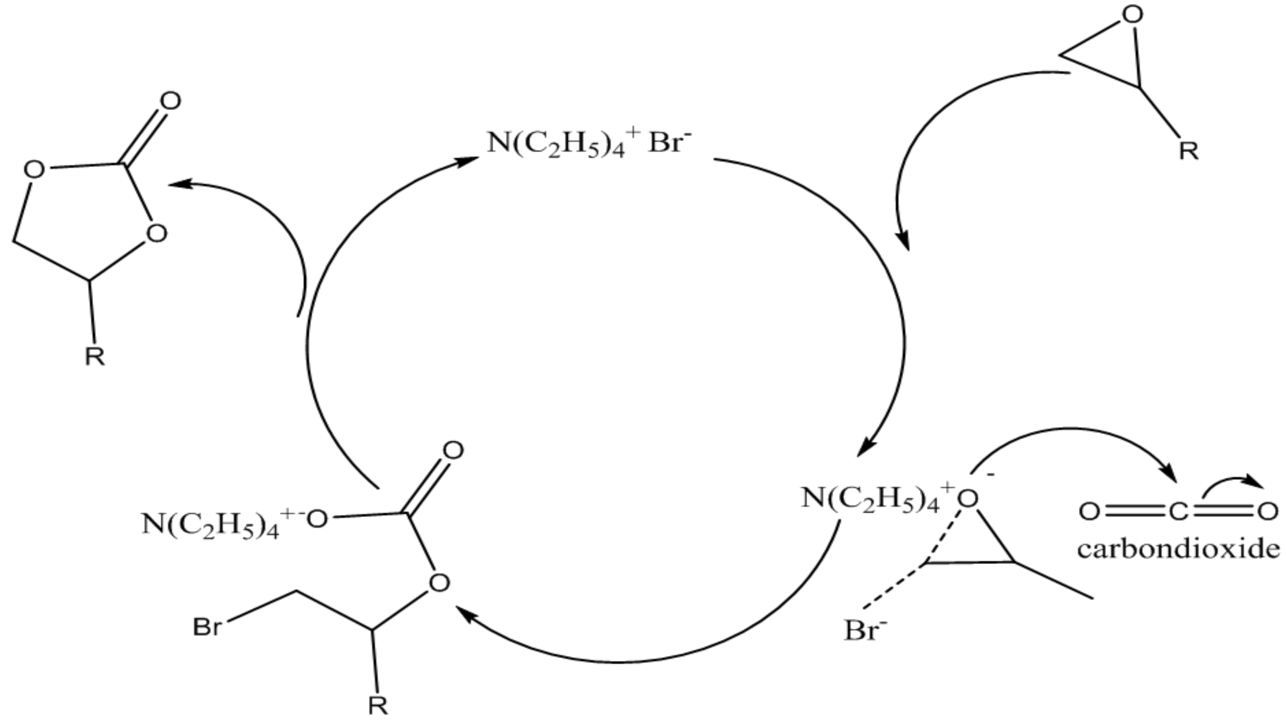
Amines and polyamines display a considerable affinity in presence of catalyst to react with cyclic carbonates thorough the ring opening addition reaction. Particularly the reaction rate of this type of addition reaction is very slow at room temperature in comparison with epoxy-amine reactions. Therefore, the higher temperature can accelerate the reaction rate of amines with cyclic carbonates. Also, in the reaction of amines with cyclic carbonates, the polyaliphatic amines are more reactive than aromatic amines. However, the polyurethane materials containing aliphatic amine functional groups represent the lower tensile strength than ones containing aromatic amine functional groups[20]. The alkyl/aryl amines should possess at least two primary amine functional groups in order to create a cross-linked polymer network with the multifunctional cyclic carbonate materials. However, the secondary and tertiary amine functional groups are not capable to carry out this specific reaction with cyclic carbonate compounds. Polyamines such as polyoxypropylene diamine and polyoxypropylenetriamine and other alkyl amines such as ethylenediamine, tris(2-aminoethyl)amine and heptamethylenediamine have dual amine functional groups in order to react with multifunctional cyclic carbonate compounds [8b, 21].

The backbone structure of polymer and the kind of cross-linking reagents used for polymerization reaction can determine the polyurethane properties. For example, if the structure of cyclocarbonate oligomers only possesses the cyclocarbonate functional groups, this kind of oligomers belong to the non-isocyanate polyurethane compounds while if the backbone structure of cyclocarbonate materials contains other functional groups such as carboxyl, hydroxyl, ether and epoxy groups, this kind of materials can produce hybrid-non-isocyanate polyurethane compounds. Specifically, the backbone structure of these two kinds of polyurethane materials can create the different polymers with various properties[7, 13].

The hydroxyurethane polymer compounds containing the amine functional groups can be synthesized through extra amounts of diamines or amines. These compounds represent different reactivities that can be used as cross-linking reagents or diluents for the adhesives and painting industries[22]. Also, Polyhydroxyurethane materials containing cyclocarbonate functional groups have been synthesized in presence of excess amounts of a bis-glycidyl ether of 1,4-cyclohexanedimethanol with a polyoxypropylenediamine[23].

## IV. Preparation and Synthesis of Cyclic Carbonate Oligomers and Polymers via Catalysts

The different kinds of catalysts are employedto synthesize the cyclic carbonate materials. The general process of making cyclic carbonate compounds is two step processes including the ring opening of epoxides via a catalyst and a simultaneous incorporation of carbon dioxide into the transition state of catalyst-alkoxides (Scheme 7)[24].



*Scheme 7 :* The role of quaternary ammonium salt (catalyst) for preparation of cyclic carbonate

The insertion of carbon dioxide into the epoxide groups is an effortless reaction which can produce the considerable yields of favorable compounds (cyclic carbonates) at either atmospheric or high pressure. The catalysts used in this reaction act as a driving force in order to begin (commence) the process by activating either one reactant or both reactants at the same time. For example, the oxygen of ethylene oxide can be activated by Lewic acid. Then, this transition state is attacked by a nuclephilic group leading to the ring opening of etylene oxide[25].

The nickel complexes containing phosphine groups, tribenzene phosphine, quaternary ammonium compounds and ribenzenephosphoniumchloride containing ehter functional groups have been investigated as a ring opener catalyst in the past [26]. Moreover, the homogeneoussalen comlexes including aluminum and chromium salen complexes display the highly active and selective catalysts to activate the reaction of epoxides with carbon dioxide. The zinc complexes containing alkoxide and phenoxide functional groups and also cobalt(III) complexes are shown as the efficient catalysts at low temperatures creating cyclic carbonates from oxiranes and carbon dioxide[27]. The halide salts such as potassium bromide, sodium iodide, lithium bromide and etc, are not relatively soluble in the organic solvents which result the low conversion of oxiranes to the cyclocarbonates[17, 28].However, these halide salts such as potassium iodide are activated as the very effective catalysts in presence of crown ethers [29].

Furthermore, the utilization of tetraalky-ammonium halides such as tetrabutyl- ammonium bromide (TBAB) and tetrabutylammonium iodide (TBAI) is considered as the most commonly used ionic liquids to catalyze the ring opening reaction of epoxies with carbon dioxide [16, 30]. The homogenous ionic liquid catalysts such as TBAB and TBAIcan selectively covert the epoxides to the cyclic carbonates or poly-cyclic carbonates in presence of carbon dioxide. In other words, these homogenous catalysts are strongly contributed in the process of capture of carbon dioxide by epoxides to selectively produce the high yield of desired products (poly-cyclic carbonates)[30b].

Moreover, the heterogeneous catalysts such as quaternary ammonium salts immobilized on the silica supports have been reported to give the remarkable yields of cyclic carbonates materials under supercritical carbon dioxide conditions [18]. The high temperature and pressure are required for this process. Therefore, this process is not considered as a cost effective process because it consumes much more energy. Thus, the utilization of silica supported-organic catalysts could be used as an alternative strategy in order to achieve a high yield of poly-carbonate materials which are produced from reaction of epoxides and carbon dioxide under atmospheric pressure[31].

Particularly, the silica surface (Si-OH) possesses the weak acidic reactive sites releasing (which can release) the protonto activate the epoxides and simultaneously the nucleophilic reagent like a halide anion attacks to the epoxy ring to initiate the ring opening reaction[32]. Generally, the organic salts and ionic liquids like phosphonium salts have lower catalytic activities than organic salts/ ionic salts supported onto the silica surface. This phenomenon probably is due to the synergistic effect between hydroxyl groups of silica and acidic sites of organic salts/ionic liquids that can be employed to activate carbon dioxide. Also, the immobilization or functionalization of organic salts/ionic liquids onto the surface of silica materials creates a good opportunity to readily recover the heterogeneous catalysts by a simple filtration and reusing them for several times without loss of their catalytic activity (performance) [32].

In theambient conditions, the catalytic systems including the tetra-nuclear zinc complexes and TBAI have been investigated to synthesize cyclic carbonates via capturing carbon dioxide. These systems represent the highest conversion of epoxides to the cyclic carbonates and the lowest impurities under mild conditions [33].

In the homogenous system, the separation of catalysts from the reaction solution is a main problem. Therefore, the catalytic systems based on the solid-state chemistry have been introduced to overcome with this problem[34]. For example, the different kinds of metal oxide and the ion-exchange resin systems have been investigated to easily recycle the catalysts from the reaction solution [35]. Nevertheless, these catalytic systems based on heterogeneous systems are not recommended because they produce by-products and also they are very expensive.

Recently, the synthesis of the ionic liquids functionalized or grafted onto surface of heterogeneous catalysts has been investigated for production of cyclic carbonates. This catalytic system possesses the properties of both homogenous ionic liquids and heterogeneous solid catalysts to activate both epoxides and carbon dioxide monomer to promote the production of cyclic carbonates. In particular, the ionic liquids such as sodium dodecylsulfate and 1,3-bis-(4-allyl-2,6-diisopropylphenyl) imidazolium chloride are respectively functionalized onto surface of polymer and mesoporous silica materials in order to introduce the ring opening or cycloaddition reaction of epoxides with $CO_2$[36].

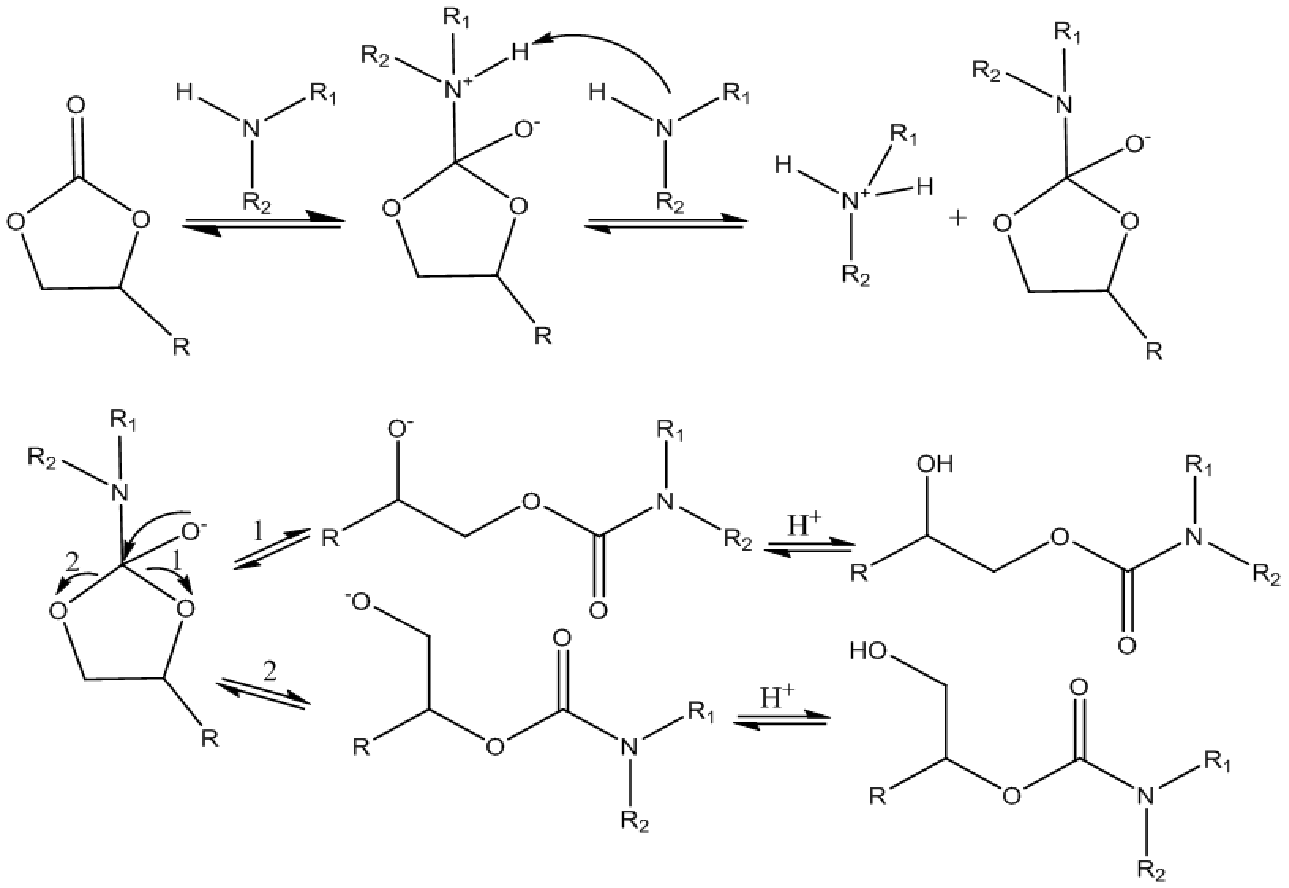
In addition, the carboxylic acid functional groups based on imidazolium ionic liquids have been synthesized and incorporated onto the surface of silica materials for the cycloaddition reaction of carbon dioxide with epoxides[37]. Also, the amino acids have been modified with ionic liquids to investigate the ring opening reaction of epoxides with $CO_2$[38]. The ionic liquids functionalized onto the chitosan, cellulose and silica supports have been effectively investigated for their catalytic activities in the cycloaddition reaction between $CO_2$ and epoxides [39].

Moreover, a novel catalytic system based on the polymer supported ionic liquids containing diol functional groups has been developed to promote the cycloaddition reaction rate of $CO_2$ with epoxide compounds. The remarkable content of adjacent hydroxyl groups on the surface of ionic liquid has been observed to increase the reaction rate through the strong hydrogen bonds between oxygen atom of epoxide and hydrogen atom of hydroxyl groups. In the process of ring opening, this catalytic system has become more effective than Ionic liquids including monohydroxyl functional groups[40].

Basically, the reaction of cycloaddition of carbon dioxide with epoxide is carried out at elevated temperatures in the oil bath. However, the microwave irradiation system under controlled pressure and temperature has provided the more effective heating method than oil bath system. The microwave irradiation system is based on non-thermal effect which uses less thermal energy leading to a remarkable decline in the activation energy of cycloaddition reaction[41].

## V. The Addition of Amines or Polyamines to Cyclic Carbonate for Synthesizing Isocyanate Free and Hybrid Polyurethanes

The addition of amines or polyamines to cyclic carbonate is considered as a nucleophilic attack followed by a deprotonation reaction (Scheme 8). Firstly, the nitrogen atom from amine group reacts with carbon atom from carboxyl group of cyclic carbonateto form a tetrahedral transition state. The ring opening reaction of cyclic carbonate using an amine is very slow which is due to the relative chemical stability of cyclic carbonate at a room temperature. In the second stage, another amine functional group is attacked to the tetrahedral transition state to remove the hydrogen atom followed by breaking the carbon-oxygen bond which in turn leads to generation of the alkyl-oxygen anion. Then, this stable compound is rapidly protonated in order to createthe final product[42]. The reaction between the amines and cyclic carbonates mainly produce two different isomers of hydroxyurethane. The major product of this reaction is hydroxyurethane which contain the secondary alcohol. The reaction selectivity towards forming hydroxyurethane containing secondary alcohol is relatively corresponded to types of amines and solvents used for this reaction [43].



*Scheme 8 :* The mechanism of ring opening reaction of cyclic carbonate with amine

*The different resources for synthesis of isocyanatefree polyurethane*

a) *Isocyanate free polyurethane from cyclic carbonate polymers*

The utilization of cyclic carbonate for synthesis of polyurethane polymeric compounds is due to elimination of materials containing toxic isocyanate functional groups. Also, the cyclic carbonate materials have a strong capability to react with amine groups in order to produce hydroxyurethanes[17a].

The various types of polyurethane materials, which possess the modest and low molecular weight, are employed to produce different polymeric materials such as synthetic fibers, adhesives, painting and varnishing compounds, thermoplastic and thermosetting polymers. There are several strategies that can be used to synthesize cyclic carbonate compounds which contain five members. Basically, the reaction of oxirane materials with alkali metals containing hydrogen carbonate can produce cyclic carbonates [44]. Moreover, the reaction of ethylene or dimethyl carbonate with 1,2-glycols or glycerol can create cyclic carbonates with different properties. In addition, the reaction of propylene epoxide with butyrolactonecan generate different kinds of cyclic carbonates[45].

Nevertheless, the most facile strategy for synthesis of cyclic carbonates is through the reaction of carbon dioxide with epoxides. There are several examples of cyclic carbonates prepared from carbon dioxide and epoxides (Figure 1).

Vinyl ethylene carbonate is a cyclic carbonate monomer which can be introduced (inserted) to the backbone structure of the vinyl polymer. This monomer is synthesized from reaction of carbon dioxide and 3,4-epoxy-1-butene. Furthermore, this material has a strong capability to carry out the copolymerization reaction with styrene and various types of acrylates such as ethyl or butyl acrylates [46]. Another unsaturated monomer, which is used in the backbone structure of polymer, is vinyl carbonate that can be used in the coating formulation. This compound is synthesized from ethylene carbonate followed by the chlorination and dehyrochlorination reactions [47]. Another type of cyclic carbonate is the glycerol carbonate vinyl ether which is synthesized through the reaction of glycidyl vinyl ether with either$CO_2$ or sodium hydrogen carbonate [47a].

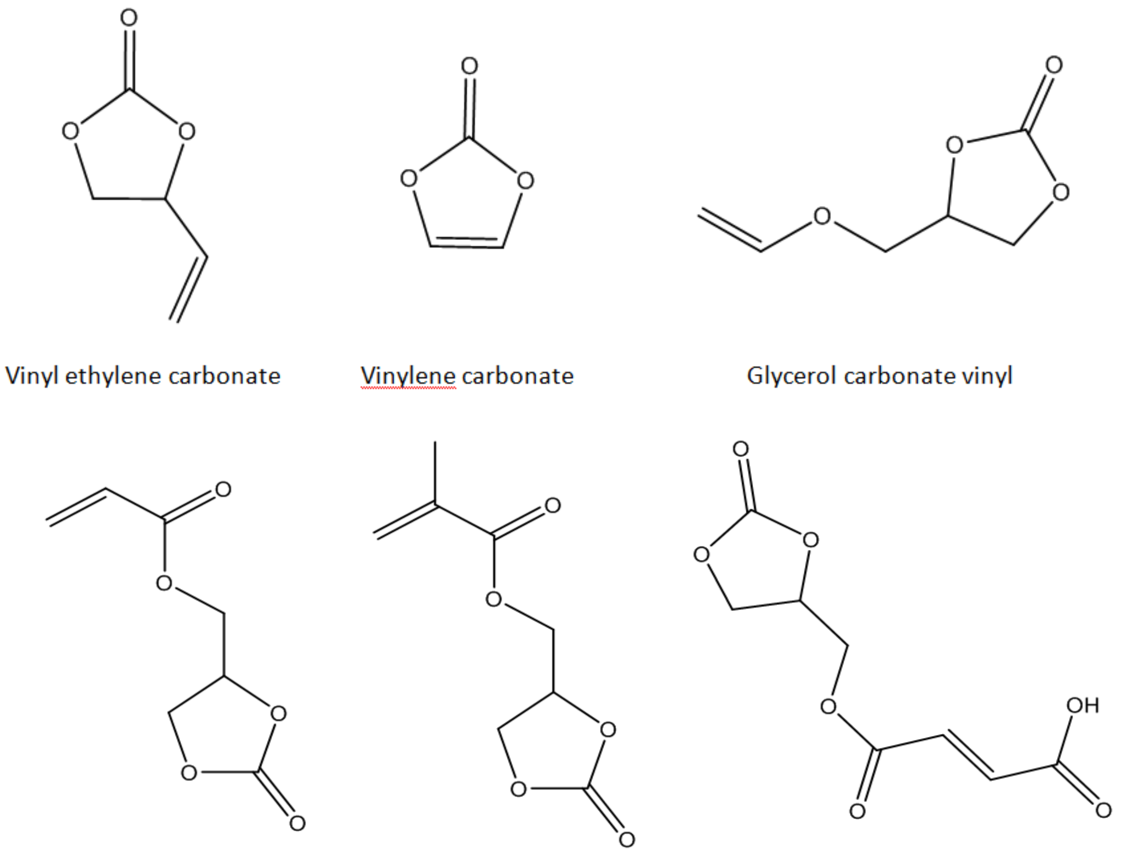
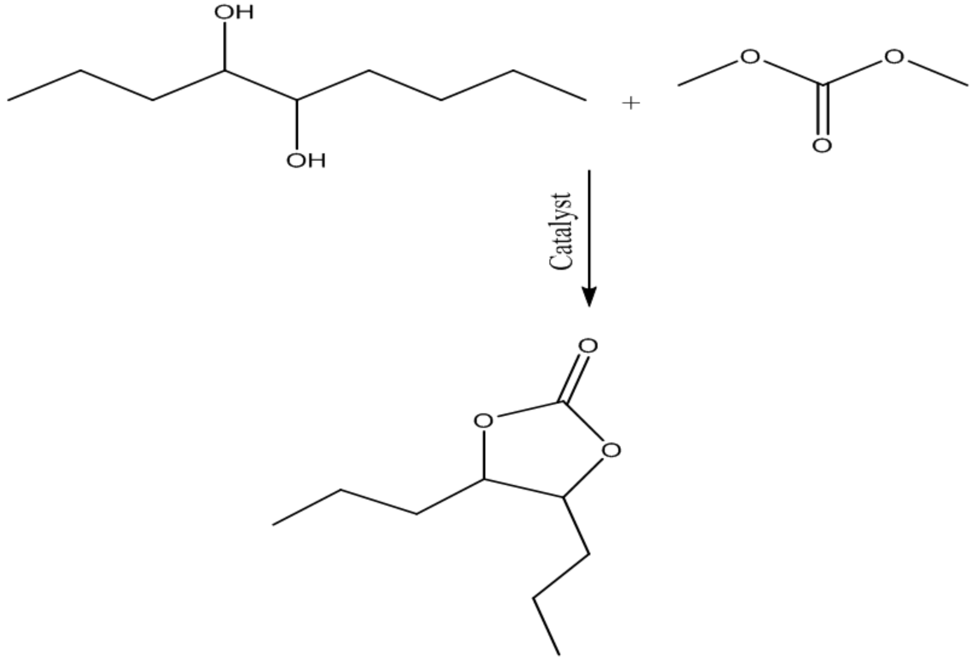
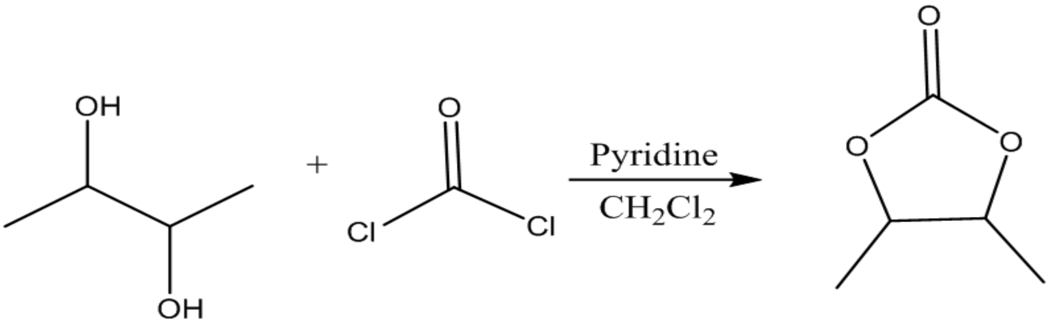


*Fig. 1 :* General structures of various cyclic carbonate materials

Moreover, the cyclic carbonates can be prepared from the reaction of dimetyl carbonate with the compounds containing vicinal-hydroxyl functional groups such as ethylene glycol and glycerol derivatives. The catalysts such as aluminum and magnesium hydrotalcitesare used to enhance the rate of reaction (Scheme 9)[48]. However, the corrosive and toxic route of cyclic carbonate production is based on phosgenation reaction of compounds containing hydroxyl functional groups in presence of a basic catalyst such as pyridine (Scheme 10) [49].



*Scheme 9 :* The reaction of dimethyl carbonate with a compound containing adjacent hydroxyl groups



*Scheme 10 :* The reaction of phosgene with hydroxyl containing material

Furthermore, the glycerol carbonate synthesis displays a green route(which is) based on the transesterification of carbon dioxide with a non toxicdialkyl carbonate such as dimethyl carbonate[41, 50]. The synthesis of glycerol carbonate is a solvent free process (which is) performed in the presence of catalysts such as Magnesium oxide and calcium oxide, zeolites, enzymes, hydrotalcite and alkyl-amine metal oxides [45c, 48b, 51].

The glycerol carbonate can be modified with maleic acid or anhydride through esterification process in order to produce cyclic carbonate materials containing unsaturated acidic moieties which in turn can be used as a monomer in polymer synthesis [45a].

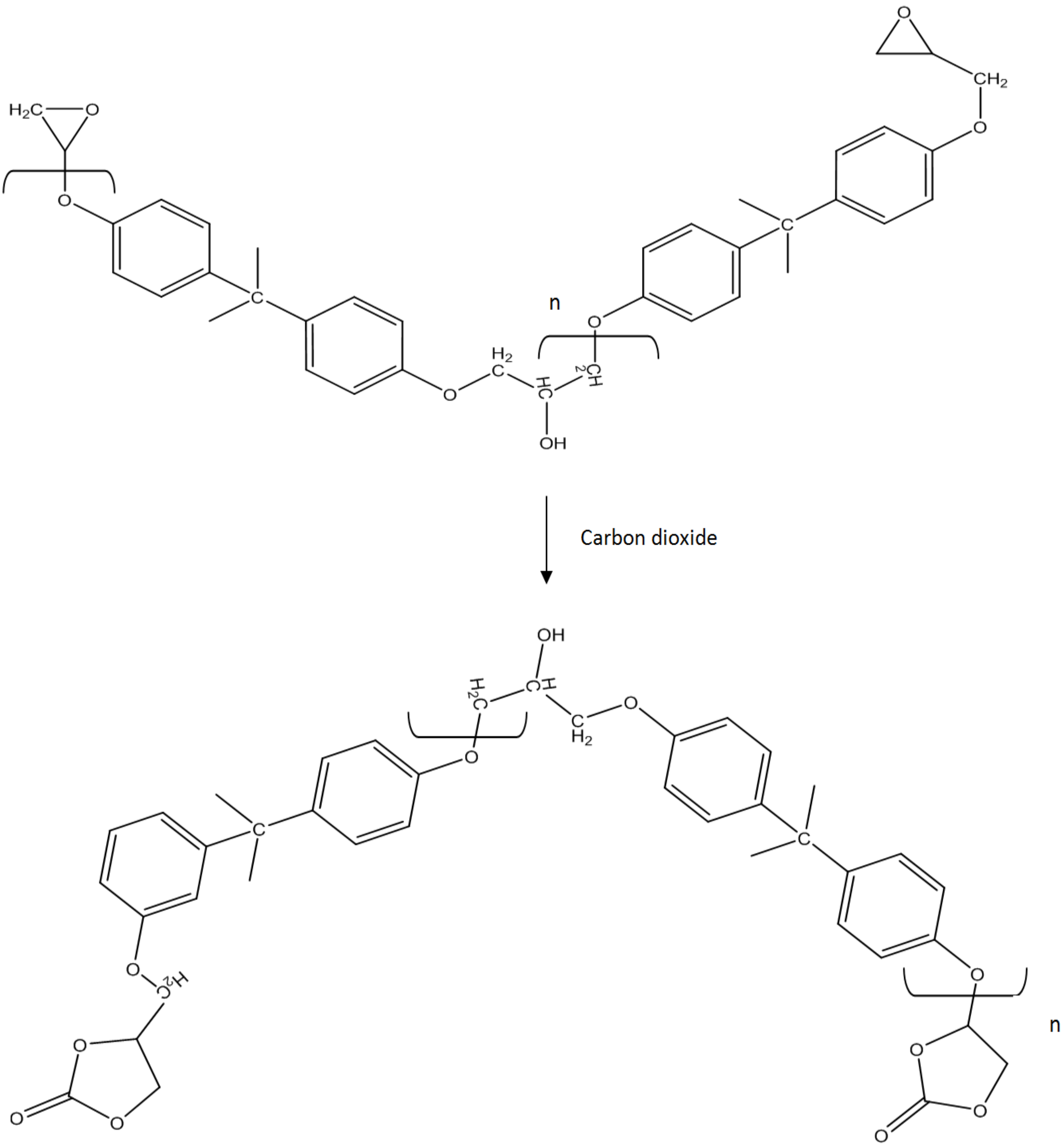
In addition, the halohydrins can react with carbon dioxide in the presence of catalyst in the room temperature to generate cyclic carbonates. Also, the halogenated carbonates in the elevated temperatures can be converted to cyclic carbonate. This reaction is performed in presence of catalyst such as mercuric acetate. The substituted propargyl alcohols undergo the cycloaddition reaction with $CO_2$. This process leads to synthesis of cyclic carbonates under relatively highertemperature[13, 52].

Moreover, the utilization of bi-functional cyclic carbonate polymers can be taken into account as cross-linking and modifying reagents for adhesive and coating industries. The cyclic carbonates containing reactive functional groups undergo the cycloaddition or condensation reaction with the oligomers containing other functional groups to generate the cyclic carbonate polymers which have outstanding properties. For instance, the esterification reaction of glycerol carbonates and di-functional carboxylic acid materials can produce cyclic carbonate materials containing ester linkages. These materials possess two different functional groups which make (cause) them to be a suitable candidate as cross linking reagents in coatings [53].

Bi-functional cyclic carbonate materials containing thioehthers have been prepared through one step reaction of thiol-ene compounds with glycerol carbonate derivatives. This process is solvent free and can produce the high yield of desirable materials which represent the lower glass transition ($T_g$) which in turn lead them to be functioned for exterior applications. Also, these materials don't possess the ester linkages and aromatic functional groups. Therefore, they are not hydrolysable and degraded towards the moisture and UV irradiation[54].

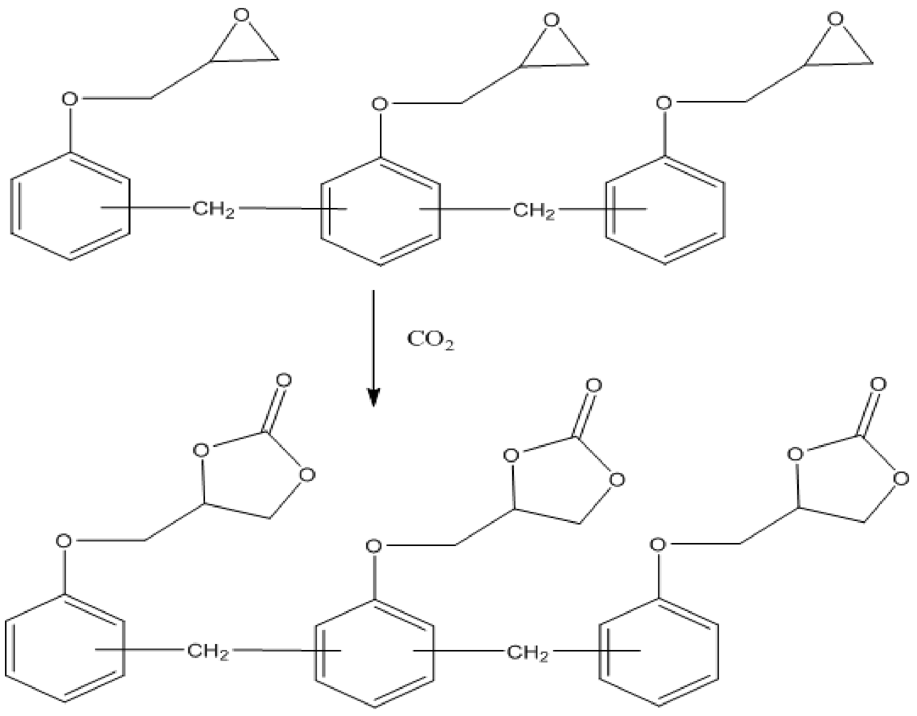
## VI. Isocyantefree Synthesis of Polyurethanes from Epoxy Resins

The Epoxy resin is considered as a class of polymers which have various applications such as adhesives, coatings and composites. The epoxy resins have remarkable properties which can be used in the various fields. The reaction of the glycidyl ether of bisphenol-A containing terminal epoxy groups and $CO_2$ is used to generate bis-cyclic carbonate materials (scheme 11)[29a]. These oligomers have been prepared according to the various preparation methods and catalysts. The cyclic carbonate materials based on epoxy resins can be functionalized or cured with amines, diamines and polyamines functional groups to produce polyurethane compounds which can be used in the coating industry [55].



*Scheme 11 :* Cyclocarbonate synthesis from epoxy resin

The novalac epoxy resin, which is produced from the reaction of phenol with formaldehyde (F/P<1 molar ratio), can be employed in industrial coatings. This type of resin can be used to prepare isocyanate-free polyurethane materials as well (Scheme 12) [56]. These materials should possess outstanding features for both coatings and adhesives industries. Nevertheless, the aromatic ether functional groups which are sensitive to UV irradiation undergo the photo oxidative degradation of this kind of polyurethane compounds. This phenomenon is restricted the use of these materials for only interior applications and therefore they are not used for exterior applications. In addition, the utilization of toxic bisphenol-A (BPA) has been limited. Consequently, there is a serious concern to find alternative bio-resources which are classified asenvironmentally friendly resources to synthesize green polyurethane compounds.



*Scheme 12 :* Cyclic carbonated materials obtained from epoxy novalac resin

The isocyanate-free polyurethane based polyester resins have been prepared for coating applications. These materials possess high performance. In particular, carboxylic acid compounds such as adipic acid and multifunctional alcohols such as hexanediol and trimethylol propane have been reacted with each other to prepare the acrylated polyester oligomer. Then, this oligomer has been incorporated to the product of the reaction of diamine with cyclic carbonate in order to generate the polyester resins containing flexible urethane segments. The formation of intermolecular hydrogen bonds between amine groups from urethane segments and carbonyl groups from ester groups has enhanced the polymer viscosity and its chemical resistance[57].

The modification of the cyclic carbonate with bis(4-glycidyloxy phenyl)phenyl phosphine oxide (BGPPO), and poly(propyleneglycol)diglycidyl ether (PPG-DGE) has been reported to prepare a novel cyclic carbonate. Then, the hexamethylene diamine was introduced(inserted) to the cyclic carbonate to synthesize a polyurethane material. Subsequently, the sol-gel method is used to incorporate the different concentrations of silica compound into the polyurethane. Therefore, the polyurethane-silica hybrids can be prepared through the isocyanate free strategy. In particular, the modulus and stiffness of polyurethane-silica hybrids were enhanced a long with increasing the concentrations of silica and phosphine oxide. Furthermore, an increase in the char percentage values and degradation temperatures in the thermal gravimetric analysis displays that the thermal stability of nanocomposites was improved[58].

## VII. SYNTHESIS OF ISOCYANATE-FREE POLYURETHANE MATERIALS FROM BIO-RENEWABLE SOURCES

The most chemicals produced from oil resources are considered as hazardous and toxic materials which can threaten both environment and human' life. Particularly, the rising environmental pollutants caused all people and researchers throughout the world to be concerned toward these serious issues. Consequently, there is a fundamental need to find alternatives to replace the harmful and toxic oil resources. The abundant bio-renewable resources are considered as environmentally friendly assets. Therefore, the use of these resources to produce eco-friendly materials is taken into account as a desirable effort. Also, the utilization of the sustainable bio-resources is being substantially investigated throughout the world[59].

The low price epoxidized soybean oil is considered as an abundant renewable resource which can be used as plasticizer in the production of polyvinyl chloride. The epoxidized soybean oil is efficiently reacted with carbon dioxide to produce the high yield five-membered cyclic carbonate soybean oil (Figure 2). Subsequently, this specific cyclic carbonate material can undergo the amine addition reaction to generate (give) the isocyanate-free polyurethane networks. These polyurethane materials based on epoxidized soybean oil possess the high tensile strength and other outstanding properties. The polyurethane characteristics are corresponded to the type of amines and cyclic carbonate oligemers in the polyurethane back bone structure [60].

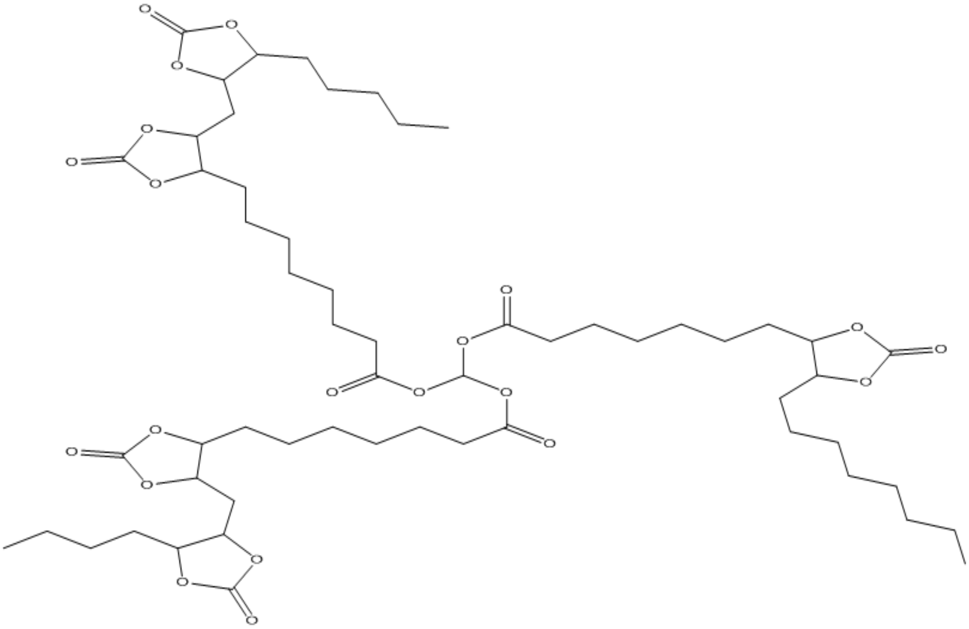


*Fig 2 :* Molecular structure of carbonated soybean oil

The utilization of different types of amines can affect the polyurethane properties. For instance, meta and para xylyenediamines, aliphatic diamines, cycloaliphatic diamiens can be used as softening reagents in the synthesis of isocyanate-free polyurethane materials. However, the amines or polyamines containing aromatic functional groups can be applied as hardeners in the structure of polyurethane networks because the aromatic functional groups leads to a remarkable increase in the tensile strength and elongation-to-break compared to the aliphatic ones[20].

Furthermore, the preparation of cyclocarbonate linseed oil has been successfully achieved by adding carbon dioxide monomers to epoxide functional groups. In this reaction, the different catalysts such as a homogenous tetra butyl ammonium bromide and the heterogeneous silica materials functionalized with alkyl pyridinium iodide have been employed effectively to accelerate the cycloaddition reaction of $CO_2$with epoxides. Also, in this strategy the catalyst can be readily recovered by simple filtration method which eliminate the solvent extraction process [28].

The number of cyclic carbonate functional groups is considerably high in the carbonated soybean oil, whereas the number of those groups is low in the carbonated linseed oil. A mixture of these two carbonated materials influenced the content of cyclic carbonate groups which in turn altered the concentration of cross-linking agents for curing purposes. Consequently, the variation of cross-linkers concentration has significantly affected the thermal and mechanical features of these novel polyurethane materials. The stiffness and glass transition temperature of polymers are significantly increased with enhancing the curing agent density. In this case, the isophrone diamine enhanced the glass transition temperature for 40°C [61].

Sometimes, the curing reaction of these cyclic carbonate oils can be accompanied with breaking the linkages of ester groups which leads to the remarkable reduction in the network density and tensile strength of polymer structure. Thus, the cyclic carbonate compounds should not have ester linkages for applications which require the high tensile strength[62].

Moreover, the difunctional limonene dioxide is a commercially available compound which originates from limonene. This material can be used as a solvent or diluents in the preparation of epoxy based resins. The limonene belongs to the terpenes family that can be employed as a bio-sustainable resource containing the high number of carbon-carbon double bonds. Also, limonene can be used as a suitable candidate for polyurethane synthesis because it is a free ester material[63]. This highly unsaturated material has a strong capability to react with the large scale of carbon dioxide monomers to generate the cyclic carbonate materials with a high content of cyclic carbonate functional groups.

In particular, the limonene dicarbonate compounds have stiff monomers which can increase the brittleness and the thermal deformation strength of isocyanate-free polyurethane materials[28, 62]. The multifunctional amines and diamines can cure the rigid structure of cyclic carbonate polyurethane for generation of stiff and brittle polyurethane networked structure. The high glass transition temperature, high Young's modulus and low elongation at break can reflect the rigid outstanding properties of polyurethane networks[28, 63].

Furthermore, the lignin is takeninto account as the first aromatic sustainable bio-renewable resource and one of the most abundant sustainable bio-polymers composed of different kinds of phenylpropane moieties in the earth[64]. The replacement of petroleum based polyol materials with lignin which is a bio-based polyol compound containing the high content of hydroxyl groupsh as been extensively studied to produce high value added materials[65]. Therefore, lignin can be employed as the bio-polyol resource to produce eco-friendly polyurethane materials.

The synthesis of bio-polyurethane materials obtained from both lignin and cyclic carbonate soybean oil has been successfully achieved. The 3-aminopropyltriethoxysilane has been used as a bridging reagent between lignin and cyclic carbonate soybean oil. This coupling agent can react with cyclic carbonate functional groups to generate the polyurethane segments. Then the lignin can be substituted with hydroxyl groups on the silica surface of coupling agent. This bio-based polyurethane elastomer represents the high tensile strength which is due to incorporation of lignin into the polyurethane network. This material can be used as thermoplastic films, adhesives, coatings and elastomers[66].

In addition, the novel lignin-glycerol based polyurethane materials have been prepared through the addition reaction of amines or diamines to the cyclic carbonate materials. The cyclic carbonate compounds have been extracted from lignin. The lignin-based polyurethane (which is) synthesized from non-isocyanate route has a higher glass transition temperature than traditional polyurethanes synthesized from bisphenol-A based on isocyanate route [67]. This novel isocyanate-free synthesis of polyurethane reveals (opens up) the new horizons in the synthesis of environmentally friendly polyurethanes.

## VIII. Application of Isocyanate-Free Polyurethane Materials in Nanotechnology

The excellent performance of non-isocyanate polyurethane systems could be employed in the nanostructured networks. The nanocomposites based silica-polyurethane materials possess the high stiffness, transparency and strength towards break. The silica nanoparticles functionalized with cyclic carbonate compounds, are synthesized from the reaction of tetraethylorthosilicate and cyclic carbonated glycidoxysilanes through the sol-gel strategy. Basically, the silica nanoparticels can act as cross-linking agents in order to strongly increase the properties of nanocomposite coatings and reduce the moisture adsorption on the coating surface[68].

Moreover, the preparation of reactive organic precursors has been successfully archived through isocyanate-free technology. The synthesis of polyurethane materials containing organic silane groups from 1,3 propane diamine and cyclic carbonated glycidoxypropyltrimethoxysilane has been reported. The reactive organic compound possesses six methoxy functional groups, which are susceptible for hydrolysis, can facilitate the sol-gel process. In this process, the coatings containing both organic and inorganic functional groups were applied as a surface protection in the aluminum alloys[69].

## IX. Isocyanate Free Polyurethane Materials made of Six-Membered Cyclic Carbonates

The various six-membered cyclic carbonate compounds can be employed effectively in the polyurethane synthesis. The different routes have been used to synthesize these materials. For instance, trimethylene carbonate is produced from reaction of 1,3-propanediol with phosgene derivatives. However, the green route for synthesis of six-membered cyclic carbonate is the carbon dioxide cycloaddition reaction with oxetanes at higher temperature and pressure in presence of a homogenous catalyst[70].

Furthermore, the transesterification of 1,3-diols with dialkyl carbonates that is an environmentally friendly procedure has been offered for synthesis of six-membered cyclic carbonates[70]. In addition, the homogenous metallic catalysts, metal oxides, metal carbonates and phosphazene materials have been employed to synthesize the various types of six-membered cyclic carbonates in the past [71].

Moreover, the green conversion oftrimethyol propane and dialkyl carbonates to six-membered cyclic carbonates through a lipase mediated reaction has been successfully achieved [72]. The six-membered cyclic carbonate materials derived from trimethyol propane could be modified (incorporated) with different functional groups for specific applications.

The six-membered cyclic carbonate materials are susceptible to undergo the ring-opening polymerization in presence of anionic reagents to generate the corresponding linear polycarbonates without the loss of $CO_2$ and volume degradation. In the presence of anionic reagents, the six-membered cyclic carbonates are less thermodynamically stable than the linear polycarbonates[73]. However, in the presence of cationic reagents the six-membered cyclic carbonates underwent the partial elimination of $CO_2$ in order to produce linear polycarbonates containing the ether moieties [74].

The five-membered cyclic carbonates are not readily polymerized to yield linear polycarbonate materials because they possess the stable five-membered rings but the partial formation of polyethercarbonates could be achieved by loss of carbon dioxide in presence of catalysts such as metal alkoxides, metal acetylacetone and metal alkyls. Nevertheless, the five-membered cyclic carbonates significantly undergo the amine addition reaction to yield the desired polyhyroxyurethanes[75].

The larger ring size of cyclic carbonates leads them to become more susceptible to react with amines or polyamines in order to form hydroxyurethane or polyurethane materials. Therefore, the cyclic carbonates containing six or seven members represent the higher activity for polymerization than five-membered cyclic carbonates [76].

In particular, the reaction of five-membered cyclic carbonates with amines is relatively slow at ambient temperature. Furthermore, the molecular weight of polyhyroxyurethane materials generated from cyclic carbonate is lower than that of conventional polyurethane compounds obtained from diisocyanates and diols. These disadvantages have relatively restricted the widespread utilization and production of isocyanate-free polyhyroxyurethanes[77].

## X. Properties of Isocyanate-Free Polyurethane Coatings

The isocyanate-free polyurethane coatings contain very low volatile organic compounds. Also, they can be classified as non-porous materials. They do not react with moisture as well. Therefore, these materials have higher coatings performance compared to conventional polyurethane systems. The chemical and thermal stabilities of these materials are relatively higher than those polyurethanes obtained from conventional method. The basic properties of these specific coatings are strongly dependent to the type of cross-linking agents[78].

Furthermore, the stoichiometric ratios of amine-to-carbonate can generate the regular structured networks in the polymer. These networks have high density, stiffness, $T_g$ and tensile strengths. Nevertheless, the non-stoichiometric ratios of amine-to-carbonate could lead to a significant decrease in coating performance properties. In addition, the samples prepared from the excess amounts of amine or diamine display the higher elongation at break than those obtained from an equal stoichiometric ratio of amine-to-carbonate[79].

Moreover, the various amines or diamines with different molecular weights can considerably affect the properties of polymers. For instance stiffness, hardness and tensile strength of polymers obtained from short chain diamines are much higher than those of polymers obtained from long chain diamines. This phenomenon is related to the different density of cross-linking agents. Also, the different diamines possess the various capabilities to create intermolecular hydrogen bonds in order to increase the chemical resistance of the polymer[78-79].

The isocyanate-free polyurethane materials cannot be employed efficiently in the interior applications such as floor and furniture adhesives because they are not able to perform the fast curing processes in the room temperature. Basically, the cyclic carbonates rapidly react with amines or diamines at elevated temperature. In contrast, diisocyanate materials have a strong capability to react with polyols at any conditions. Also, the mechanical and chemical features of isocyanate-free polyurethanes are comparable to polyurethane materials obtained from traditional conventional system[80].

## XI. The Benefits of Isocyanate Free Polyurethanes over Conventional Polyurethanes

The toxic isocyanates are employed in the conventional process of generating the linear and networked polyurethane materials. However, the isocyanate-free polyurethane compounds are produced from diols, polyols, carbon dioxide and diamines which are based on eco-friendly chemical substances. The production process of isocyanate-free polyurethane materials is based on fixation of $CO_2$ in coatings. These materials don't have any pores and they are not permeable towards chemical solutions and microorganisms. Therefore, they are not easily degraded in the environment. Also once they are exposed to the moisture, they don't react with water on their surfaces. Thus, an essential care, when applying diisocyanates to prevent the carbon dioxide formation resulting inporosity, is not required. Moreover, in the conventional method of polyurethane synthesis the free-solvent curing process should be performed with a great care in presence of diisocyanates to exclude water from atmosphere. This is process is eliminated in the synthesis of isocyanate free polyurethane materials.

## XII. Applications of Isocyanate Free Polyurethane Materials

The isocyanate-free polyurethane polymers have some applications in the coatings and polymer industries. In particular, the isocyanate free polyurethane could be functioned for thermo-stable adhesives, UV-resistant coatings and monolithic adhesives or coatings [81]. The main promising way to enhance the chemical and thermal stability of isocyanate-free polyurethane materials is utilizing the difunctional hyroxyalkyl urethane glycols as an additive. These glycols containing the urethane bonds can be used as diols for synthesis of polymer materials as well [81-82].

The aminosilanes and cyclic carbonates are specifically used for synthesis of thermosetting polymers. These coatings can be used in the various fields such as non-porous monolithic coatings, the protection against corrosion for coverings and linings, wood and metallic surfaces, retention of color and in the marine environment[81]. The isocyanate-free polyurethane materials can be used as a corrosion protection in a long period of time because they have a non-porous structure which leads them to have an effective performance in the highly basic or acidic conditions. Also, they have much better durability than polyurethanes materials obtained from isocyanate compounds [82a].

The isocyanate-free polyurethane materials are sensitive to light and once they are exposed to light, they may gradually turn to the yellow color. Therefore, they are not suitable for transparent application. Moreover, the UV stable coatings can be synthesized from acrylic materials which contain the cyclic carbonate functional groups. These materials have excellent mechanical properties [83].

The waterborne polyurethane dispersions obtained from non-isocyanate chemistry contain low volatile organic compounds. These specific dispersions have superior mechanical properties. The presence of hydroxyl, carboxyl and urethane functional groups in these materials cause them toact as highly efficient pigment dispersing resins[84].

Moreover, the polyurethane resins are obtained from reaction of multifunctional hydroxyalkylene carbonates with methylene diphenyldiiso cyanates in presence of potassium acetate. These particular polyurethane materials can be reacted again with aliphatic diamines to prepare the highly value-added polyurethane materials with the high content of urethane motifs [24]. The cycloaliphatic diamines are susceptible reagents to react with alkylene carbonates to produce the polyurethane adducts. Then the other terminal amine group is reacted with epoxy-urethane resins to form superior polyurethane coatings without use of diisocyanates[24].

The polyurethane materials obtained from isocyanate-free procedure (process) can be used in the sealants to protect the electronic devices and their components in aircraft and rocket construction towards hydrolysis and gasoline[85]. Furthermore, these materials have the various applications in the civil engineering because they can be employed as glues or adhesives with high performance and longevity to join all kinds of materials such as glass, metal, ceramics. These materials are used as reinforcing and filling polymers in the chemical and civil engineering[86].

Furthermore, the isocyanate free polyurethanes can be functioned in the textile industries for finishing purposes as well. For instance, an isocyanate-free UV-curable polyurethane resin has been recently prepared using polyetheramine and bisphenol based epoxy resin containing cyclic carbonate for treatment of hydrophilic textile[87].

The isocyanate-free polyurethane compounds possess the outstanding adhesive properties and therefore they can be used as adhesives and sealants. The different types of multifunctional acrylate materials containing urethane groups are extensively employed in inks, varnishes and adhesives. These particular compounds can be utilized in the various fields as cross-linking agents. For example, they can be employed for anaerobic adhesives, co-monomers in acrylic materials for laminating coatings and flexibilizers in protective coatings[88].

In addition, the hardeners such as dendro-aminosilanes can be employed in the synthesis of isocyanate-free polyurethane sealants. These hardeners can increase the thermal stabilities of polyurethanes. Also, the organosilaneshave extremely affected the mechanical and viscoelastic properties of isocyanate-free polyurethane coatings which can be employed in the steel and glass industries [89].

The inorganic nanoparticle materials have been functionalized with isocyanate-free polyurethanesto create the hybrid inorganic-organic nanocomposites which can be used in the coating industry. The incorporation of isocyanate-free polyurethane materials onto the surface of zinc oxide nanoparticles has significantly enhanced the mechanical and anticorrosive properties of new materials[90].

## XIII. CONCLUSION

Basically, the chemical industry is increasingly demanding for environmentally benign processes in order to produce the eco-friendly chemicals. The carbon dioxide accumulation can cause global warming. Therefore, there have been several investigations to reduce the carbon dioxide concentration in the atmosphere to reduce the consequences of global warming. Also this useful monomer can be used for synthesis of different polymers. The utilization of isocyanate free strategies for synthesis of polyurethane materials has been attracted the considerable attention because these strategies have not introduced the use of toxic and environmentally dangerous compounds such as phosgene and isocyanates. The isocyanate free processes create a novel route for developing world by incorporation of carbon dioxide into the epoxide rings.

The polyurethane materials, which are generated from isocyanate free procedures, can replace the conventional method of polyurethane synthesis. These materials can be used effectively in a variety of applications. In particular, the design of cyclic carbonates backbone structure and their oligomers play an essential role to improve the performance of isocyanate free polyurethane materials. The recent preparations and developments of materials containing cyclic carbonates are providing the new opportunities for synthesis of polyurethane materials. Six-membered cyclic carbonates open a new window for synthesis of isocyanate free polyurethane materials. A variety of cyclic carbonates functionalized with different functional groups have been prepared and polymerized. These novel compounds have high performance properties which can be used for both industrial and household applications. The reaction of peracid or hyrgoen peroxide with unsaturated moieties of polymer compounds leads to the formation of epxides which in turn can undergo the cycloaddition reaction with carbon dioxide to generate cyclic carbonates for synthesis of the green isocyanate free polyurethane materials. This process leads to eco-friendly production of coatings that doesn't apply harmful phosgene and isocyanates. The toxic and hazardous materials have been replaced with safe and nonirritating molecules such as carbon dioxide and hydrogen peroxide.

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# Susceptibility of States and Properties of Metallic Systems at a Threshold Breakdown of the through Holes under Power Laser Action

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*GJSFR-B Classification : FOR Code: 039904*

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## I. INTRODUCTION

One of the promising parameter, allowing to describe in detail the states of the matter under laser action, is an exit diameter of threshold hole [1] in metallic foils resulting from threshold breakdown. The threshold breakdown corresponds to minimal laser fluence capable to produce through hole in a foil of a certain thickness. Minimum diameter of threshold exit hole can be considered as response of the system to an external action [2], and diameter *d* of this exit hole is a fluctuating value. This experimental approach gives possibility to connect properties of fluctuating magnitude with values characterizing behavior of matter under external action [2]. Formally, response *d* is expressed through susceptibility operator $\alpha$ [2]:

$$d = \hat{\alpha} f \qquad (1)$$

here *f* - is time function of generalized force.

## II. MODEL

The incident electromagnetic field of laser radiation interacts with the electronic subsystem of metal and enlarges chemical potential $\mu_e$ of electrons in region of interaction. (Ponderomotivepotential $V = (q^2/4c \cdot m \cdot \omega^2) \cdot E^2$ is about $10^{-6} \div 10^{-4}$eV under experimental conditions λ = 694 nm and intensity $J \sim 10^{6} \div 10^{10}$ W/cm$^2$[3]). As a result the electrons will start moving into area, in which the electron chemical potential is smaller or where the electron density is less. Into metal their density remains unchanged. Therefore, the excited electrons move into place, where their number is small, i.e. from a metal to the interface of "metal-gas". In particular, this sort of movement arises, when the initially solid matter is quickly heated up to high temperature [4]. Kinetic energy of motion of electrons and ions at these densities (densities of metals in solid and liquid states) turns out comparable with coulomb energy of their interaction. Electrons are concentrating at a "gas- metal" interface. It leads to original polarization at an "interface" which is expressed as difference of chemical potentials

$$(\mu_{e\_interface} - \mu_{e\_volume}) = e \cdot (\varphi_{interface} - \varphi_{volume}) \quad (2)$$

here $\mu_{e\_interface}$ and $\mu_{e\_volume}$ is the chemical potentials of electrons on interface and in volume. Therefore, the arising electric field of *E*, is determined as ($\partial\varphi/\partial r = (1/e) \cdot (\partial\mu_e/\partial r) = -E,\ \mu_e = \varepsilon_{Fermi}$. For cooper $\varepsilon_{Fermi} = 7eV,$ so the order of magnitude of electric field strength corresponds to – $E \sim 7 \cdot 10^{8}$V/cm$^2$), which is enough to drag out positive ions from a warmed-up volume. Accelerated ions pass through the "gas-metal" interface. Due to comparable values of the kinetic energy of motion and the coulomb energy of interaction, the ions capture electrons, and abandon a metal.

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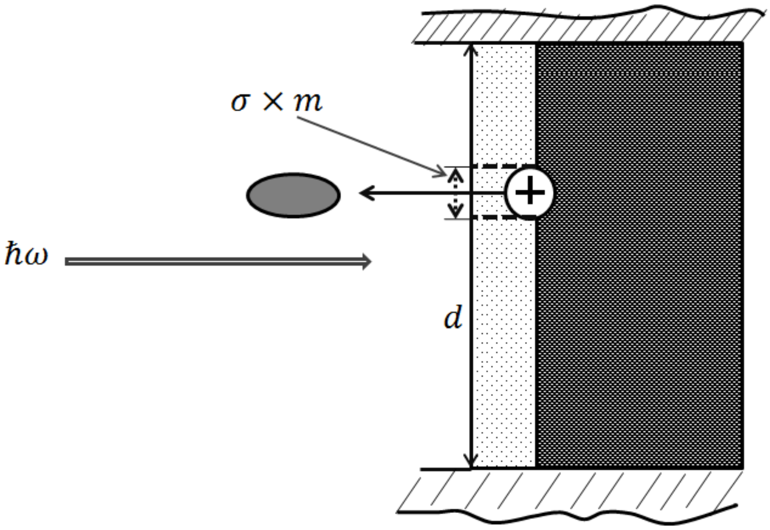

*Fig. 1 :* Creation (annihilation) of element of interface, σ, on leaving of ion from the volume of metal

Therefore, an ion, passing through an interface, participates in formation of surface, increasing (or decreasing) its area (Fig.1). Moreover, an ion, passing through an interface, transforms itself into an atom, and represents the same fluctuation part of the surface, which is the response of the system on the external field *f*, (Appendix A). Therefore, the elemental act of displacement (crossing of interface) can be considered as an act of moving away (or joining) of element of interface area per time. This element of area $\sigma$ is approximately equal to the "area of surface» of shade of atom (Appendix A). Elemental area $\sigma$ per time is connected with mass *m* of atom. Therefore, we can talk about moving away (formation) per time of area in the interface, by the characterized composition *N·σ·m*, where *N* is an amount of atoms in this region. Then the value *z* measureable in an experiment on the threshold breakdown of the through holes [1] is connected to the mean value of *d* (Appendix A)

$$N \cdot \sigma \cdot m = \pi(d/2)^2 \cdot m = (\pi/4) \cdot \left(z \cdot \sqrt{m}\right)^2 \qquad (3)$$

Effective diameter of the threshold exit, $d = z \cdot \sqrt{m}$, is the response of the system on external action *f*. In general, the threshold diameter *z*depends on time, and *d* is the function of time *t* :

$$d = d(t) \qquad (3a)$$

It is possible to construct generalized force *f* conjugated to the chosen response *d* [2]. In our case

$$f \sim (v \cdot \mathcal{E}/\omega)^{1/2}$$

here $\mathcal{E} = (1/c) \cdot \sqrt{\xi \cdot \mu} \cdot E \cdot H$ is electromagnetic energy density; $E$ and $H \sim e^{+j\omega t}$ or $e^{-j\omega t}$ are tensions of the monochromatic field with cyclic frequency $\omega$; $v$ is volume accepting $\mathcal{E}$.

Dropping details of calculations [2]and taking into account that external perturbation is monochromatic, we will write down connection (1) between the response *d (t)* of the system and external perturbation *f* in Fourier components:

$$d_\omega = \alpha(\omega) \cdot f_\omega \qquad (4)$$

here *α(ω)* is generalized susceptibility. Symbol ω means Fourier component of value, for example:

$$d_\omega = \int_{-\infty}^{+\infty} d(t) e^{j\omega t}\, dt$$

Then, fluctuation-dissipative theorem [2] allows writing down Fourier component of square of diameter (areas) (3a) nascent hole in a form:

$$\langle d^2 \rangle_\omega = 2 \cdot \hbar\alpha_2 \cdot \left[\frac{1}{2} + \frac{1}{e^{\hbar\omega/kT} - 1}\right] \qquad (5)$$

here $\alpha_2$ is imaginary part of generalized susceptibility (1) and (4):

$$\alpha(\omega) = \alpha_1 + j\alpha_2$$

$\hbar, k$ are Plank and Boltzmann constants, *T* is absolute temperature. The important feature of $\langle d^2 \rangle_\omega$ is that it consists of the composition area of the threshold hole, as functions of temperature, on a delta function *δ (ω)* (Appendix B).

## III. SOLUTION AND RESULTS

*a) Determination of imaginary part of generalized susceptibility*

Inverting expression (5), we will find the temperature of the electron-ion system depending on the "diameter" of the threshold hole

$$T = \frac{\frac{\hbar\omega}{k}}{\ln\left[\frac{1 + \hbar \cdot \alpha 2/d^2}{1 - \hbar \cdot \alpha 2/d^2}\right]} \qquad (6)$$

The expression (6) describes the dependences of imaginary part of generalized susceptibility for different diameters versus temperature (see Fig. 2). It is seen from Fig. 2 that these dependences intersect nowhere, and each one starts with the minimum of real value. Each of the curves corresponds only to a certain diameter of exit hole.

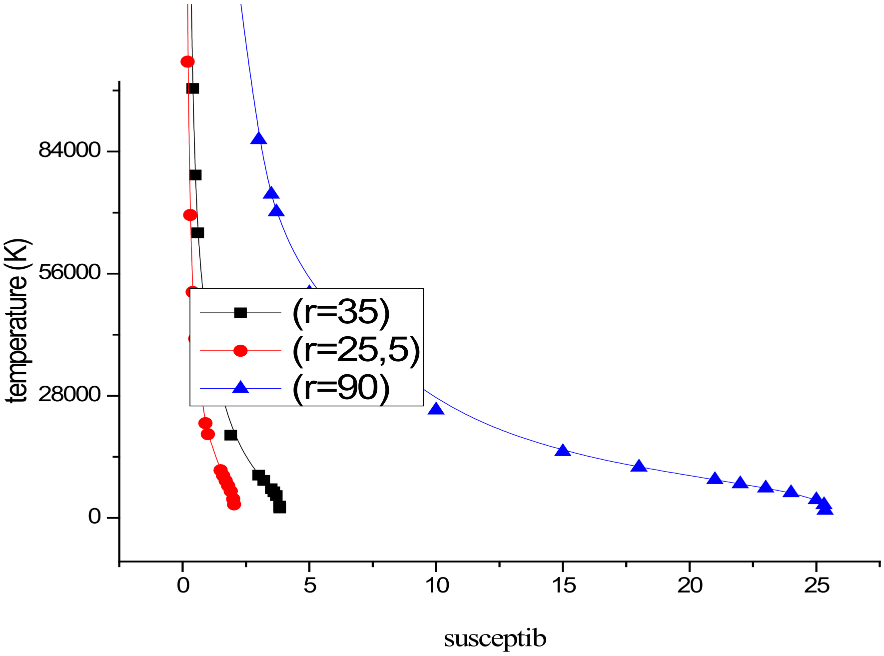

*Fig. 2 :* The temperature of the electron-ion system depending on $\alpha_2$. (Dimeter of exit hole $(\mu m) z = 2 \cdot r$ )

The behavior of these curves allows finding of the values of imaginary part of generalized susceptibility$\alpha_2$ at different temperatures and also the real value of critical temperature (within the framework of the chosen approaching).

Each curve in Fig. 2 reveals the inflection point (see Fig. 3). An inflection point on dependence of $dT/d\alpha_2$ (to be more correct value, reciprocal to $dT/d\alpha_2$, i.e. $\frac{d\alpha_2}{dT} \sim \left(\frac{\hbar\omega}{kT}\right) \cdot \frac{1}{T}$ ) indicates the way how the energy of single quantum $\hbar\omega$ is adopted by the system at temperature of $T$.

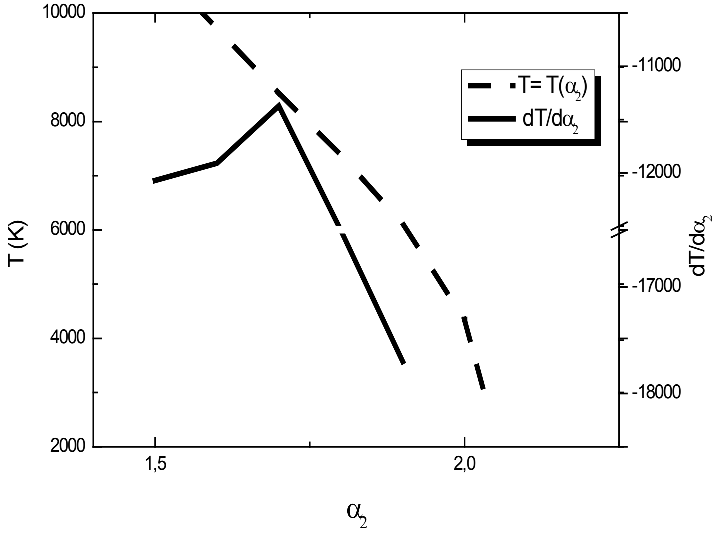

*Fig. 3 :* The inflection point of a derivative $dT/d\alpha_2$ (solid line), and temperature dependence $T(\alpha_2)$ for $r \sim 25{,}5\ \mu m$ (dashed line)

i. *State of the electro-ion system*

Imaginary part of susceptibility $\alpha_2$ is fully determined by the state of electronic subsystem and its interaction with ionic subsystem. Behavior of two subsystems depends on the absorbed energy amount at interaction with laser field, which, in turn, depends on a reflectivity (absorptions) coefficient. From dependence (6) and Fig. 2, it is possible to specify behavior of the electron-ion system at critical temperature and around. Within the framework of Drude approaching [5-12] we can determine the reflectivity of metals [6, 7]. Note that the temperature range of research of reflectivity for metals is rather limited, both in a theoretical and in experimental way [9-11]. To calculate reflection coefficient we use (6) and take into account our experimental data of response fig.2. According to Drude approximation dielectric permittivity ε (ω) can be expressed through external field frequency ω plasma frequency $\omega_p$ and electron-ion collisions frequency of ν [3, 5-12]:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega\cdot(\omega + j\nu)} = \varepsilon_1(\omega) + j\varepsilon_2(\omega) \qquad (7)$$

(value ν can be considered as relaxation time $\nu^{-1}$ of electronic distribution [10] or, as relaxation time of electrons interacting with both electrons and ions [6]). From another side, permittivity ε(ω) and susceptibility α(ω) are connected by relationships [5,6]:

$$\varepsilon(\omega) = 1 + 4\pi\cdot\alpha(\omega) = 1 + 4\pi(\alpha_1 + j\alpha_2) \qquad (8)$$

Expressions (7) and (8) yield $\alpha_1$ and $\alpha_2$:

$$\begin{cases} \varepsilon_1 = 4\pi\cdot\alpha_1(\omega) \\ \varepsilon_2 = 4\pi\cdot\alpha_2(\omega) \end{cases} \qquad (9)$$

Coming back to (7) we find:

$$\begin{cases} \varepsilon_1 = 1 - {\omega_p^2}\Big/{(\omega^2+\nu^2)} \\ \\ \varepsilon_2 = {\omega_p^2\cdot\nu}\Big/{\omega(\omega^2+\nu^2)} \end{cases} \qquad (10)$$

here ω is frequency of the external field of radiation (for a ruby laser $27\cdot 10^{14}s^{-1}$, $\omega_p$ is plasma frequency, ν is the frequency of electron-ion interaction.

In the threshold breakdown of the through hole conditions [1] temperatures exceeds few thousand Kelvin, so that $\hbar\omega \sim kT$, which result in ratio $|\varepsilon_1| \sim |\varepsilon_2|$. It means that calculations of conductivity and reflectivity, which are usually performed under conditions $|\varepsilon_1| \ll |\varepsilon_2|$,[12], cannot be carried out since this inequality is not fulfilled.

Electron-ion frequency νis expressed from second equation of (7a) system:

$$\nu^2 - \frac{\omega_p^2}{\varepsilon_2\cdot\omega}\cdot\nu + \omega^2 = 0 \qquad (11)$$

$$\nu_{(+),(-)} = \frac{\omega_p^2}{2\varepsilon_2\cdot\omega}\left(1 \pm \sqrt{1 - 4\cdot\left(\frac{\omega}{\omega_p}\right)^4\cdot(\varepsilon_2)^2}\right) \qquad (11a)$$

The equation (11a) shows that the frequency of electron-ion interaction has two roots. These two roots imply two different states of electronic subsystem. First root (+ sign) responds the case when electrons of conductivity with the increase of temperature more often collide with ions (mean free time of these electrons diminishes sharply). The system is kept in metallic state. The second one describe situation when frequency of collisions falls down. And it is possible (at temperatures below critical, when the volume, occupied by the system also below, than at a critical temperature) only at reduction of number of electrons participating in conductivity. Reduction of number of electrons of conductivity says that the electrons are localized on ions (or original ionic bubbles). Thus, a metal passes to the dielectric state.

Since both of these roots are interchangeable at identical temperatures, the matter represents itself coexistence liquid metal and dielectric. Thus, there is the only condition at which these two roots to coincide:

$$\nu_{(+)} = \nu_{(-)} \qquad (12)$$

It implies that square root in (10a) is equal to zero, i.e. $\omega_p^4 - (2\varepsilon_2\omega^2)^2 = 0$or

$$\varepsilon_2 = \frac{1}{2}\cdot\left(\frac{\omega_p}{\omega}\right)^2 \qquad (13)$$

The value $\varepsilon_2$can be found from imaginary part of susceptibility $\alpha_2$(8), which corresponds to critical temperatureFig.3. From (11a), (12), and (13) the electron-ion colliding frequency at critical temperature is found$\nu_{(+)} = \nu_{(-)} = \nu$ :

$$\nu = \frac{\omega_p^2}{\varepsilon_2\cdot\omega} = \omega \qquad (14)$$

Thus, at critical temperature the external perturbation distributes electrons and ions in such a way, that frequency of their interaction, $\nu$, becomes equal frequency of the external field. Under laser irradiation ($\omega = 27{\cdot}10^{14}s^{-1}$) on a metal at a critical temperature, this frequency equals to $\nu = 27\cdot 10^{14}s^{-1}$.

b) *Temperature behavior of parameters of the electron-ion system*

i. *Plasma frequency*

The temperature behavior plasma frequency$\omega_p$ (Fig. 4) is determined from the following consideration. In our approach we consider copper atoms, which are singly ionized (valence Z = 1) from melting temperature up to the critical one. We accept $\omega_p = 4\pi\cdot\frac{n^2}{m} = 31{,}80795\cdot 10^{-8}$, where $n = 6{,}022\cdot 10^{23}\cdot Z\cdot\frac{\rho}{A}$; $A = 64$. Temperature dependence of copper density $\rho$ is adopted from [15]. The metal density is taken into account in the temperature range from melting up to boiling. The value $\omega_p$ was determined from (12) at the critical temperature $T_{cr} = 8522K$, got from our results, Fig.3, preliminary defining $\varepsilon_2$ on $\alpha_2$. In addition, experiment determined imaginary part of susceptibility and, accordingly, to the permittivity, and the value of critical temperature do not allow fluctuating of plasma frequency, due to correlation (11).

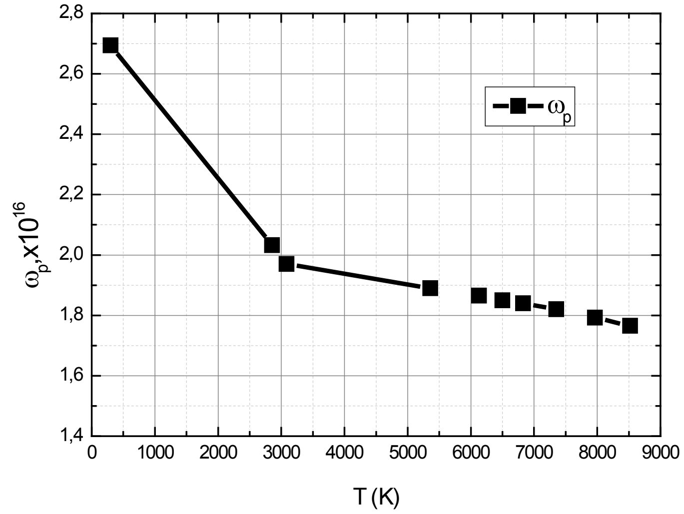

*Fig. 4 :* The temperature dependence of plasma frequency $\omega_p$

ii. *Electron-ion interaction frequency*

Electron-ion interaction frequency ν consists of two branches $\nu(+)$ and $\nu(-)$ Fig.5. First of the branches corresponds to "metallic» part, and second - to "dielectric" part of the electron-ion system at the examined conditions. $\nu(+)$ demonstrates growth of frequency of electron-ion collisions, and $\nu(-)$ is shows reduction of frequency of electron-ion collisions due to localization of electrons by capture of them on ionic bubbles. It leads to growth of dielectric constituent of a metal.

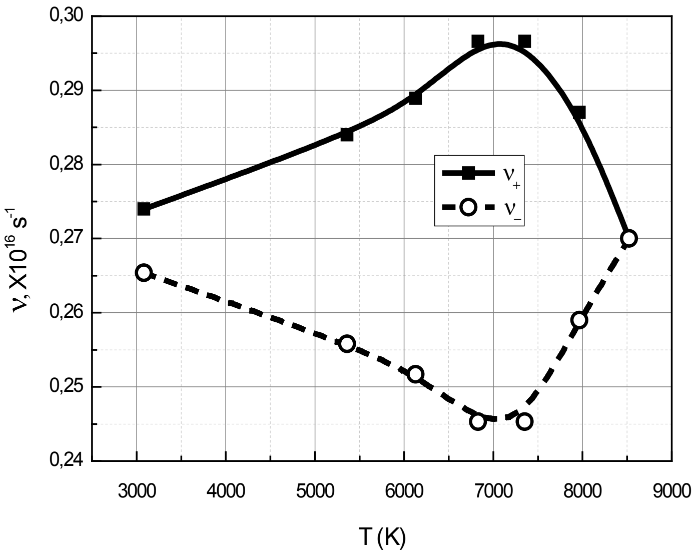

*Fig. 5 :* Frequency $\nu$ is temperature dependence of electron-ion interaction .Upper curve corresponds $\nu(+)$ metallic part of the electron-ion system, $\nu(-)$ corresponds to "dielectric" part of the electron-ion system

iii. *Reflectivity coefficient*

In order to determine reflectivity, *R*, and its temperature dependence has to know temperature behavior of permittivity, plasma frequency, and frequency of electro-ion interaction. These values are bound by the standard set of relationships (9) - (11a), which include imaginary part of susceptibility α (ω). Therefore the experimental dependence of temperature versus imaginary part of susceptibility, (Fig.2, and Fig.3), can be used to find temperature dependences $\varepsilon_2, \omega_p$,

(Fig. 4), $\nu$ (Fig. 5) and reflectivity coefficient (Fig. 6). *R* calculated in accordance with the appendix C. Fig.6 demonstrates complicated behavior of reflectivity in the temperature range from boiling up to critical temperature of phase transition of liquid metal to gas state.

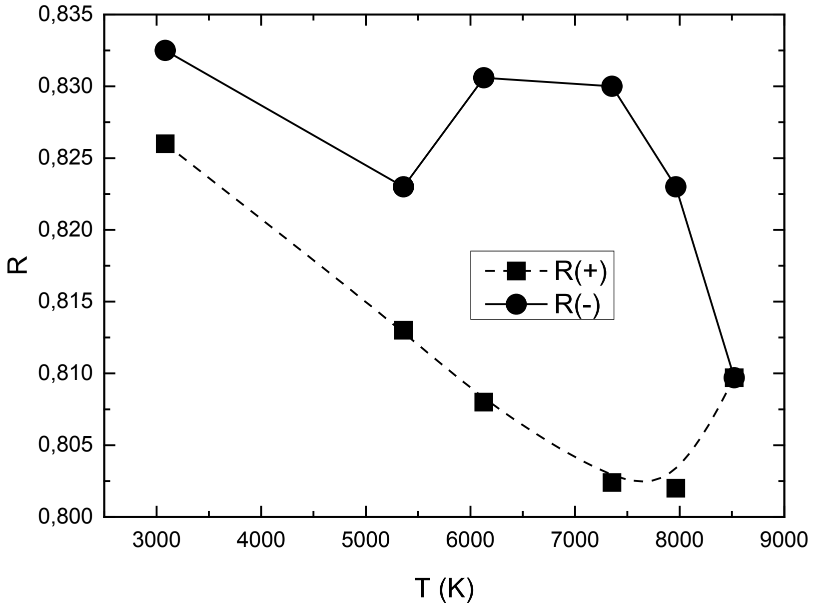

*Fig. 6 :* Reflectivity coefficients R (+) and R (-) for metallic and dielectric constituents of the electron-ion system

Dielectric constituent part of reflectivity R(-) plays substantial role. In a liquid metal near-by the critical temperature of R(-) is significantly lager than reflection of R(+) caused by a metallic constituent. Quite possible, that such situation is caused not only by appearance of the constrained localized states of electrons on ions or ionic bubbles, but also by origin of overlapping between such constrained states [21, 22] leading to generalization of the localized states. In such regions electrons work again as in a metal. Herein, presumably, and essence of the critical phenomenon at what distinction between a liquid metal and gas disappears.

### iv. *Critical temperature*

Critical temperature, $T_{cr}$, arises from specific behavior of electron-ion system (fig. 5, 6). Thus, a critical temperature for a copper is approximately equal to $T_{cr} = 8522\,K$. In literature a few different values of critical temperatures for a copper are presented. A critical temperature was measured by method of explosion of thin wire by a large current [13]: $T_{cr} = 8390$ *K*. In [14] a theoretical value $T_{cr} = 7800K$was obtained from calculations of modeling a phase diagram. But in such calculations, if reflectivity (absorptions) was used, then for such temperatures it would be obtained only by extrapolation on high temperatures, as a direct measuring of these coefficient at high temperatures, higher *3000K* in literature are not presented. In [15] $T_{cr} = 9000$ *K* was found by extrapolation of density of the gas state of copper from the boiling temperature.

## IV. CONCLUSION

The idea of threshold breakdown of the through holes and application of fluctuation-dissipative theorem allowed to find the value of critical temperature, and also temperature dependences of the generalized susceptibility of the system. This combination opens the prosperity of more thin and detailed high temperature measuring and possibilities of management by the electron-ion system at high temperatures.

## V. APPENDIX A

To estimate the mean (quantum mechanical) value of *d* from (1) and (3), we will include next moments:

(1). At the densities of liquid metal and temperatures in thousands of Kelvin, coulomb energy of interaction of electrons and ions is comparable with their kinetic energy of motion [4]. In these conditions a liquid metal is the electron-ion system, being mixture of electron-ion gas (constrained electron-ion pairs) and electron-ion liquid. Such state is substantially heterogeneous and non-ideal. The last properties suppose a presence, both disconnected electrons and ions, providing the metallic state ("zone of conductivity" and level of Fermi in her), and appearing electron-ion pairs (atomic metallic gas) that can decompose in next moments. And at approaching of the liquid metallic state to the critical condition (critical temperature) frequency of origin of such virtual pairs grows (see for example, рис.5, behavior $\boldsymbol{\nu}$(-)).

(2). In this electron-ion system, electrons can be considered, as electrons of the strongly excited state of atom, at which peripheral electron of atom appear far remote from a positive ion [16]. The similar situation takes place when the electron being at long distance from a nucleus may attribute to the large main quantum number n (and orbital number $\ell = 0$. So the electron corresponds to excited S-state). Motion of such electron (or such ion in the field of electron) can be considered as mutual motion in the coulomb field of atomic remain (ion) with the effective charge of Z = 1 [16]: electric-field tension arising between the charges at that rate $\sim E_{n,l,m} \cdot (a \cdot e)^{-1}$ , ($E_{n,l,m}$ is own energy of electron, *e* is an electron charge, *a* is a Bhor radius).

(3). The conduction band in a copper appears as a result of hybridization *4s* and *3d* shells of atom [17]. So that the wave function of electron in the conduction band can be decomposed on ball functions with certain quantum numbers [ 16, 17, 18] including those that correspond to the states of electrons participating in interaction with the external field. Part of them participates in dispersion of the external field, another part – in absorption (in optical transitions). For example optical transitions in cooper correspond transitions $3d^{10}5s - 3d^{10}4p$ , $3d^{10}6s - 3d^{10}4p$ ,$3d^{10}5,6,7d - 3d^{10}4p$ [19].

Taking into account these facts, and (1) - (3), we can do the following estimations

(a) Remoteness of electron from a nucleus in approaching of hydrogen-like atom [16, 18] is determined by quantum mechanical mean distance of electron in an atom

$$\langle r \rangle_{n,l} = \frac{a}{2 \cdot Z} \cdot [3n^2 - l \cdot (l+1)] \sim d/2$$

Then the distance of 5S -state (at Z = 1, looks higher, point (2)) equals to $\langle r \rangle_{5,l=0} = 19{,}838 \cdot 10^{-8} cm$, i.e., an electron is remote from a nucleus on mean distance $19{,}838 \cdot 10^{-8} cm$ (These distances are in Thomas-Fermi approaching [20]) Tension of electric-field of such electron operating on rest atom (ion) equaled to $\frac{E_{n,l,m}}{e \cdot \langle r \rangle_{5,0}}$ is the same, what $\frac{1}{e} \cdot \frac{\partial \mu_e}{\partial r} \approx 3{,}5 \cdot 10^7 \, {}^{V}\!/_{cm} = -E$

(b) The electromagnetic field of laser radiation interacting with target is changing slower than time of electron-electron $\tau_{e-e}$ interaction (period of oscillation for a ruby laser $\tau = 23 \cdot 10^{-16} s$and $\omega_p^{-1} \sim \tau_{e-e} = 2.32 \cdot 10^{-16} s$, where $\omega_p$ is plasma frequency). It implies that an electronic subsystem will have time to be tuned under external influence. Thus, electrical fields of interaction between charged particles will look like slowly changing. Atom of copper in exited state is considered in hydrogen-like atom approaching. Character (potential) of electric field allows to split up of wave function of atom $\Psi(x_\alpha, y_\alpha, z_\alpha;\ X, Y, Z) = \varphi_e(x, y, z) \cdot \Phi(X, Y, Z)$ in the adiabatic approaching on the wave function of electron $\varphi_e(x, y, z)$(here *a* numbered electrons in an atom; (x,y,z) are coordinates of relative motion of electron, (X,Y,Z) coordinates of center-of-mass of atom ) and wave function of ion of atom $\Phi_n(X, Y, Z)$ so, that equalization of Schrodinger for the ion of atom will be written down, as

$$i\hbar \frac{\partial}{\partial t} \Phi_n = -\frac{\hbar^2}{2M} \Delta_{X,Y,Z} \Phi_n + \left[\mathcal{U}(X,Y,Z) + E_{n,l,m}(X,Y,Z)\right]\Phi_n \qquad \text{(A1)}$$

Because de Broglie wavelength of ion of atom is very small a wave function for wavelength is searched in a form [16 ]

$$\Phi_n = A \cdot exp\left(-{}^{iS}\!/_{\hbar}\right) \qquad \text{(A2)}$$

Where S, is an action [16 ], equals to

$$S = H \cdot t - P_X \cdot X - P_Y \cdot Y - P_Z \cdot Z \qquad \text{(A3)}$$

Substitution of (A2) in (A1) with an account (A3) yields to Hamiltonian

$$H = {}^{\vec{P}^2}\!/_{2M} + \mathcal{U}(X,Y,Z) + E_{n,l,m}(X,Y,Z) \qquad \text{(A4)}$$

It corresponds to classic behavior of ion of atom of copper, in the external field created by surroundings of ion, $\mathcal{U}(X,Y,Z)$ and by field $E_{n,l,m}(X,Y,Z)$created by remote valence electron.

We consider that $E_{n,l,m}(X,Y,Z)$ at moving of center-mass does not change. The external field for the ion of $\mathcal{U}(X,Y,Z)$is expressed through the difference of chemical potentials of electrons in the "interface" and in a "volume"

$$\mathcal{U}(X,Y,Z) = \left(\mu_{e_{interface}} - \mu_{e_{volume}}\right) = e \cdot \left(\varphi_{interface} - \varphi_{volume}\right)$$

It is accepted for simplicity the vector of tension of electric-field is directed on a normal to the "interface" Fig.1. Then equations of motion of center-of-mass of remain of copper atom take the following form

$$M \frac{d^2X}{dt^2} = 0$$

$$M \frac{d^2Y}{dt^2} = 0$$

$$M \frac{d^2Z}{dt^2} = -\frac{\partial}{\partial Z}\left(\mathcal{U}(X,Y,Z) + E_{n,l,m}(X,Y,Z) + \frac{q^2}{4mc\omega^2} J\right)$$

Value $|V| \ll |\mathcal{U}(X,Y,Z)|$, where $V = \frac{q^2}{4cm\omega^2} E^2$

It is accepted that the initial value of speed of remain in the moment of t = 0 is equal to zero $\left(\frac{dX}{dt}, \frac{dY}{dt}, \frac{dZ}{dt}\right) = 0.$ It followes, the conserved values are $X - X_0, Y - Y_0 \sim \langle r \rangle_{n,l}$ and $(X - X_0) \cdot (Y - Y_0)$. In other words, an area $(X - X_0) \cdot (Y - Y_0) = \sigma$ is equal to the area formed by the projection of atom on normal to moving of atom of plane, is conserved. Values of $M \cdot \sigma$ and $N \cdot M \cdot \sigma$ also are the invariants of motion during the process of transition of remained atom from one position in other. Distance overcame by the remain of atom is

$$Z - Z_0 = -\frac{1}{2M}\left[\frac{\partial}{\partial Z}\left(\mathcal{U}(X,Y,Z) + E_{n,l,m}(X,Y,Z)\right)\right] \cdot \tau^2$$

Let us assume, that $Z - Z_0 = \langle r\rangle_{4,l=1} - \langle r\rangle_{5,l=0} = |7{,}671 \cdot 10^{-8}|\, cm$ then the remained of atom will overcome this distance after $\tau \sim 10^{-14} s$ before will go across from the state $|n = 5, l = 0\rangle$ in $\langle n = 4,\ l = 1|$. We note that the$\tau$ correspondsto creation time of new phase (or aggregate) state of substance [1].

## VI. Appendix B

Calculation of spectral density of square of diameter of the threshold breakdown of the through hole $\langle d^2\rangle_\omega$

Formation of hole is the temporal phenomenon. And the diameter of minimum exit hole depends on a diameter in the moment of time previous to the breakdown. So that it is possible to talk about temporal´correlation function

$$\langle d(t) \cdot d(t')\rangle \qquad \text{(B1)}$$

in which $t'$ is time moment of through breakdown of minimum exit hole by the diameter of *d*. $t = 0$ is the preceding moment of time is chosen as point of reference. It means an exit hole arises up at $t' - 0 = \tau$. Spectral density of square of diameter of the through breakdown of minimum exit hole with respect to [2] is written down

$$\langle d^2\rangle_\omega = \int_{-\infty}^{+\infty} \langle d(0) \cdot d(\tau)\rangle e^{j\omega t}\, dt \qquad \text{(B2)}$$

It is assumed that diameter during $\tau$ is changed poorly the $d\,(\tau)$ is decomposed into row

$$d(\tau) = d(0) + \dot{d} \cdot \tau \qquad \text{(B3)}$$

(B2) is rewritten with taking into account (B3):

$$\langle d^2\rangle_\omega = \int_{-\infty}^{+\infty} \langle d(0) \cdot (d(0) + \dot{d} \cdot \tau)\rangle e^{j\omega t}\, dt =$$

$$= \int_{-\infty}^{+\infty} \langle d(0) \cdot d(0)\rangle e^{j\omega t}\, dt + \int_{-\infty}^{+\infty} \langle d(0) \cdot \dot{d} \cdot \tau)\rangle e^{j\omega t}\, dt =$$

$$= \langle d(0) \cdot d(0)\rangle \int_{-\infty}^{+\infty} e^{j\omega t}\, dt + \tau \cdot \int_{-\infty}^{+\infty} (d(0)\dot{d}(0)) e^{j\omega t}\, dt = \qquad \text{(B4)}$$

one should notice

$$\int_{-\infty}^{+\infty} e^{j\omega t}\, dt = \delta(\omega) \qquad \text{(B5)}$$

$$\int_{-\infty}^{+\infty} (d(0) \cdot \dot{d}(0)) e^{j\omega t}\, dt = \langle d(0) \cdot \dot{d}(0)\rangle \qquad \text{(B6)}$$

Continuing equality (B4) and taking into account relations (B5) and (B6), then (B4) :

$$= \langle d(0) \cdot d(0)\rangle \cdot \delta(\omega) + \tau \cdot \langle d(0) \cdot \dot{d}(0)\rangle \qquad \text{(B7)}$$

It is assumed that change of diameter $\dot{d}$ versus time and size of diameter $d$ in one and the same moment of time are not correlated. Then the second member in (B7) equals to the zero. So, finally

$$\langle d^2\rangle_\omega = d^2(0) \cdot \delta(\omega)$$

## VII. Appendix C

Reflectivity coefficient (relation of Fresnel of electromagnetic radiation for the normal incidence on interface)

$$R = \left|\frac{\sqrt{\varepsilon} - 1}{\sqrt{\varepsilon} + 1}\right|^2 = \left|\frac{n - j \cdot k - 1}{n + j \cdot k + 1}\right|^2 = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

$$\varepsilon^{\frac{1}{2}} = n - j \cdot k$$

$$n = \left\{\frac{1}{2} \cdot \left[\varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}}\right]\right\}^{\frac{1}{2}}$$

$$k = \left\{\frac{1}{2}\cdot(\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}} - \varepsilon_1\right\}^{\frac{1}{2}}$$

$$\varepsilon = \varepsilon_1 + j\cdot\varepsilon_2 = 1 - \frac{\omega_p^2}{\omega^2 + \nu^2} + j\cdot\frac{\omega_p^2\nu}{(\omega^2+\nu^2)\cdot\omega} =$$

$$= 1 - \frac{\omega_p^2\cdot\omega - j\omega_p^2\cdot\nu}{(\omega^2+\nu^2)\cdot\omega} = 1 - \frac{\omega_p^2\cdot(\omega - j\nu)}{(\omega + j\nu)\cdot(\omega - j\nu)\cdot\omega} = 1 - \frac{\omega_p^2}{\omega\cdot(\omega + j\nu)}$$

$$\varepsilon_2 = 4\pi\cdot\alpha_2$$

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# Synthesis of Zirconium Containing Mesoporous Material for the Efficient Catalytic Esterification of Benzyl Alcohol and Acetic Acid

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*Keywords:* *Zr-MCM-41, benzyl alcohol, acid acetic, esterification, calcinations.*

*GJSFR-B Classification :* *FOR Code: 250399p*

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## I. INTRODUCTION

Esterification is an industrially important reaction, which is one of the methods used to produce ester compounds. These organic esters are intermediates in the synthesis of fine chemicals, drugs, plasticizers, food preservatives, pharmaceuticals, cosmetics and auxiliaries [1]. Esters are normally produced by a batch process in industries using mineral acid catalysts such as hydrofluoric acid, sulphuric acid or Lewis acid catalysts like $AlCl_3$ or $BF_3$ [2]. Mineral acids are known as corrosive and virulent, so they need to be neutralized after the completion of the reaction, while in the process catalyzed by metal containing Lewis acid catalysts, the excess water has to be removed carefully after the reaction [3].However, it leads to the formation of large amounts of waste [4, 5]. Moreover, all these catalysts are typically categorized as hazardous substances and hence undesirable from the environmental point of view. Therefore, there is a global effort to replace hazardous and environmentally harmful catalysts with ecofriendly alternatives [1, 5].The purely siliceous Si-MCM-41 is structurally stable towards thermal treatment, hydrothermal treatment with steam at mild conditions, mechanical grinding and also towards acid treatment at mild condition. Since, mesoporous materials do not have efficient catalytic properties due to absence of catalytically active sites, so MCM-41 is often modified by incorporating certain active materials such as metal oxides, metal complexes and strong acid compounds [6].

The aim of this work is to develop a new kind of catalyst containing zirconium with ordered mesoporous structure and strong Lewis and Brönsted acidity for the esterification of benzylalcohol. The surface acidity of the silicate mesoporous molecular sieves wasgreatly enhanced by modification of the framework by the incorporation of $Zr^{+4}$ ions into the Si-MCM-41.

## II. CHEMICALS

The chemicals used for the synthesis of isomorphic substitution of Zr-MCM41 are summarized in the Table 1. All the chemicals were used as received without purification.

*Table 1 :* List of chemicals used in the synthesis of catalyst

| Chemicals | Chemical | Manufacture | Purity (%) |
|---|---|---|---|
| Cetyltrimethylammonium bromide (CTABr) | $C_{19}H_{42}NBr$ | Fluka | 99 |
| Tetraethyl orthosilicate (TEOS) | $C_8H_{20}O_4Si$ | Merck | 98 |
| Zirconium propoxide (70% in propanol) | $C1_2H_28O_4Zr$ | Aldrich | 98 |
| Ammonium hydroxide (27 wt %) | $NH_3.H_2O$ | - | - |

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## III. EXPERIMENTAL

### a) *Catalyst Synthesis*

Direct synthesis or isomorphic substitution of Zr-MCM-41 was carried out by using the method proposed by Chen, L.F. *et al*. with some modifications [7]. The Zr-MCM-41 solids were prepared using tetraethyl orthosilicate (TEOS) as Siprecursor and zirconium propoxide (70% in propanol) as Zr source, along with cetyltrimethylammonium bromide (CTABr) as surfactant template. The typical preparation procedure of a Zr-MCM-41 sample with a molar ratio of Si/Zr =5, 10, and 20 is as follow: first of all, two solutions were prepared, the first solution was made by adding given amount of zirconium tetra-propoxide (0.0475,0.095 and 0.19 mol) into given amount of TEOS (0.95 mol) with stirring; the second solution was made by adding given amount of CTABr (0.35 mol) into 110mL hot water (around 50° C) with stirring, followed by addition of 110 mL $NH_3.H_2O$ (28wt %).

Then, the first solution was added gradually into the second solution. The mixture was strongly stirred during the addition for about 2 hours. After that a gel was formed. The gel is left in the ambient temperature to be cooled. Then, the gel is loaded into stoppered Teflon bottle and it maintained at 100°C for two days. Once the gel is cooled to room temperature, the solid powder was recovered by filtration and it was washed with 500mL of deionized water for several times. The white solid powder was heated in the oven for one day at 70°C. After that, the sample was placed into the furnace and calcined at 600°C for about 6 hours in the air. The heating rate is 1°C/min. It can be seen from Table 2 that the molar composition of the gel mixture is the following: 0.95TEOS : 0.35CTABr : $0.65NH_3.H_2O$ : X-zirconium tetrapropoxide : $0.55H_2O$. In this study, the amount of X was varied according to desired Si/Zr molar ratios of 5, 10, 20.

*Table 2 :* Sample codes for different Si/Zr **molar** ratio of the materials

| Sample | Si/Zr | Si content, mole | Zr content, mole |
|---|---|---|---|
| Si/Zr=20 | 20 | 0.95 | 0.0475 |
| Si/Zr=10 | 10 | 0.95 | 0.095 |
| Si/Zr=5 | 5 | 0.95 | 0.19 |

### b) *Characterization of Zr-MCM-41*

In this study, comprehensive characterization techniques were utilized in order to elucidate and provide unambiguous structural information and physicochemical properties ofZr-MCM-41. The Powder X-Ray Diffraction (XRD)is Bruker D8 Advance powder diffractometer with Cu-Kα as the radiation sources with λ= 1.5418 Å at 40 kV and 40 mA. The Fourier Transform Infrared Spectroscopy is done using a Perkin Elmer One FTIR Spectrometer. The FTIR spectrums are recorded in a spectral range of 4000-400 $cm^{-1}$. The Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-Vis DR) is a Perkin-Elmer Lambda 900 spectrometer. A spectrum was measured in the wavelength scale of 190-800 nm. The Scanning Electron Microscopy (SEM) is Philip XL40 field emission scanning electron microscope operating at 15kV. The nitrogen adsorption measurements were carried out at 77 K on ASAP 2010 volumetric adsorption analyzer. The evaluation and analysis of the strength and type of acid site, pyridine adsorption on the samples was performed on the 170SX FTIR spectrometer.

### c) *Catalytic testing*

The performance of Zr-MCM-41was measured in terms of conversion of benzyl alcohol and selectivity to benzyl acetate in competition with etherification reaction. The Blank reactions were also carried out in the absence of a catalyst. The main product was found to be benzyl acetate. Experiments were designed by varying the amount of the catalyst, the molar ratios of the reactants, the reaction temperature and the reaction period.

## IV. RESULTS & DISCUSSION

### a) *Characterization of Zr-MCM-41 catalyst*

#### i. *XRD analysis*

XRD patterns of the as-made and calcined Zr-MCM-41(Si/Zr = 20) is displayed in Figure 1a. The Samples have four peaks that are indexed to (100), (110), (200) and (210) reflections, which correspond to well ordered hexagonal pore systems, characteristic of MCM-41-type mesoporous materials. In comparison with the as-made solids, after calcination at 600°C, several variations were observed: the positions of the (110) peak shifted towards larger 2θ values which results a reduction in the spacing distance between the (100) planes ($d_{100}$) and lattice parameters ($a_0$). The groups of Si-OH and/or Zr-OH condensate considerably during calcinations which leads to the contraction of unit cell dimension towards fresh solids. There is a remarkable enhancement in the intensities of the diffraction peaks after calcination, which must be corresponded to the surfactant removal molecules in the process of calcination. As shown in the Table 3, the pore wall thickness ($t= a_0- d_p$) is obtained from lattice cell parameter ($a_0= 2d_{100}/3^{1/2}$) and the pore diameter ($d_p$), is thicker relative to that of Si-MCM-41(t=1.92 nm). The slight increase in pore wall thickness (t) is coincident with the enhancement of zirconium content which points out the incorporation of zirconium into the framework. Particularly, after calcination, the intensities of the XRD peaks increase significantly in the Zr-MCM-41(Si/Zr=20), indicating that the structural ordering is increased and ordered hexagonal pore system retained without collapsing. It is remarkable that in the calcined MCM-41 solids, the intensities of the XRD peaks vary with zirconium content. The calcined sample with a Si/Zr=10 shows a lower peak intensity than the calcined sample with a Si/Zr=20 (see Fig. 1b).The intensities of all the peaks decrease as the Si/Zr molar ratio decreases from 20 to 10 and then, decrease with further increase of the zirconium content.

The calcined sample with a Si/Zr=20 shows the highest peak intensity, and the calcined sample with Si/Zr=5 shows the lowest peak intensity, indicating that a too high zirconium content may lower the structural ordering in the resultant material (see Fig. 1c). It is possible that too many zirconium ions incorporated into the framework of Si-MCM-41, might result in a partial collapse of the mesostructure. As shown in Table 3, the wall thickness largely increases by increasing the zirconium content, until the Si/Zr molar ratio decreases to 5, indicating the incorporation of zirconium into the framework.

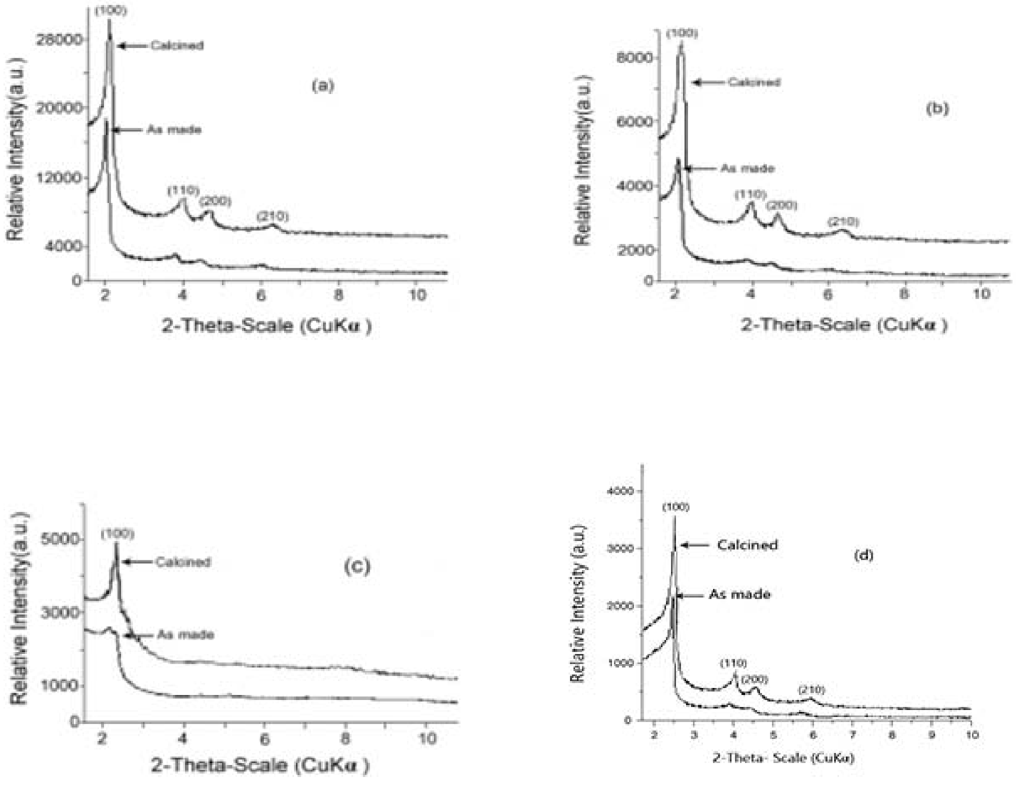


*Figure 1 :* XRD patterns of the as-made and calcined Zr-MCM-41:(a)Si/Zr=20, (b)Si/Zr=10, (c) Si/Zr=5 and (d) Si-MCM-41

*Table 3 :* Structural data obtained from $N_2$ physical sorption isotherms and XRD of Zr-MCM-41

| Si/Zr | hkl | 2θ(CuKα) | $d_{100}$(nm) | $a_0$(nm) | $d_p$(nm) | t(nm) |
|---|---|---|---|---|---|---|
| 20 | 100 | 2.38 | 3.76 | 4.38 | 2.45 | 1.93 |
| 10 | 100 | 2.34 | 3.83 | 4.43 | 2.48 | 1.95 |
| 5 | 100 | 2.32 | 3.87 | 4.49 | 2.51 | 1.98 |
| ∞ | 100 | 2.41 | 4.02 | 4.64 | 2.72 | 1.92 |

### ii. *Textural properties*

Figure2 (a, b, c) shows the loops of the $N_2$ adsorption-desorption isotherms of the calcined Zr-MCM-41 samples. Four regions are observed: The first stage, at $P/P_0 < 0.2$, is due to a monolayer adsorption of nitrogen molecules on the walls of the mesopores. The second stage, at $0.3 < P/P_0 < 0.4$, determined by a high increase in adsorption, is due to capillary condensation inside the mesopres. The third stage, the adsorption isotherm is the horizontal section beyond the $P/P_0$ of 0.4, which is corresponds to multilayer adsorption on outer surface of the particles. The last stage at $P/P_0 > 0.9$ can be related to capillary condensation in the solid with high zirconium content. The pore diameter distribution of the samples with low zirconium content, Si/Zr=20 and 10, shows only a single peak around 21.90 and 22.5 Å. However, in the sample with high zirconium content, Si/Zr=5, some larger pores appear, which is due to the formation of mesopores between particles. The Si/Zr=5 sample shows a single peak around 24 Å which is higher than single peaks for both samples of Si/Zr= 20 and10. This is due to the collapse of mesopores in the solids with high zirconium content. The high zirconium content in the mesoporous solids reduces the pore volume and the surface area. The determination of the mesopore volume was based on the $N_2$ adsorbed at $P/P_0=0.4$. The surface area of the mesoporous solids were 997, 811 and 446 $m^2/g$ for Si/Zr= 20, 10 and 5 respectively.

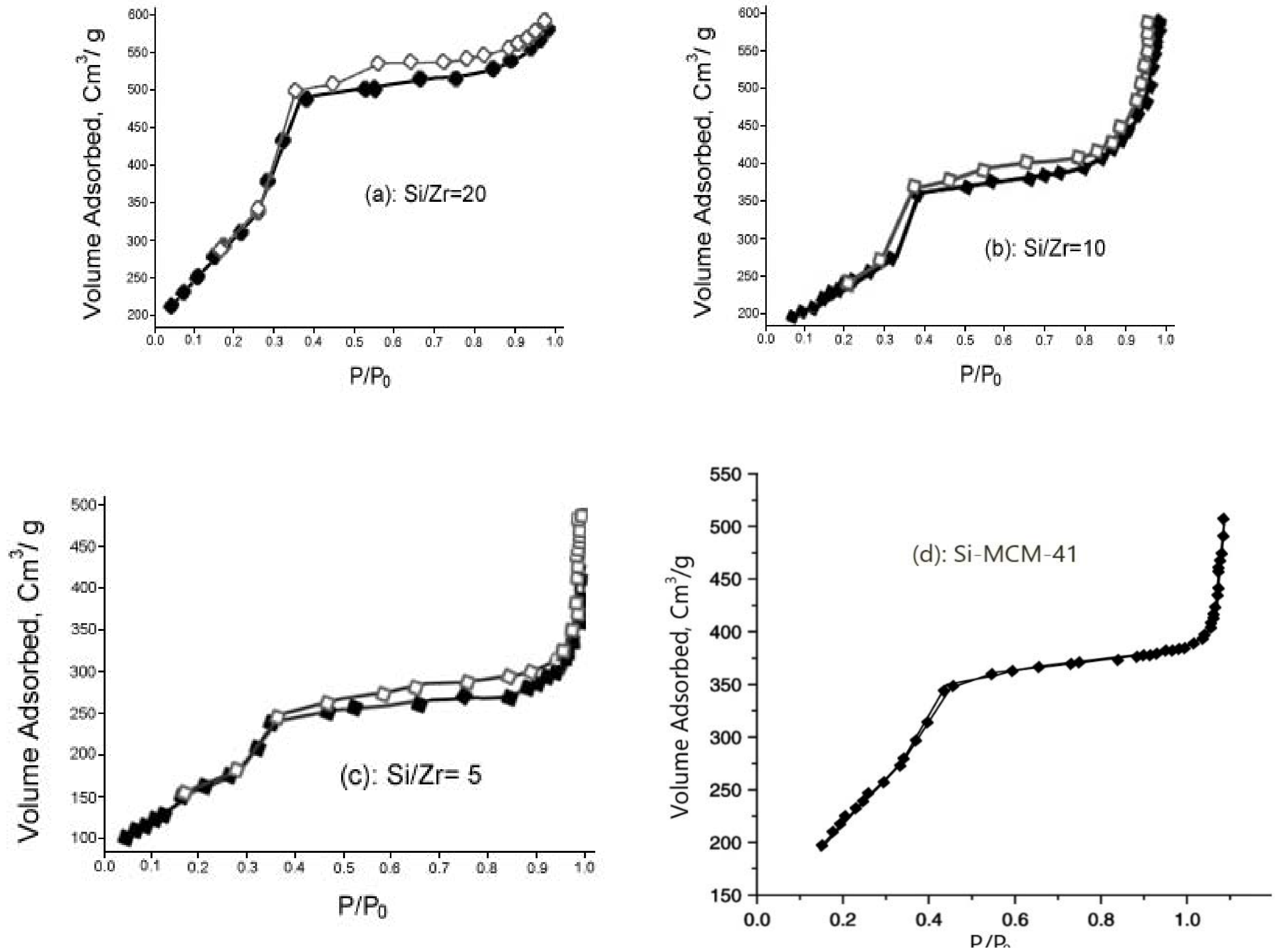
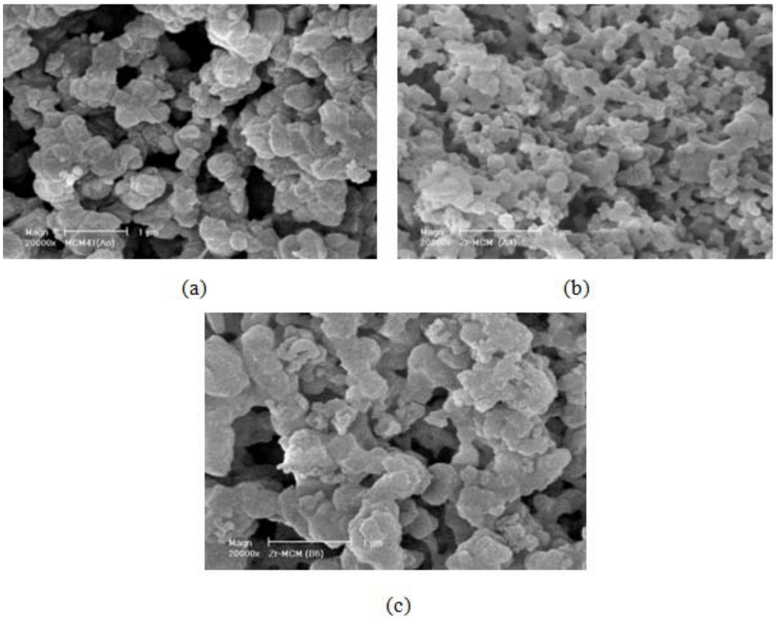


*Figure 2 :* N2 adsorption-desorption isotherm of the calcined Zr-MCM-41:(a) Si/Zr=20, (b)Si/Zr=10,(c) Si/Zr=5 and (d)Si-MCM-41

iii. *Morphology features*

The morphology of MCM-41 and Zr-MCM-41 materials was studied by scanning electron microscopy. Typical SEM images are given in Figure 3. It can be seen that, whatever the zirconium loading of MCM-41 and Zr-MCM-41 (Si/Zr=10 and 20), the morphology of parent MCM-41 and Zr-modified samples consist of particles less than 1$\mu$m with irregular shapes, probably due to agglomeration of particles. It is obvious that smaller particles can be recognized in the sample of Si/Zr=20.


(a) (b)

(c)

*Figure 3 :* SEM image of the samples (a)MCM-41, (b) Zr-MCM-41 (Si/Zr=20), (c) Zr-MCM-41(Si/Zr=10)

iv. *UV-Vis DR analysis*

The calcined Zr-MCM-41 solids were also characterized with UV-Vis DR spectroscopy. For the purpose of comparison, the UV-Vis DR analysis of the pure Si-MCM-41 sample was also included as reference. All the Zr-MCM-41 solids show a band around 200 nm which is due to the charge-transfer transition from an oxygen ion to a Zr(IV) ion (see Fig.4), relating to the excitation of electrons from the valence band (2*p* character in O) to the conduction band (4*d* character in Zr).

The Si-MCM-41 sample did not display any peak in the same wavelength range, between 190 and 800 nm. Usually, in the UV-V is spectrum, an absorption band around 250 nm corresponding to $Zr^{+4}$ in monoclinic $ZrO_2$ phase and an absorption band at around 300 nm of octahedral $Zr^{+4}$ in the perovskite-type $SiZrO_3$ can be observed [8].Our results suggest that the zirconium ions in the Zr-MCM-41 samples are in a different state than in pure $ZrO_2$ or $SiZrO_3$ (or pure Si-MCM-41 solid) and no separated $ZrO_2$ phase was formed in our samples. This is another strong evidence of zirconium incorporation into the framework of the mesoporous materials. The intensity of the band increases as the zirconium concentration increases, once again, indicating that more zirconium ions are incorporated into the Si framework at higher zirconium contents.

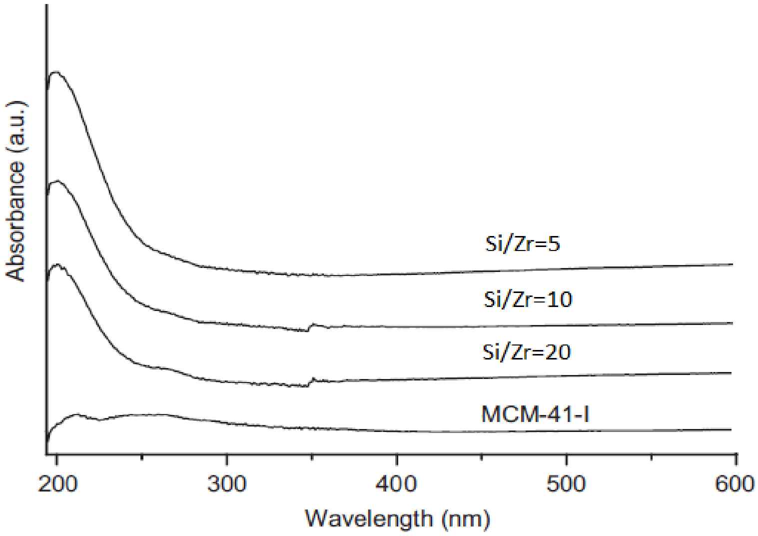


*Figure 4 :* UV-Vis defuse reflectance spectra of MCM-41 and Zr-MCM-41(Si/Zr=20, 10 and 5)

### b) *FTIR studies*

The FTIR technique was used for the surface characterization of the Zr-MCM-41catalyst [9]. As shown in Figure 5, the bands at 1621–1641 cm$^{-1}$ are aroused by the vibration of the adsorbed water molecules; the band around 811 cm$^{-1}$corresponds to the bending vibration of Si–O; the band about 460 cm$^{-1}$ is from the bending vibration of Si–O. The band around 3500 cm $^{-1}$ was attributed to the Si-OH stretching bond. As can be observed in Figure 5, for the pure silica MCM-41 sample, the band at 1081 cm$^{-1}$ is from the anti symmetric stretching vibration of Si–O–Si. The Si–O–Si bands of the Zr-MCM-41 shifted to 1079 cm$^{-1}$, at the same time, we can also observe that the intensity of the band 1081 cm$^{-1}$ is gradually reduced as the zirconium content increases. The red shift in the Si–O–Si band of Zr-MCM-41 sample with the increase in the zirconium content is probably due to the replacement of Si ions in the framework by Zr$^{+4}$ ions.

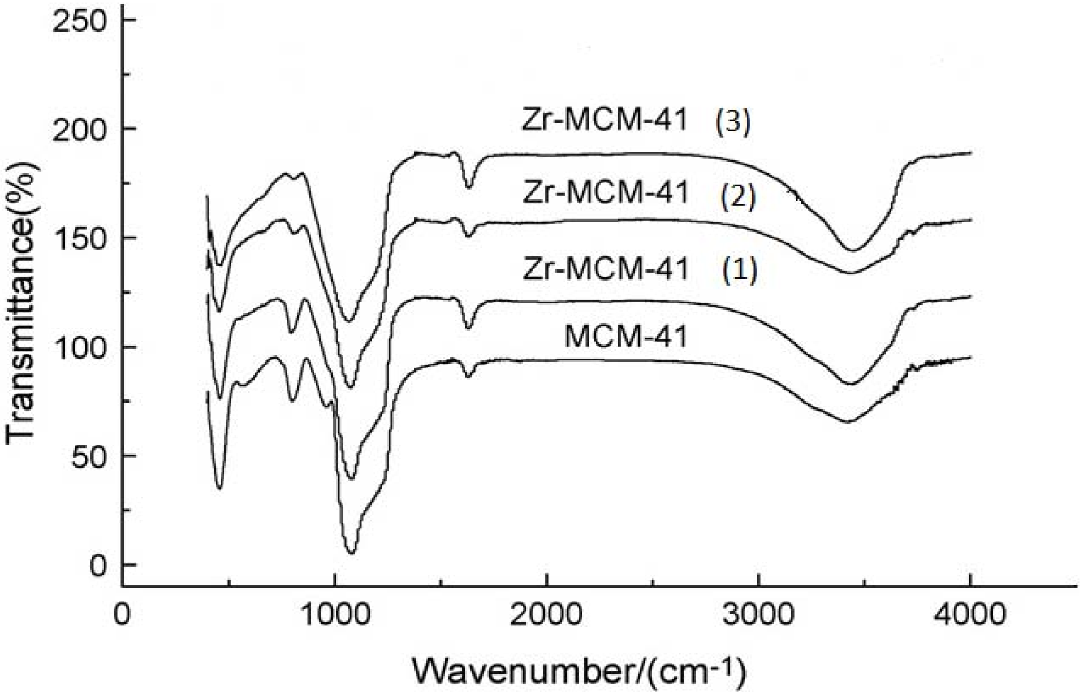


*Figure 5 :* FTIR Spectrums of Zr-MCM-41(Si/Zr=20 (1),Si/Zr=10 (2),Si/Zr=5 (3)) and MCM-41

### c) *Surface acidity of the Zr-MCM-41 solids*

Figure 6 shows a set of in situ FTIR spectra of pyridine adsorption on the samples of Zr-MCM-41. In the Zr-MCM-41 both Lewis and Brönsted acid sites are formed. These mesoporous solids are heated to 100°C inside IR cell under vacuum. Lewis acid sites formed on the samples with the Si/Zr molar ratios 20, 10 and 5 characterized by the absorption bands at 1445, 1580 and 1598cm$^{-1}$. The absorption band corresponding to pyridine associated with both Lewis and Brönsted acid sites was observed at 1490 cm$^{-1}$. Brönsted sites appeared in these solids as indicated by the band at 1540 cm$^{-1}$. The band at 1640 cm$^{-1}$was attributed to pyridine adsorbed on the hydroxyls ions. The intensities of all the bands corresponding to Lewis acid sites are considerably decreased with the enhancement of zirconium content; simultaneously the intensities of all the bands corresponding to the Brönsted acid sites are almost unchanged. It is known that the surface acidity of mesoporous solids is influenced by incorporation of zirconium ions in the framework. The diameter of Zr$^{+4}$ ions is much larger than that of Si$^{+4}$.Therefore, the replacement of Zr$^{+4}$ ions with smaller Si$^{+4}$ ions in the framework of solid creates the bond length of Zr-O-Si which is obviously different from that of Si-O-Si that leads to micro-strain within lattice cell. As can be seen from Fig. 6 the presence of silanol groups and small amounts of zirconium may affect the strength of Si-OH bond in the structure. Furthermore, there are several structural defects located in the framework that led to the unbalance situation in the electron charges. The variation of electron density around Si nuclei which can be considered as a result of charge unbalance, variations in electronegativity and local deformation resultig from the introduction of Zr$^{+4}$ ion into the vicinity of the hydroxyls groups carrying silicon can decrease the strength of SiOZr-O-H and SiO-H bonds [10]. This can be taken into account as one of origins which lead to an increase in the number of Brönsted acid sites on the zirconium containing mesoporous materials (Zr-MCM-41). I rewrote this part again and I made several changes and correction to it.

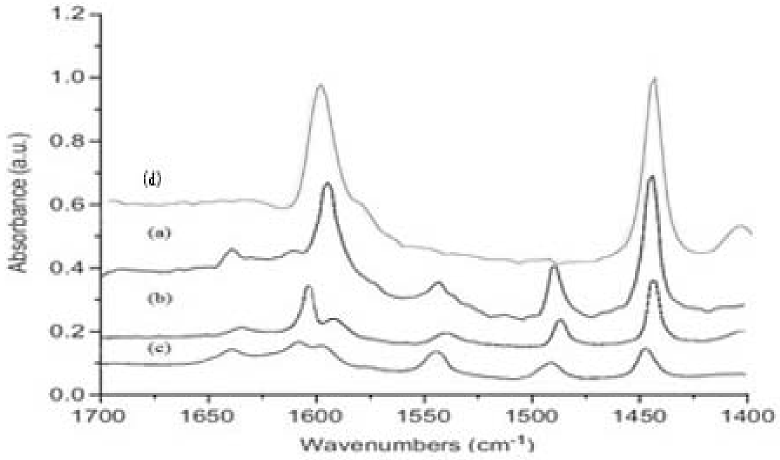


*Figure 6 :* In situ FTIR spectra of the pyridine adsorption on the various solids. The spectra were recorded at 100°C under vacuum condition; (a): Si/Zr=20, (b): Si/Zr=10, (c): Si/Zr=5 and (d): Si-MCM-41

### d) *Catalytic Test*

In this study, the acidic strength of the silicate molecular sieves (MCM-41) was greatly enhanced by the incorporation of $Zr^{+4}$ ions into the Si-MCM-41 framework. The $Zr^{+4}$ components created Brönsted acid sites on the mesoporous Zr-MCM-41.

Initial investigations of the effect of the catalyst type on the reaction yielded some interesting results (Table 4). Conversion of benzyl alcohol is between 15 and 48% for all different loadings of zirconium, selectivity for benzyl ester product is 100%. It seems that because of the less number of acidic active sites in the samples can inhibit the ether formation, since ether formation required more active acidic sites than ester formation, also the pore size of all Zr-MCM-41 samples, are probably medium, therefore they cannot accommodate the large ether molecule, and thus hinders its formation. The fact that dibenzyl ether is not formed when the reaction is carried out in the absence of any catalyst indicates the involvement of acid sites for the ether formation and the presence of these active sites within the pores of the mesoporous. The deterioration of catalytic activity observed when the Si/Zr molar ratios decreased which in turn increased the zirconium content in the mesoporous solids. The enhancement of zirconium content in the mesoporous materials leads to the variation of electron density around Si nuclei which results to the distortion of mesoporous structures with high zirconium content. Consequently, the incorporation of a proper amount of zirconium can remarkably increase surface acidities and Brönsted type acid sites in the solids.

*Table 4 :* Esterification of benzyl alcohol with acetic acid: effect of catalyst type. Acetic acid(AA):benzyl Alcohol(BA), 2:1(mol/mol); reaction time 1h; catalyst weight 0.5 g, in 383 K

| Type of Catalyst | Conversion % |
|---|---|
| Blank (MCM-41) | 15 |
| Si/Zr=5 | 19 |
| Si/Zr=10 | 35 |
| Si/Zr=20 | 48 |

#### i. *Influence of molar ratio of the reactants*

The reaction was carried out over Zr-MCM-41(Si/Zr =10 and 20) using different molar ratios of acetic acid to benzyl alcohol. In all cases, only benzyl acetate was formed. The conversion of benzyl alcohol was found to decrease with the increase in concentration of benzyl alcohol in the reaction mixture. In the all cases, the conversion decreased as the molar ratio of acid: alcohol was varied from 2:1 to 1:3. The selectivity towards the ester was constant. Also, the selectivity towards dibenzyl ether was unchanged. Selectivity towards ester and dibenzylether was always 100% and 0%, respectively. For example, in the case of Si/Zr=20, the conversion of benzyl alcohol was found to decrease with the increase in the concentration of benzyl alcohol in the reaction mixture. In the case of Si/Zr=20, the conversion decreased from 50 to 37% as the molar ratio of acid: alcohol was varied from 2:1 to 1:3. In the case of Si/Zr=10, the conversion decreased from 39 to 10% on varying the acid: alcohol molar ratio from 2:1 to 1:3.

#### ii. *Influence of catalyst concentration*

In the case of Zr-MCM-41(n=20), the amount of the catalyst was varied from 0.5 to 1.5 g while keeping the molar ratio of acid: alcohol at 2:1. The reaction was carried out at 383 K for 1 h. The conversion of benzyl alcohol increased from around 50 to 80% on increasing the weight of from 0.5 to 1.5 g. In the case of Zr-MCM-

41(n=10), the conversion increased from around 40 to 68% in the same catalyst range of 0.5–1.5 g.

iii. *Influence of temperature*

The esterification reaction was carried out in the temperature region 383–403 K while keeping the acid: alcohol molar ratio at 2:1 and the catalyst weight at 0.5 g (Table 5). In general, the conversion of benzyl alcohol increases with increase in reaction temperature. The selectivity for the ester was found constant over Zr-MCM-41(Si/Zr=5, 10 and 20).

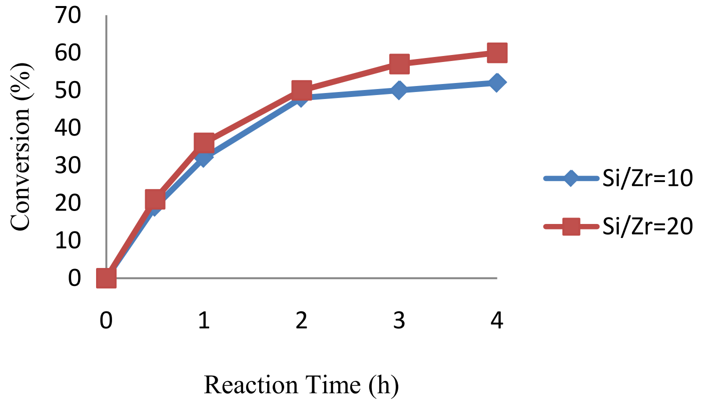
Over Zr-MCM-41(Si/Zr=5, 10 and 20), the selectivity for the ester was found to be 100% regardless of the reaction temperature. This suggests that over all samples of Zr-MCM-41, high temperatures favor the ester formation, whereas such formation is less facile at lower temperatures. Also, the temperature effect on Zr-MCM-41(Si/Zr=20, 10) was higher than Si/Zr molar ratios of 5, because the pores diameter of Zr-MCM-41(Si/Zr=20 and 10) was more regular and smaller than Si/Zr molar ratios of 5 that increased formation of ester in higher temperatures.

*Table 5 :* Esterification of benzyl alcohol with acetic acid: effect of reaction temperature AA:BA= 2:1(mol/mol); reaction time 1 h

| Si/Zr | 5 | | | 10 | | | 20 | | |
|---|---|---|---|---|---|---|---|---|---|
| T (K) | 383 | 393 | 403 | 383 | 393 | 403 | 383 | 393 | 403 |
| Conversion% | 30 | 40 | 50 | 30 | 50 | 65 | 40 | 60 | 77 |

iv. *Influence of reaction time*

The conversion of benzyl alcohol increases rapidly in the beginning and gradually levels off after 2 h (Figure7). For example, over Zr-MCM-41(Si/Zr=20) the conversion increased from around 21% in the first 30 min to around 57% in 3 h; on increasing the reaction time to 4 h, the conversion increased only to 60%. There is no significant difference in the formation of ether. The ether formation is independent of the esterification reaction.



## V. CONCLUSION

In this study, effort has been devoted to direct synthesis of highly ordered Zr-based mesoporous molecular sieves MCM-41-type through a surfactant-template approach. The molar Si/Zr ratio greatly influences the structural regularity and textural properties. XRD data show that the range ordering of the mesoporous structure of the catalyst decrease extremely as a result of the incorporation of higher amount of zirconium species. The presences of zirconium in tetrahedral coordination were indicated by UV-Vis DR spectra, which show an absorption band around 200 nm in the Zr-MCM-41. Calcination may significantly improve the structural ordering of the resultant materials. This catalyst can be applied in the esterification reaction of benzyl alcohol with acetic acid with a high yield.

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# A Comparitive Study on the Electrode Kinetics and Mechanism of Pesticides Having Different Electro Active Centres at Carbon Nano Tubes Paste Electrode

By T. Raveendranath Babu, P. Sujana & S. Rajasekhar Reddy

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*GJSFR-B Classification : FOR Code: 250603*

# A Comparitive Study on the Electrode Kinetics and Mechanism of Pesticides Having Different Electro Active Centres at Carbon Nano Tubes Paste Electrode

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## I. Introduction

Although pesticides have many harmful effects on environment they have been used in agriculture field to increase yield, improve food quality and save time and money. But the uniform use of pesticides can cause soil, water and food contamination. Their detection concerns agriculture health care professionals and regulatory agencies. At present, they are mostly determined in the laboratory by methods such as chromatographic and spectroscopic methods. Although they have high sensitivity, these methods suffer from many disadvantages, in requiring skilled technicians, being complex, costly and time consuming and their use online for continuous monitoring is impractical. Because large number of samples have to be measured, the development of fast automated and inexpensive methods are of great interest. voltammetric methods are suitable, sensitive and reproducible and can be applied for the analysis of pesticides in environmental matrices[1-10].

More recently electrochemical techniques become extremely useful for the monitoring of pesticides in environmental samples. This can be attributed to the introduction of highly sensitive commercial instrumentation, which yields easily interpretable data for routine quantitation at low levels. The approach has been demonstrated to have utility for number of hygienic and toxicological problems. The early voltammetric methods experienced number of difficulties making them less ideal for routine analytical uses. However, in the 1960's and 1970's significant advances were made in all areas of voltammetry, which enhanced the sensitivity and expanded repertoire of analytical methods. The coincidence of these advances with the advent of low cost operational amplifiers also facilitated the rapid commercial development of relatively inexpensive instrumentation. The common characteristic of all voltammetric techniques is that involve the application of potential (E) to an electrode and monitoring the resulting current (i) flowing through the electrolytic cell. In many cases, the applied potential is varied or the current is monitored over a period of time (t). Thus, all voltammetric techniques can be described as some function of E, i and t. Concentration of electro active species is forced to change by the applied potential which electrochemically reduce or oxidizes it's activity at the electrode surface. Thus, they are considered as active techniques.

Phenothrin containing >C=C< as electro active group is broad spectrum pyrithroid ester insecticide which is widely used for weed control in many agricultural crops.

Chlorpropham containing >C=O as electro active group is a plant growth regulator used for the pre-emergence control of grass weeds in falfa, Lima and snap beans, blueberries, cane berries, carrots, cranberries, ladino clover, garlic, eed grass, onions, spinach, sugar beets, tomatoes, safflower, soybeans, gladioli and woody ursery stock. It is also used to inhibit potato sprouting and for sucker control in tobacco.

Fenclorim containing >C=N- as electro active group is broad spectrum herbicide which is widely used for weed control in many agricultural crops like corn, wheat, maize and barley.

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## II. Experimental

### a) Apparatus and electrodes

Voltammetric determinations were performed using a model Meterohm Auto Lab 101 PG stat (Netherlands)Fig I. CNTPE was used as working electrode for differential pulse adsorptive stripping voltammery and cyclic voltammetry. pH measurements were carried out with an Eutech PC_510 cyber scan. Meltzer Toledo (Japan) Xp26 delta range micro balancer were used to weigh the samples during the preparation of standard solutions. All the experiments were performed at 250C.

*Fig 2 :* Meterohm Auto Lab 101 PG stat (Netherlands)

### b) Reagents and solutions

All reagents used were of analytical reagent grade. Double distilled water was used throughout the analysis. In the present investigation universal buffers of pH range 2.0 to 6.0 are used as supporting electrolytes and are prepared by using 0.2 M boric acid, 0.05M citric acid and 0.1Mtrisodium orthophosphate solutions. Samples obtained from nagarjuna agrichem and syngat india limitted

### c) Calculation of Ep And Ip

Cyclic voltammetry is perhaps a most versatile electroanalytical technique for the study of electroactive species. Its versatility combined with ease of measurement has resulted in the extensive use of cyclic voltammetry in the field of electrochemistry, inorganic chemistry, organic chemistry, and biochemistry. It is rarely used for quantitative determinations, but it is widely used for the study of the redox process, for understanding reaction intermediates and for obtaining stability of reaction products.

In this technique, the potential applied between the working electrode and the reference electrode is varied with time in known fashion in a triangular sweep mode. The forward or cathode potential sweep gives a reduction wave where as backward or anodic potential sweep gives an oxidation wave. Generally linear diffusion conditions are employed in cyclic voltammetry. Fast scan rates minimize diffusion problems.

This technique is based on varying the applied potential at working electrode in both forward and reverse directions (at some scan rate) while monitoring the current for example. The initial scan could be in the negative direction to the switching potential. At the point, the scan would be reversed and run in the positive direction. Depending on the analysis, one or more potential cycles can be performed, hence the term 'Cyclic Voltammetry'. The potential of working electrode (usually CNTPE) is controlled verses a reference electrode such as saturated calomel electrode or silver electrode. The controlling potential, which is applied across these two electrodes, can be considered in excitation signal. The excitation signal for cyclic voltammetry is liner potential scan with triangular wave form. If only a single anodic / cathodic sweep is performed the technique usually called linear potential sweep voltammetry.

The peak current in a reversible process is quantitatively expressed by

$$i_p = KACD^{1/2} V^{1/2} n^{3/2}$$

where, $i_p$=peak current in microamperes

K=Randles-Sevcik constant

A=area of working electrode in $cm^2$

C=concentration of the depolarizer in mM

D=diffusion coefficient of electroactive species in $cm^2s^{-1}$

V=scan rate in $mVs^{-1}$

n=number of electrons

Delahay indicated 2.75 x $10^5$ as the reliable value for the 'K' in the case of reversible process.

For an irreversible processes

$$i_p = 3.01 \times 10^5 n (\alpha\, na)^{1/2} AD^{1/2} CV^{1/2}$$

where, α=transfer coefficient.

$n_a$=number of electrons involved during the rate determining step and other terms have their usual significance.

The above equations are used for evaluating diffusion coefficient values of reversible and irreversible electrode processes respectively.

The nature of the irreversible process is known from following equations

(i) $E_{p/2} - E_p = 0.0565/n$ volts

(ii) $(E_p)_{anodic} - (E_p)_{cathodic} = 0.058/n$ volts

where, $E_p$=peak potential in volts

$E_{p\backslash 2}$=half-peak potential in volts

Any deviation from the above equations leads to irreversible nature of the electrode process. Absence of anodic signal on the reverse scan indicates irreversible nature of the electrode process.

$\alpha_{na}$ values can be evaluated from the equation

$E_{p/2} - E_p = 0.048/\alpha_{na}$ volts

The forward rate constant values for all irreversible processes can be evaluated using the equation

$$E_p = \frac{-1.14RT}{\alpha n_a F} + \frac{RT}{\alpha n_a F} \ln \frac{k^0_{f,h}}{D^{1/2}} - \frac{RT}{2\alpha n_a F} \ln(\alpha n_a v)$$

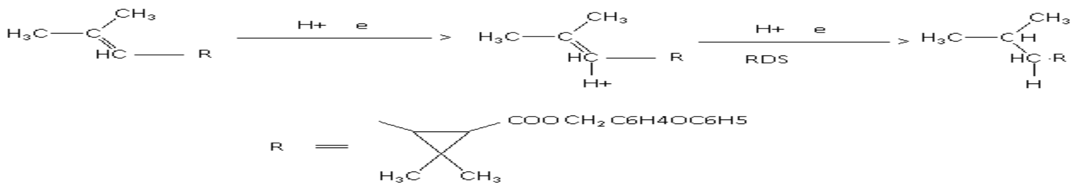
where, all the terms have their usual significance.

The most useful aspects of cyclic voltammetry[11-15] is, its application to the qualitative diagnostic of the electrode reactions which are coupled to the homogeneous chemical reactions. Cyclic voltammetry provides a particularly convenient means to study adsorption phenomena in detail. For adsorption controlled waves, the current function ($i_p / Cv^{1/2}$) increased rapidly with an increase in scan rate.

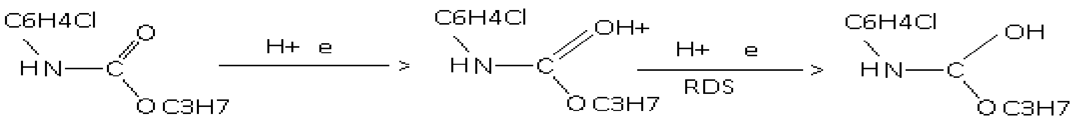
## III. Result and Discussion

Based on the nature of the peak it is found to be diffusion controlled and adsorbed on the electrode surface in the buffer systems taken, as shown by the linear plot of ip vs $v^{1/2}$ (Fig. III) which is found to pass through origin. The irreversibility of the electode process was confirmed by log plot analysis of the peak. The variability of the peak potential with scan rate also indicates the irreversible nature of the electrode process. Further Ep values are observed to have shifted towards more negative values with increasing concentration of the depolarizer. The Ep values were found to be dependent on pH and shift towards more negative values with the increase in pH of the buffer solutions, indicating proton involvement in the electrode process.

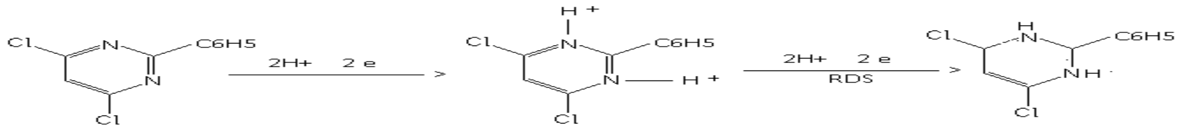
The values for transfer coefficient ($\alpha$), diffusion coefficient (D) and heterogeneous forward rate constant ($k^o_{f,h}$) at various pH values in cyclic voltammetry technique were given in Table I. The variation of diffusion current and peak current with the pH of the supporting electrolyte influences the diffusion coefficient values. Because the slight variation in diffusion coefficient values with increase in pH for isopropalin may be attributed to the decrease in the availability of protons. The forward rate constant ($k^0_{f,h}$) values were found to decrease with increase in pH. This trend shows that the electrode process becomes more irreversible with increase in pH of the solution.



*Scheme I :* Electrode mechanism of Phenothrin (at pH 4.50)



*Scheme II :* Electrode mechanism of Chlorpropham(at pH 4.50)



*SchemeIII :* Electrode mechanism of Fenclorim(at pH 4.50)

Cyclic voltammetry is mainly employed to study the mechanism and nature of the electrode process (Scheme I, II and III). Cyclic voltammetry has been specially used for the detection of reactive intermediates, if any during the electrode process. Apart from general applications of all the techniques, differential pulse adsorptive stripping voltammetry has been extensively used to establish experimental and instrumental parameters for analytical estimations of the above said pesticides and their determination. Controlled potential electrolysis has been used for the isolation of the reduction products. Determination of total number of electrons participated in the electrode process has been carried out by milli coulometric technique. The experimental data obtained from these techniques has been used to evaluate the kinetic parameters such as diffusion coefficient, transfer coefficient and heterogeneous forward rate constant values to understand the mechanistic nature and kinetics of the electrode process in universal buffer systems.

Information concerning the voltammetric properties and electron stoichiometry of pesticide and the knowledge of the reduction behaviour of similar classes of pesticides reported in literature should permit us to propose a reasonable mechanism for the reduction of the studied compounds. The reduction mechanisms proposed for the electrode processes studied are presented in Schemes I, II and III.

Phenothrin exhibits a single well-defined wave / peak obtained in pH 2.0 to 6.0 in all the techniques, corresponding to the reduction of >C=C< group in two electron process.

Chlorpropham exhibits only one voltammetric wave / peak over the pH range 2.0 to 6.0 with all techniques. This wave / peak is attributed to the simultaneous reduction of carbonyl group involving 2 electrons.

Fenclorim exhibits a single well-defined wave / peak obtained in pH 2.0 to 6.0 in all the techniques, corresponding to the reduction of azomethine group in two electron process. Typical cyclic voltammograms for three samples are shown in Fig. 1.0.

## IV. RECOVERY EXPERIMENTS

### a) *Analysis*

Based on the results obtained with Dp Asv at a CNTPE, differential pulse adsorptive stripping voltammery has been used for quantitative estimation of samples using both calibration and standard addition methods.

Investigated compounds was found to exhibit well resolved peak at pH 4.0, and the sharp well resolved peak was chosen for quantitative studies. Peak currents were linear over the concentration range of $10^{-7}$ M to $10^{-12}$ M with lower detection limits of 1.02x $10^{-11}$ M. The relative standard deviation and correlation coefficients for phenothrin, chlorpropham and fenclorim are found to be 1.30%, 0.998, 1.25%, 0.996 and1.26%, 0.997respectively for 10 replicates.

### b) *Recommended analytical procedure*

Standard solutions (1.0 x 10-8M) prepared in dimethyl formamide[16-18]. 1 mL of standard solution were transferred into a voltammetric cell and made up with 9 mL of supporting electrolyte (pH 4.50) and de oxygenated with nitrogen gas for 10 min, subjected to voltammetry. After obtaining the voltammogram, a small increment of standard solution of samples is added to voltametric cell and deoxygenated for 10 min and voltammogram recorded under similar conditions. In the same manner 10 voltammograms are recorded for 10 standard additions. The optimum conditions for analytical determination were found to be at pH.4.50.

### c) *Determination of samples in spiked water samples*

To the filtered water known amount of samples are added. Aliquots of water samples were taken in a 25mL graduated tube buffer solution is added and analysed as described above. The recoveries of samples ranged from 99.60 to 99.80% and the results are summarized in Table II.

## V. CONCLUSION

From the results, it is concluded that phenothrn, cloropropham and fenclorim are found to exhibit a single well resolved wave / peak in the buffer systems studied (pH 4.50) owing to the reduction of electro active group. It can be seen from the above mentioned results and findings that modern electro analytical methods may even today play a very useful role in the field of monitoring the persistence of various pesticides having different electro active groups in different matrices such as environmental samples, food and drinks, aquatic samples etc. Remarkably new electrode materials and arrangements can greatly stimulate further development in this field.

*Table I :* Typical cyclic voltammetric data of phenothrin, chlorpropham and fenclorim at pH:4.50

| Sample | -Ep/V | Ip/nA | $\alpha n_a$ | DX$10^6$/cm$^2$S$^{-1}$ | $K^0_{f,h}$/cm S$^{-1}$ |
|---|---|---|---|---|---|
| Phenothrin | 1.60 | 6.5 | 0.42 | 2.12 | 7.20 x $10^{-2}$ |
| Chlorpropham | 0.60 | 5.8 | 0.30 | 1.60 | 3.32 x $10^{-3}$ |
| Fenclorim | 1.15 | 7.5 | 0.52 | 2.10 | 6.89 x $10^{-6}$ |

*Table II :* Recoveries of phenothrin, chlorpropham and fenclorim in spiked water samples

| Name of the sample | Amount added (µg/mL) | Amount found (µg/mL) | *Recovery (%) | Standard deviation% |
|---|---|---|---|---|
| Phenothrin | 3.0 | 2.97 | 99.80 | 0.30 |
| Chlorpropham | 5.0 | 4.89 | 99.60 | 0.25 |
| Fenclorim | 7.0 | 6.95 | 99.70 | 0.26 |

**Average of 10 replicates*

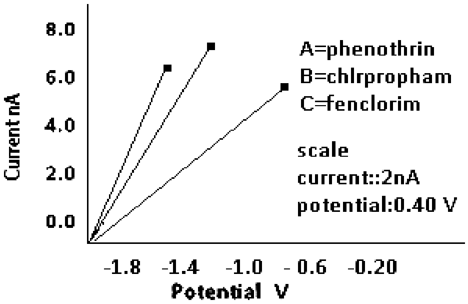


*Fig. I :* Peak current Vs half wave potential curves of samples at CNTPE , pH 4.50, Concentration: 0.5 mM; scan rate : 45 mVs$^{-1}$

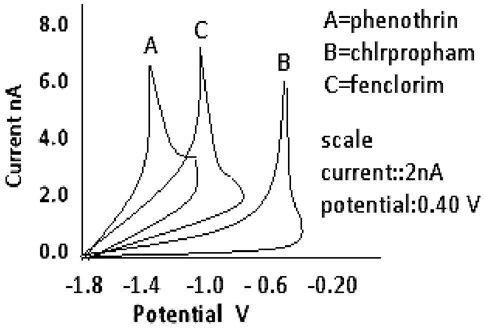


*Fig. II :* Typical cyclic voltammogram of samples at CNTPE, pH 4.50,Concentration: 0.5 mM; scan rate : 45 mVs$^{-1}$

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# Spectrophotometric Determination of Sodium Salicylate in Pharmaceutical Preparations by Coupling with Diazotized Para-Amino Benzoic Acid

By Mohauman Mohammad AL-Rufaie

*Kufa University*

*Abstract-* A rapid, sensitive and simple spectrophotometric procedure for the assay of the smaller amounts measures from sodium salicylate at pharmaceutical preparations (topical-solution) was examined. The procedure is focus on a diazotization and reaction coupling between sodium salicylate and diazotized para-amino benzoic acid in alkaline medium for the formation of an intensive bright yellow soluble water colour which was being stable, which gives highly absorption at 452nm. The law of Beer was Introduced on the range of concentration from(2-30) μg.ml$^{-1}$ of sodium salicylate, the molar absorptivity and the sensitivity of Sandell index were $8.5013\times10^{3}$ l mol$^{-1}$ cm$^{-1}$, 0.0188 μg/cm$^{2}$ subsequently, The procedure does not need to the control of temperature and the extraction by the solvent. The perfect circumstances for all colour increasing are portrayed and the examined procedure has been very good application on the assay of sodium salicylate at topical- solution preparations. The general excipients materials and additives did not affect the examined procedure.

*Keywords: diazotization coupling reaction, spectro- photometric determination, sodium salicylate, para-amino benzoic acid.*

*GJSFR-B Classification : FOR Code: 030599*

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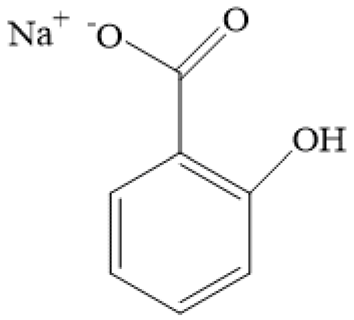
*Keywords: diazotization coupling reaction, spectrophotometric determination, sodium salicylate, para-amino benzoic acid.*

## I. INTRODUCTION

Sodium salicylate is the crystalline powder and white or almost white colour, or crystals with small, colourless or flakes shiny, water freely soluble, ethanol sparingly soluble (96per cent).It is a sodium 2-hydroxybenzene carboxylate, $C_7H_5NaO_3$, where as its chemical structure is [1]



Sodium salicylate was a salt for sodium with salicylic acid. It was formed by the reaction between sodium phenolate and carbon dioxide by using higher pressure and temperature. In the literature ,Where it had extracted by methyl salicylate that it was obtaining from winter green plants or from sweet birch tree that result from the bark ) by adding it with surplus of consented solution (sodium hydroxide) and making reflux operation for it with heating.[2]

The substance is utilized as therapy as an antipyretic and a pain relieving. Sodium salicylate additionally performs about as non-steroidal calming (NSAID) drug , also it affects as anti cancer in the Infected cells [3][4][5 and otherwise necrosis.[6] It was using as Potential alternative for aspirin drug that was giving to sensitive people for this drug .It may additionally be utilized as a phosphor for the discovery of vacuum ultraviolet radiation and electrons.[7]

In the present work, the stable diazotized para-amino benzoic acid reagent has been proposed to determine sodium salicylate in pharmaceutical preparations(topical-solution) by the reaction (azo-coupling) in basic medium. The serious splendid yellow that was resulting in the product .it was spectrophotometrically computed at 452 nm. The new analytical method is accurate, rapid and simple. The procedure was making a very good application in the investigation for sodium salicylate in pharmaceutical preparations(topical-solution).

## II. EXPERIMENTAL

*a) Apparatus*

- every absorbance and spectral estimations were performed on double - beam applied UV-Visible 160 digital recording spectrometer (japan).
- Heating-cooling water bath (Haake, Fe3).
- Analytical balance (Sartorius BL 210S).
- pH meter, Jenway 3020.

## III. MATERIAL AND REAGENTS

The Chemical substances that were utilized in the procedure with very high purity degree and did not

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required to purification, all solutions were obtained by the next steps .

a) *Sodium salicylate (500 µg.ml$^{-1}$ ) solution*

This solution is supplied by dissolution for (0.05g) of sodium salicylate (SDI) in( 100) mL deionized water. This solution is at that point exchanged to a dim bottle where it is steady for no less than 1 month [1].

b) *Para-amino benzoic acid (3 x10$^{-3}$M) (Diazotized reagent solution)*

It was obtained by dissolution (0.01 gm) of para-amino benzoic acid (Fluka) with highly purity in (5mL) of deionized water after that. (2 mL) of 1 M HCl (BDH) was added and shacked well, then Continued by adding of ( 0.009 gm) from sodium nitrite (BDH) shake completely, after that the volume was diluted to (25 mL) and the was cooling at temperature degree (5°C) for 30 min, The solution was taken to a dark bottle and leaved in the refrigerator that was steady for two weeks.

c) *Hydrochloric acid (BDH) (1M)*

It was provided by dissolution reasonable measure of concentrated hydrochloric to (100 mL) by deionized water.

d) *Sodium hydroxide (BDH) (0.5M)*

It was supplied by dissolution (2.0 gm) of sodium hydroxide at (100 mL) volumetric flask, the volume was completed to the lebal with deionized water.

*Procedure:*

Separately, volumetric flasks (25mL), the volumes was increasing of (500 µg.ml$^{-1}$) sodium salicylate from the standard working solution were exchanged to cover a range between (2-30) µg.ml$^{-1}$ in the end dissolution, (0.5M) sodium hydroxide (1mL) solution, (2 mL) form diazotized para-amino benzoic acid solution ( 0.003M) are added and dissolute to the lebal by deionized water. After that it was mixing very good, then it was leaving for (15min) at (25°C), the intensive bright yellow colour for the result was gave the highly absorbance measured at 452 nm against a blank reagent that was including all the materials without the sodium salicylate and the calibration curve was built .

*Assay Procedure for salicylic acid in Pharmaceutical Preparations.*

A topical-solution sample (25 mL) was conveyed to volumetric flasks (100 mL) then it was dissolute to the mark with deionized water. An aliquot for this solution (1mL) was put in volumetric flask (25 mL), (2mL) (0.003M) diazonium agent, 1mL(0.5M NaOH), that were adding, the completed volume to the lebal by deionized water, put away for (15 minutes), the measured absorbance for this solution was at 452 nm. the salicylic acid concentrations was given by utilizing the calibration curve officially made and portrayed previously.

This procedure was obtained for 3 trade kinds for topical-solution that was giving in the following:

1- *Avomack topical –solution (MECP.Riyadh-KSA):* containing 16.7% w/w Salicylic acid according to the product label.

2- *Duofilm topical – solution ( ITD,Sligo,IRELAND):* containing 16.7% w/w Salicylic acid, according to the product label.

3- *NOCAL topical – solution ( JORDAN ):* containing 10% w/w Salicylic acid, as indicated by the item mark.

Furthermore, the % Salicylic acid produced by the suggested technique is as per the following.

*Table (1) :* Salicylic acid investigation in some pharmaceuticals by utilizing the suggested technique:

| المستحضر الصيدلاني | Conc. Salicylic Acid µg. ml$^{-1}$ | | E % | Rec. % | RSD % n=5 | Conc. Sod.Salicylate µg. ml$^{-1}$ * |
|---|---|---|---|---|---|---|
| | taken | found | | | | |
| Avomack Topical-solution | 4 | 3.977 | - 0.575 | 99.425 | 0.679 | 4.609 |
| | 16 | 15.890 | - 0.687 | 99.313 | 0.930 | 18.416 |
| | 26 | 25.770 | - 0.884 | 99.116 | 1.300 | 29.867 |
| Duofilm Topical-solution | 4 | 4.030 | + 0.750 | 100.750 | 0.590 | 4.670 |
| | 16 | 16.200 | + 1.250 | 101.250 | 1.010 | 18.775 |
| | 26 | 25.880 | - 0.461 | 99.539 | 0.903 | 29.994 |
| NOCAL Topical-solution | 4 | 3.960 | - 1.000 | 99.000 | 0.499 | 4.712 |
| | 16 | 15.920 | - 0.500 | 99.500 | 0.841 | 18.451 |
| | 26 | 26.400 | + 1.538 | 101.538 | 1.410 | 30.597 |

**Every of the values that was utilizing in the table, It was relates with the quantity of Sodium salicylate, It was result from the multiply of the quantity of the salicylic acid per the sample by the conversion factor of 1.159, which was being equal to the output of dividing the molecular weight of sodium salicylate on the molecular weight of the salicylic acid.*

## IV. Results and Discussion

The perfect reaction circumstances was studied, The impacts of different parameters on the optical characteristics for the azo colour have been examined and the reaction circumstances are given.

1- *Reagent volume effect:-* The diazonium reagent (0.003M) volumes was examined by utilizing the range between (0.1-5 mL) on the absorbance intensity, it was has been studying (2 mL ) volume was the perfect volume.

2- *Acid volume effect:-* the presence of acid that was adding in the suggested procedure resulted in a increasing on the absorbance intensity for the formed product, so thus, acids like $CH_3COOH$, HCl, $H_2SO_4$ and $HNO_3$ are checked up, all these acids was giving verging on equivalent intensity, therefore; HCl was chosen for the next tests and, (2 mL) volume was the perfect from the chosen acid that was obtaining Highly sensitive which it utilized in following experiments.

3- *Base volume effect of:-* the colour product formed was giving highly absorbance and it was making more stable and intense in basic medium, so that, the various basic solutions effect on the colored result were examined like ammonium hydroxide sodium hydroxide, sodium acetate, sodium carbonate and potassium hydroxide. highly stability and sensitivity were given just when the reaction was performed with the attendance of sodium hydroxide solution. The various concentrations of NaOH effect were examined, (0.1-4 M) volumes for the using base with concentration (0.5 M) appears to be ideal. The (0.5 M) NaOH volumes effect were as well examined between (0.1 to 5 mL) (1mL) volume was the perfect volume and utilizing in the next tests.

4- *Order Addition effect:-* the ideal order of addition that obtains the maximum absorption was (D+B+R) wherever (B=base, D=drug substance and R=reagent) which was choosing in the following experiments.

5- *Temperature effect:-* The produced compound the studied procedure were examined at various temperatures. the absorbance values that obtained from The outcomes demonstrate that it was staying about consistent in the range of temperature (0-70)°C, While, the absorbance value at the increasing temperatures was Reduced, demonstrating the disintegration of the result on the heating for a long time. The stability of the colored compound was between (15 - 20)°C. so that, this range of temperature was chosen in examined procedure.

6- *Reaction Time effect:-* The highly intensity of colour arrived after that the sodium salicylate was reacting instantly with the solution of reagent. It was making steady after time(15 minute). so that (15 minute) evolution time was taken as the prefect in the common method of assay .The colour resulted was steady for (2 days).

The practical circumstances for the investigation for sodium salicylate were instituted. The reaction Diazonium happened in the acidic medium [8]and ( 1M ) concentration for hydrochloric acid was chosen [9], the absorbance for the colour compound formed has been highly stable and intense in basic medium [10],

a) *Absorption spectra*[11]

The dilute solutions from sodium salicylate in under the the foregoing from the The Practical circumstances, was blending with diazotized para-amino benzoic acid in Attend the sodium hydroxide, the bright yellow intense colour compound instantly established. It gives highly absorption at 452nm.at the same time the reagent solution (blank) gives no absorption at the same wavelength. ( Fig. 1) gives the spectra of absorption. The highly absorption wavelength was at 452nm. it was yet utilized for the next determinations.

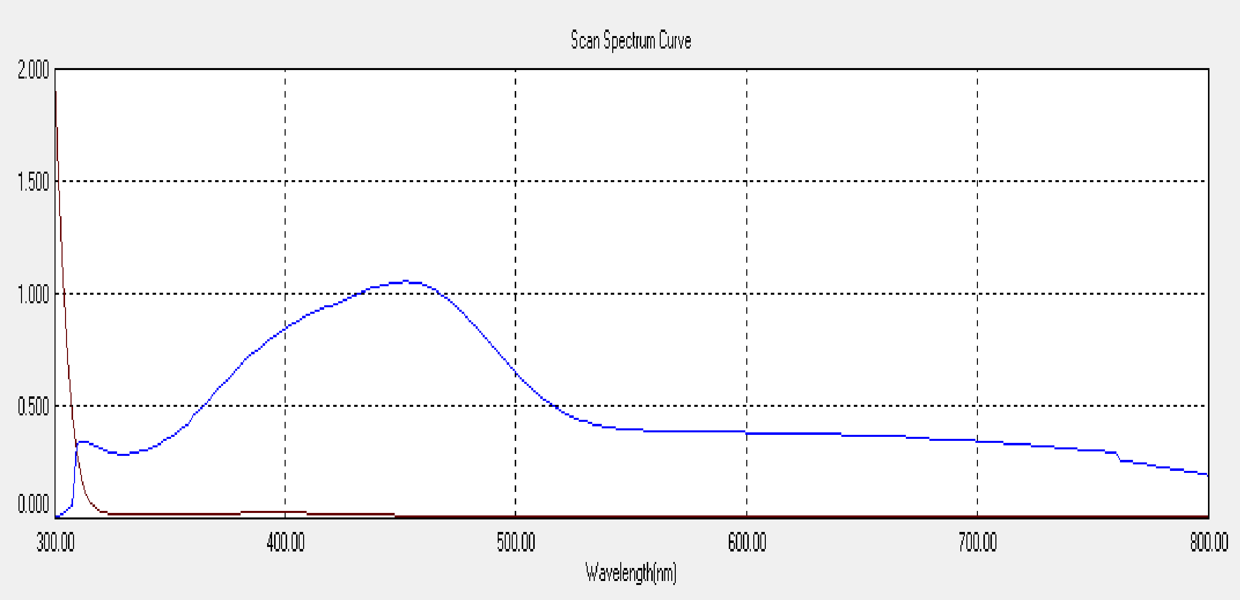


*Fig (1) :* The spectra of absorption:

A : sodium salicylate (20 µg. ml$^{-1}$) + para-amino benzoic (3x10$^{-3}$) (product compound) versus the reagent (blank).

B : the Blank reagent solution versus D.W.

b) *Calibration curve*[12]

By using the established practical circumstances. the linear relationship between the concentration of sodium salicylate and the absorbance was noted during the range of concentration (2-30µg.ml$^{-1}$) (Fig 2) and a correlation coefficient and the intercept were 0.9990, 0.0821 Respectively. The beer's law was given negative deviation at the concentrations up to (30 µg.ml$^{-1}$) from the sodium salicylate. The molar absorptivity was $8.5013\times10^3$ l.mol$^{-1}$.cm$^{-1}$.

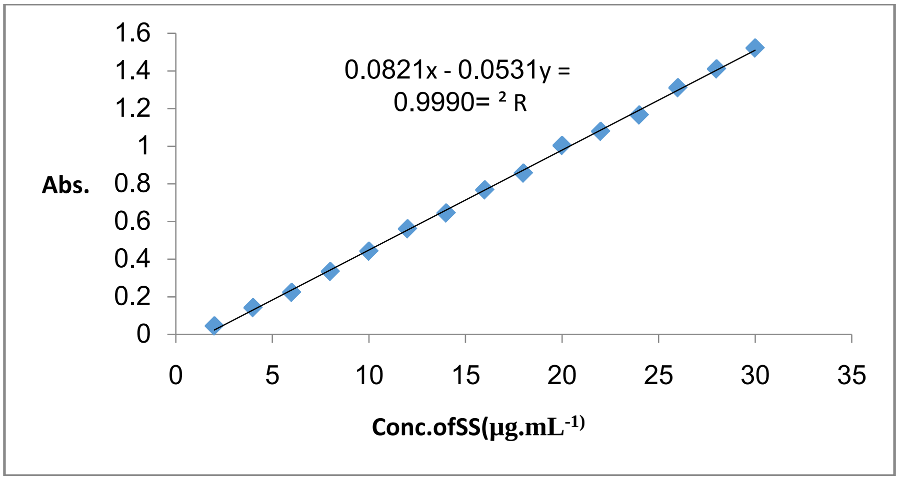


*Fig (2) :* calibration curve of sodium salicylate(ss)

c) *Precision and accuracy*[13]

To investigate the precision and accuracy of the calibration curve, sodium salicylate was designating at three various concentrations. The results appeared in Table (2) was demonstrated a good satisfactory accuracy and precision.

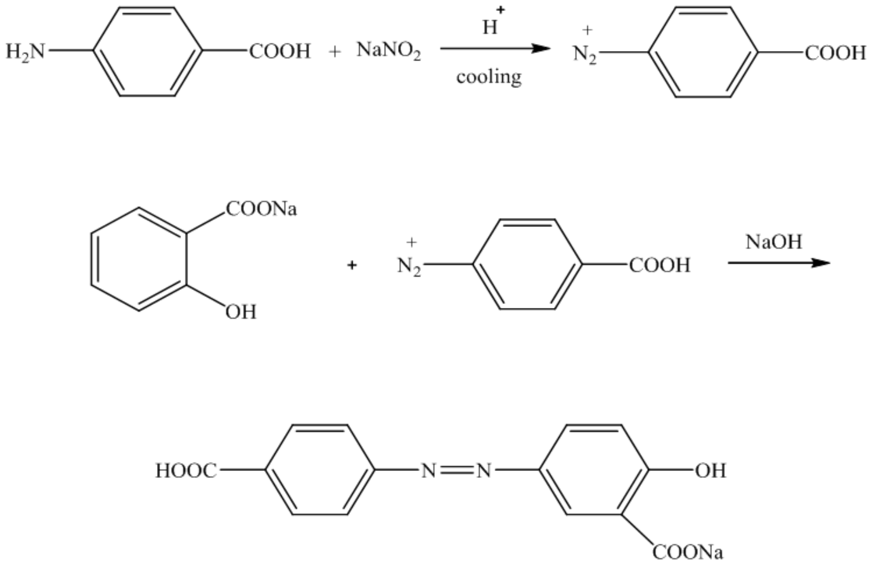
*Table (2) :* Precision and accuracy of examined procedure

| No. | Conc. of sodium salicylate mg per25ml | | Error %* | Recovery* | R.S.D %* |
|---|---|---|---|---|---|
| | present | found | | | |
| 1 | 4 | 3.964 | -0.900 | 99.100 | 0.374 |
| 2 | 16 | 16.110 | +0.687 | 100.687 | 0.990 |
| 3 | 26 | 26.200 | +0.769 | 100.769 | 1.200 |

** Average for five investigations*

*d) Product nature of and the mechanism of reaction*[14,15]

To observe the structure for the product compound (the ratio between sodium salicylate to diazotized para-amino benzoic acid) for the intense bright yellow azo colour that was resulting from reaction, mole-ratio method and Job's method of continuous variations have been utilized. The data that was resulting discover that the colour has been established by the reaction of sodium salicylate with diazotized para-amino benzoic acid with a ratio of 1:1, Fig (3&4), demonstrating a mono azo colour with possibly of the next schema:



Colored Azo dye

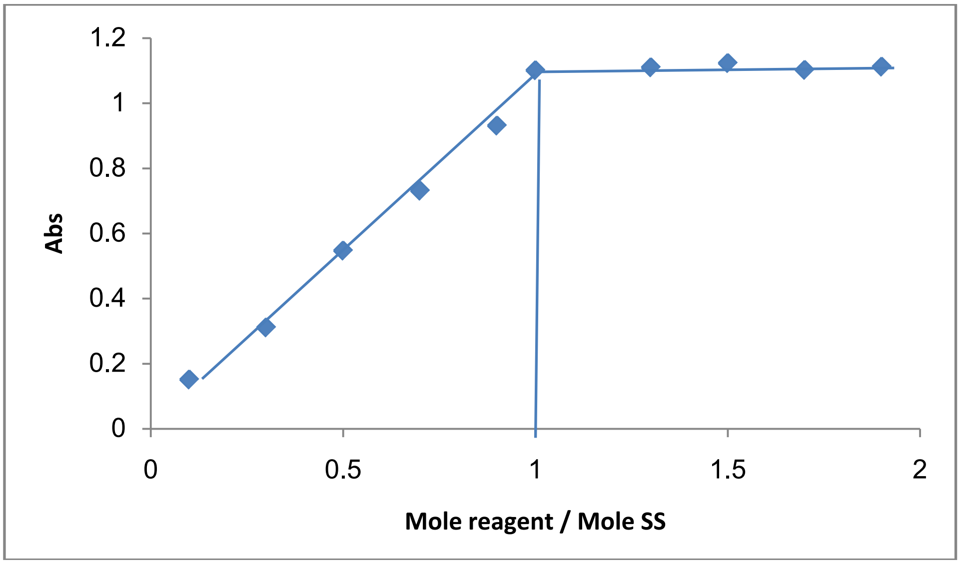
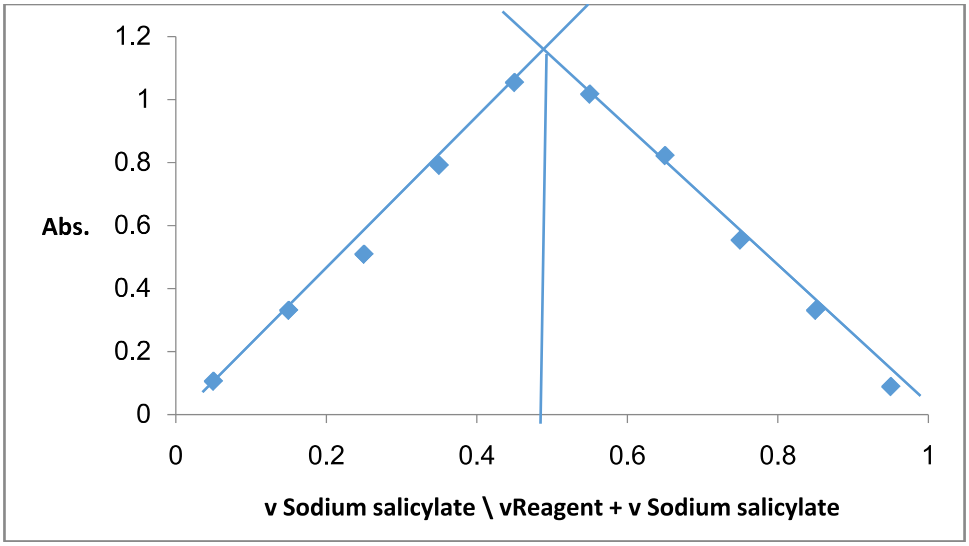


*Fig (3) :* Mole ratio plot



*Fig(4) :* Continuous variation plot

The stability constant was computed for the azo dye in the aqueous solution, by using the circumstances of practical method, the constant was equal to .28×10$^{6}$ l.mole$^{-1}$.

The regression equation was given, and the analytical data for this method are obtained in the next (Table 2).

*Table(3) :* Analytical properties of the developed method for the investigation of sodium salicylate

| Parameter | studied method |
|---|---|
| Regression equation | Y=0.0531x- 0.0821 |
| Linear range(µg ml$^{-1}$) | 2-30 |
| Correlation coefficient, r$^{2}$ | 0.9990 |
| Detection limit (µg ml$^{-1}$) | 0.064 |
| Average of recovery % | 99.702 |
| Average of RSD) % | 0.854 |
| Sandell's sensitivity (µg cm$^{-2}$) | 0.0188 |
| Molar absorptivity (l mol$^{-1}$ cm$^{-1}$) | 8.5013*10 $^{3}$ |

e) *Interferences effect*[16]

The probably analytical enforcements were evaluated for the new suggested Procedure, the interferences effect for the excipients on the different levels for the quantitative assay of (20µg.ml$^{-1}$ )of Salicylic acid by utilizing the studied procedure have been tested, the results are obtained in Table(3).

*Table (4) :* Excipients effect on the investigation of (20µg.ml$^{-1}$ ) of Salicylic acid

| Exeipient | Conc.of Salicylic acid µg.ml$^{-1}$ | E% | REC% Recovery |
|---|---|---|---|
| Talc | 19.890 | -0.550 | 99.450 |
| Lactose | 20.102 | +0.510 | 100.510 |
| Starch | 19.800 | -1.000 | 99.000 |
| Mg stearate | 19.790 | -1.050 | 98.950 |
| Poly vinylpyrolidone(pvp) | 20.220 | +1.100 | 98.900 |
| Benzoic acid | 20.125 | +0.625 | 100.625 |
| manitol | 19.880 | -0.600 | 99.400 |

* *Average for five determinations*

### *f) Application Procedure*

The examined procedure were checked up on the quantification of salicylic acid in topical- solution preparations. Three kinds of topical-solution preparations having salicylic acid were tested, they was obtaining a better precision and accuracy as appeared in (Table 5). The examined procedure were given successful comparison with the standard procedure [1].

*(Table 5) :* Application of the examined and standard procedures for the investigation of topical- solution having Salicylic acid

| Pharmaceutical preparation | Rec.* % proposed method | Rec.* % standard method |
|---|---|---|
| sodium salicylate Pure | 99.702 | 100.200 |
| Avomack Topical-solution | 99.284 | 98.000 |
| Duofilm Topical-solution | 100.513 | 102.000 |
| NOCAL Topical-solution | 100.513 | 99.600 |

* *Average for five determinations*

## V. CONCLUSION

A sensitive, simple, rapid and precise spectrophotometric procedure has been evaluation for the investigation of microgram quantities of sodium salicylate in the aqueous solution depended on the diazotization reaction coupling with para-amino benzoic acid ,the procedure does not need to the control of temperature control and solvent extraction.

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# Single Bond Lengths of Organic Molecules in the Solid State

By Peter F. Lang & Barry C. Smith
*University of London, United Kingdom*

*Abstract-* This paper discusses in detail the calculation of bond lengths of organic molecules in the solid state. It describes briefly the effect of electronegativity in covalent bond length. A set of single bond covalent radii and electronegativity values are proposed. Covalent bond lengths calculated by a modified form of the soft sphere equation (which calculated internuclear separation of different Group 1 and Group 2 crystalline salts to a remarkable degree of accuracy) show very good agreement with observed values. The results also show that electronegativity is a major influence on covalent bond lengths and the soft sphere model described here can be used to calculate covalent bond lengths of other organic/bio-organic molecules in different environments that have not yet been experimentally measured.

*Keywords: covalent bond, organic compounds, solid state, bond length calculation, electronegativity, covalent radii.*

*GJSFR-B Classification : FOR Code: 030599*

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Peter F. Lang α & Barry C. Smith σ

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## I. INTRODUCTION

Bonding and reactivity form the core in the study of chemistry. How a reaction occurs and the type of bonding that takes place depend on factors such as reaction conditions, electronegativity, covalent or ionic radii of the reacting atoms or ions. There are many different sets/series of ionic and covalent radii in the open literature and it can be confusing to the researcher or student because the values presented in the various sets can be very much different. For example, fairly recently Cordero (Cordero et al, 2008) undertook a large scale statistical exercise and published a set of covalent radii deduced from crystallographic data. Cordero discussed in detail the need of covalent radii and lack of and limitations of some experimental data. Another recent set of covalent radii (Pyykko and Atsumi, 2009) also produced by straight forward statistical exercise showed values that are completely different. It is also sometimes implied that ionic and covalent radii are additive.

It has been recognised for a long time that there are deviations from additivity of the covalent radii in the bond lengths between atoms of different elements. It was pointed out that the deviations were caused by the differences in electronegativities of the different elements (Schomaker and Stevenson, 1941). As shown in Table 1, the observed bond lengths are usually shorter than the sum of the individual covalent radii, all given in Angstrom units (Å), even for small differences in electronegativity between the two atoms forming the bond. Since experimental uncertainties are usually less than ±0.002 Å, bond lengths and radii are shown (rounded) to three decimal places of an Angstrom unit. Column 1 of Table 1 shows the particular molecule concerned and the specific bond in question is shown in bold type. Columns 2 and 3 show the covalent of the two individual atoms forming the bond, derivation of the individual covalent radii is briefly described below. Column 4 shows the electronegativity difference between the two atoms, column 6 shows the difference between the observed bond length and the sum of the two covalent radii.

*Table 1:* Difference between covalent bond lengths and simple sum of covalent radii

| (1) Molecule A-B (bond) | (2) Covalent A | (3) radii B | (4) Electronegativiy difference | (5) Observed bond length in (Å) | (6) Difference in (Å) |
|---|---|---|---|---|---|
| H-I | 0.371 | 1.333 | 0.317 | 1.609 | 0.095 |
| $H_2$-S | 0.371 | 1.072 | 0.492 | 1.336 | 0.107 |
| S-$Cl_2$ | 1.072 | 0.994 | 0.459 | 2.006 | 0.060 |
| Br-Cl | 1.141 | 0.994 | 0.284 | 2.136 | 0.001 |
| I-Br | 1.333 | 1.141 | 0.350 | 2.469 | 0.005 |
| I-Cl | 1.333 | 0.994 | 0.634 | 2.321 | 0.006 |
| B-$H_3$ | 0.848 | 0.371 | 0.186 | 1.190 | 0.029 |
| B-$I_3$ | 0.848 | 1.333 | 0.503 | 2.118 | 0.063 |
| C-$H_4$ | 0.795 | 0.371 | 0.295 | 1.087 | 0.079 |
| C-$Br_4$ | 0.795 | 1.141 | 0.372 | 1.935 | 0.001 |
| C-$Cl_4$ | 0.795 | 0.994 | 0.656 | 1.767 | 0.022 |
| $(H_3C)_2$-S | 0.795 | 1.072 | 0.197 | 1.802 | 0.065 |

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It was also pointed out that observed ionic radii differ from commonly known sets of published ionic radii with few exceptions (Adams, 1974). Our work initially concentrated on the ionic radii of Group 1 and Group 2 binary compounds (Lang and Smith, 2010). In our work we proposed a "soft" or compressible sphere approach to ionic radii and results of internuclear distances calculated by a very simple equation showed remarkable agreement with observed values (with differences between calculated and observed less than 0.01 Å in all cases).

Gaseous diatomic molecules are considered as harmonic oscillators and the covalent radii can be reliably measured (Herzberg, 1950). We used covalent radii derived from spectra (Huber and Herzberg, 1979) and radii reported in the Handbook of Chemistry and Physics (Lide, 2009) as a starting point and produced a modified equation as shown below (equation 1) to calculate bond lengths of covalent molecules in the gas phase. The derivation of the equation has been described in detail in previous work and not repeated here (Lang and Smith, 2014) .

$$D[AB] = [A]^{1} + [B]^{1} - C[\mathrm{abs}(x_a - x_b)^{r}] \qquad ...(1)$$

In equation 1 above, D[AB] is the bond length of AB and A and B. C and *r* are constants, $x_a$ and $x_b$ are the electronegativity values of A and B. C takes a value of 0.1 and the value or *r* is 0.5. We discovered that the available electronegativity scales are not completely satisfactory for use in our calculations and the electronegativity values used are taken from a new electronegativity scale (see Appendix 1) we have developed based on "adjusted" ionization energies (Lang and Smith, 2003, 2010). Calculated bond lengths of covalent compounds in the gaseous state were shown to agree very well with observed values.

## II. RESULTS

We have now extended our work to include organic compounds in the solid state and particular bond lengths calculated from equation 1 are compared with mean observed bond lengths (of specific bonds) taken from the Handbook of Chemistry and Physics and Crystal Data Determinative Tables (Donnay, Ondik and Mighell, 1973, 1979). The CRC Handbook of Chemistry and Physics provided data on bond lengths in both the gaseous and crystalline state. We have previously shown that radii in the gaseous state may be different from that in the solid state (Lang and Smith, 2014). Therefore, we have used a similar procedure as in prior work to derive covalent radii in the solid state and they are shown in Table 2.

*Table 2:* Covalent radii of some common atoms/groups and carbon bonded to different groups in Å

| Atom/group | radius | electronegativity | Atom/group | radius | electronegativity |
|---|---|---|---|---|---|
| $(sp^3)$C- | 0.770 | 2.30 | $O_2^-$C- | 0.820 | 2.77 |
| $H_3$C- | 0.761 | 2.28 | (arene)C- | 0.740 | 2.24 |
| $RH_2$C- | 0.764 | 2.29 | -C≡C- | 0.750 | 2.60 |
| $R_2$HC- | 0.771 | 2.29 | N≡C- | 0.770 | 2.80 |
| $R_3$C- | 0.794 | 2.31 | Cl- | 1.108 | 2.95 |
| -C=C- | 0.750 | 2.32 | Br- | 1.229 | 2.67 |
| OHC- | 0.760 | 2.32 | I- | 1.505 | 2.32 |
| $HO_2$C- | 0.810 | 2.80 | F- | 0.759 | 4.00 |
| HO- | 0.779 | 4.00 | O=C- | 0.764 | 2.33 |
| O=C- | 0.764 | 2.33 | $H_2$N- | 0.760 | 3.00 |

Examples of calculated bond lengths between two carbons with at least one of carbon atoms bonded to alkyl groups are shown in Table 3 below.

*Table 3:* Carbon-carbon bond lengths with calculated compared to observed values in Å

| Bond | Observed bond length | Calculated bond length | Abs % difference |
|---|---|---|---|
| $H_3C-CH_2R$ | 1.513 | 1.515 | 0.13 |
| $H_3C-CHR_2$ | 1.524 | 1.522 | 0.13 |
| $H_3C-CR_3$ | 1.534 | 1.538 | 0.24 |
| $RH_2C-CH_2R$ | 1.524 | 1.528 | 0.26 |
| $RH_2C-CHR_2$ | 1.531 | 1.535 | 0.26 |
| $RH_2C-CR_3$ | 1.538 | 1.544 | 0.38 |
| $R_2HC-CR_3$ | 1.556 | 1.551 | 0.33 |
| $H_3C-C=C$ | 1.503 | 1.491 | 0.81 |
| $RH_2C-C=C$ | 1.502 | 1.497 | 0.35 |
| $R_2HC-C=C$ | 1.510 | 1.504 | 0.42 |
| $R_3C-C=C$ | 1.522 | 1.534 | 0.79 |

The above table shows that there is very good agreement between calculated and observed with agreement of 99% or better in every case. Tables 4 and 5 show the comparison between observed and calculated results for carbon to halogen/hydroxide and other carbon bonds respectively.

*Table 4:* Comparison of carbon to halogen/hydroxide bond lengths in Å

| Bond | Observed bond length | Calculated bond length | Abs % difference |
|---|---|---|---|
| $RH_2C-Cl$ | 1.790 | 1.791 | 0.04 |
| $R_2HC-Cl$ | 1.803 | 1.798 | 0.29 |
| $R_3C-Cl$ | 1.849 | 1.822 | 1.46 |
| (arene)C-Cl | 1.739 | 1.764 | 1.42 |
| $(sp^3)C-Br$ | 1.966 | 1.939 | 1.36 |
| (arene)C-Br | 1.899 | 1.904 | 0.29 |
| -C=C-Br | 1.883 | 1.920 | 1.96 |
| $R_2HC-F$ | 1.399 | 1.399 | 0.0 |
| $R_3C-F$ | 1.428 | 1.423 | 0.35 |
| (arene)C-F | 1.363 | 1.366 | 0.24 |
| (arene)C-I | 2.095 | 2.112 | 0.83 |
| $(sp^3)C-I$ | 2.162 | 2.145 | 0.80 |
| $H_3C-OH$ | 1.413 | 1.409 | 0.29 |
| $RH_2C-OH$ | 1.426 | 1.412 | 0.97 |
| $R_2HC-OH$ | 1.432 | 1.419 | 0.89 |
| $R_3C-OH$ | 1.440 | 1.443 | 0.21 |
| (arene)C-OH | 1.362 | 1.380 | 1.79 |

*Table 5:* Comparison of other carbon bond lengths in organic molecules (in Å)

| Bond | Observed bond length | Calculated bond length | Abs % difference |
|---|---|---|---|
| $(sp^3)C-CHO$ | 1.510 | 1.516 | 0.39 |
| $(sp^3)C-C=O$ | 1.511 | 1.517 | 0.38 |
| $(sp^3)C-COOH$ | 1.502 | 1.509 | 0.49 |
| $(sp^3)C-COO^-$ | 1.520 | 1.521 | 0.09 |
| $(arene)C-CH_3$ | 1.506 | 1.481 | 1.66 |
| $(arene)C-CH_2R$ | 1.510 | 1.482 | 1.88 |
| $(arene)C-CHR_2$ | 1.515 | 1.49 | 1.74 |
| $(arene)C-CR_3$ | 1.527 | 1.508 | 1.27 |
| $(sp^3)C-C\equiv C-$ | 1.466 | 1.465 | 0.05 |
| $(sp^3)C-C\equiv N$ | 1.470 | 1.469 | 0.05 |
| $(sp^3)C-NH_2$* | 1.469 | 1.446 | 1.54 |
| (arene)C-C=C- | 1.488 | 1.462 | 1.77 |
| (arene)C-C=O | 1.488 | 1.474 | 0.94 |
| (arene)C-COOH | 1.480 | 1.475 | 0.33 |
| $(arene)C-COO^-$ | 1.484 | 1.487 | 0.22 |
| $(arene)C-C\equiv C-$ | 1.434 | 1.430 | 0.28 |
| $(arene)C-C\equiv N$ | 1.443 | 1.435 | 0.54 |
| $(arene)C-NH_2$* | 1.394 | 1.413 | 1.35 |

**(pyramidal not planer)*

Again, the comparisons as shown in Tables 4 and 5 show good agreement with the majority of values in agreement to over 99%. In order to maintain our principle of using a simple equation, the exponent *r* and the constant C are kept the same as the ones used in calculating bond lengths in the gaseous state.

## III. DISCUSSION

It was obvious from the start that covalent radii are not additive except for homonuclear bonds and for some bonds between atoms in the same group such as BrCl or where the electronegativity difference is small such as $CBr_4$. We suspect that bonds of fluorine, the hydroxyl (OH) or the amino ($NH_2$) groups with other elements may possess ionic character because they are very electronegative. If that is the case, a modified equation (Lang and Smith, 2015) should be used to calculate the bond length. Our results also demonstrate that covalent bond lengths for the same molecule may be different for the gaseous and solid states.

Research in medical and biological science has advanced by leaps and bounds in the past half a century partly as a consequence of improvements in technology and partly due to the work done and discoveries at the molecular level. For example, investigations down to the molecular level led to better understanding of cell cycle control (Twyman, 2001) may have implications in cancer research, or that hormone activity can be regulated by controlling receptor expression (Johnson and Everitt, 2000). In the study of the physiology of behaviour we know that many of the body's senses are "chemical" senses (Carlson, 2014). The properties and reactivity of biological molecules depend largely on their bonding and structure and the size and structure or molecules are broadly influenced by the length of the various bonds in the molecule. Hence, it is very useful to be able to calculate the lengths of different bonds in organic molecules. As a further example in medical science consider the replacement of damaged or diseased bone. Traditionally, it often involves patients donating their own bone tissue, which means two separate surgeries are required..In the past, ivory, which is chemically similar to bone has been used as a replacement. However, more recent work is based on the idea of using degradable material as a temporary support for the bond and enough allow natural bone to regenerate. Biodegradable materials need to be strong enough to support the human body and porous enough to all bone tissue to regenerate. To produce such material, factors such as toxicity, bond type, activity and the space between atoms forming the bonds, bond-lengths etc. need to taken into account. A new material that may be suitable have been discovered (Davies et al, 2014) but more research still need to be done.

Technetium complexes have been known for a long time as useful cancer imaging agents (Lang, 1984) and the use of other transition metals such as gold (Martin, 2010) is important as medical treatment. This shows the importance of both traditional organic and transition metal chemistry in bio-medicine Hence, there is a good case for further research into the soft/compressible spheres methodology to improve agreement between calculated and observed values.

## IV. CONCLUSION

The above calculations show that covalent radii are definitely not additive for the majority of covalent bonds in the solid state and covalent radii of atoms in the gaseous state are different from that of the solid state in many cases. Results show that our "soft" sphere approach is sound. Electronegativity differences play an important part in determining bond type and bond length. An understanding of molecular structure will become more important in drug and certain branches of medical research.

## APPENDIX 1

Electronegativities & Single Bond Covalent Radii of elements in the gaseous state

| Atomic Number | Symbol | Electronegativity | Covalent Radius (Å) |
|---|---|---|---|
| 1 | H | 2.00 | 0.371 |
| 2 | He | N/A | N/A |
| 3 | Li | 1.24 | 1.292 |
| 4 | Be | 2.14 | 0.930 |
| 5 | B | 1.81 | 0.848 |
| 6 | C | 2.30 | 0.795* |
| 7 | N | 2.82 | 0.759 |
| 8 | O | 3.39 | 0.732 |
| 9 | F | 4.00 | 0.706 |
| 10 | Ne | N/A | N/A |
| 11 | Na | 1.18 | 1.613 |
| 12 | Mg | 1.76 | 1.450 |
| 13 | Al | 1.31 | 1.200 |
| 14 | Si | 1.66 | 1.124 |
| 15 | P | 2.05 | 1.080 |

| | | | |
|---|---|---|---|
| 16 | S | 2.49 | 1.072 |
| 17 | Cl | 2.95 | 0.994 |
| 18 | Ar | N/A | N/A |
| 19 | K | 1.00 | 1.952 |
| 20 | Ca | 1.40 | 1.723 |
| 21 | Sc | 1.51 | 1.395 |
| 22 | Ti | 1.57 | 1.294 |
| 23 | V | 1.62 | 1.260 |
| 24 | Cr | 1.65 | 1.250 |
| 25 | Mn | 1.71 | 1.310 |
| 26 | Fe | 1.77 | 1.235 |
| 27 | Co | 1.84 | 1.225 |
| 28 | Ni | 1.92 | 1.187 |
| 29 | Cu | 2.02 | 1.140 |
| 30 | Zn | 2.16 | 1.199 |
| 31 | Ga | 1.31 | 1.233 |
| 32 | Ge | 1.62 | 1.234 |
| 33 | As | 1.95 | 1.230 |
| 34 | Se | 2.30 | 1.170 |
| 35 | Br | 2.67 | 1.141 |
| 36 | Kr | N/A | N/A |
| 37 | Rb | 0.96 | 2.077 |
| 38 | Sr | 1.31 | 1.880 |
| 39 | Y | 1.54 | 1.520 |
| 40 | Zr | 1.57 | 1.430 |
| 41 | Nb | 1.61 | 1.490 |
| 42 | Mo | 1.66 | 1.380 |
| 43 | Tc | 1.71 | 1.310 |
| 44 | Ru | 1.76 | 1.300 |
| 45 | Rh | 1.84 | 1.260 |
| 46 | Pd | 1.91 | 1.200 |
| 47 | Ag | 1.92 | 1.350 |
| 48 | Cd | 2.06 | 1.340 |
| 49 | In | 1.26 | 1.450 |
| 50 | Sn | 1.49 | 1.432 |
| 51 | Sb | 1.73 | 1.425 |
| 52 | Te | 2.01 | 1.340 |
| 53 | I | 2.32 | 1.333 |
| 54 | Xe | N/A | N/A |
| 55 | Cs | 0.89 | 2.200 |
| 56 | Ba | 1.20 | 2.000 |
| 57 | La | 1.28 | 1.720 |
| 72 | Hf | 1.57 | 1.428 |
| 73 | Ta | 1.73 | 1.37 |
| 74 | W | 1.81 | 1.355 |
| 75 | Re | 1.80 | 1.345 |
| 76 | Os | 1.94 | 1.350 |
| 77 | Ir | 2.06 | 1.300 |
| 78 | Pt | 2.06 | 1.220 |
| 79 | Au | 2.12 | 1.200 |
| 80 | Hg | 2.40 | 1.316 |
| 81 | Tl | 1.34 | 1.580 |
| 82 | Pb | 1.51 | 1.565 |
| 83 | Bi | 1.68 | 1.535 |
| 84 | Po | 1.90 | 1.450 |
| 85 | At | 2.12 | 1.440 |

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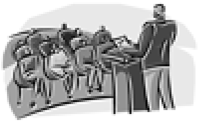

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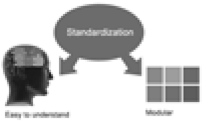

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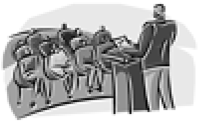
The IBOARS can initially review research papers of their institute and recommend them to publish with respective journal of Global Journals. It can also review the papers of other institutions after obtaining our consent. The second review will be done by peer reviewer of Global Journals Incorporation (USA) The Board is at liberty to appoint a peer reviewer with the approval of chairperson after consulting us.

The author fees of such paper may be waived off up to 40%.



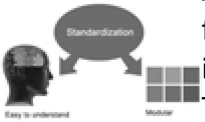
The Global Journals Incorporation (USA) at its discretion can also refer double blind peer reviewed paper at their end to the board for the verification and to get recommendation for final stage of acceptance of publication.

The IBOARS can organize symposium/seminar/conference in their country on behalf of Global Journals Incorporation (USA)-OARS (USA). The terms and conditions can be discussed separately.

The Board can also play vital role by exploring and giving valuable suggestions regarding the Standards of "Open Association of Research Society, U.S.A (OARS)" so that proper amendment can take place for the benefit of entire research community. We shall provide details of particular standard only on receipt of request from the Board.

The board members can also join us as Individual Fellow with 40% discount on total fees applicable to Individual Fellow. They will be entitled to avail all the benefits as declared. Please visit Individual Fellow-sub menu of GlobalJournals.org to have more relevant details.

We shall provide you intimation regarding launching of e-version of journal of your stream time to time. This may be utilized in your library for the enrichment of knowledge of your students as well as it can also be helpful for the concerned faculty members.



After nomination of your institution as “Institutional Fellow” and constantly functioning successfully for one year, we can consider giving recognition to your institute to function as Regional/Zonal office on our behalf.
The board can also take up the additional allied activities for betterment after our consultation.

**The following entitlements are applicable to individual Fellows:**

Open Association of Research Society, U.S.A (OARS) By-laws states that an individual Fellow may use the designations as applicable, or the corresponding initials. The Credentials of individual Fellow and Associate designations signify that the individual has gained knowledge of the fundamental concepts. One is magnanimous and proficient in an expertise course covering the professional code of conduct, and follows recognized standards of practice.

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- • This individual has learned the basic methods of applying those concepts and techniques to common challenging situations. This individual has further demonstrated an in–depth understanding of the application of suitable techniques to a particular area of research practice.

**Note :**

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- In future, if the board feels the necessity to change any board member, the same can be done with the consent of the chairperson along with anyone board member without our approval.
- In case, the chairperson needs to be replaced then consent of 2/3rd board members are required and they are also required to jointly pass the resolution copy of which should be sent to us. In such case, it will be compulsory to obtain our approval before replacement.
- In case of “Difference of Opinion [if any]” among the Board members, our decision will be final and binding to everyone.

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The Area or field of specialization may or may not be of any category as mentioned in 'Scope of Journal' menu of the GlobalJournals.org website. There are 37 Research Journal categorized with Six parental Journals GJCST, GJMR, GJRE, GJMBR, GJSFR, GJHSS. For Authors should prefer the mentioned categories. There are three widely used systems UDC, DDC and LCC. The details are available as 'Knowledge Abstract' at Home page. The major advantage of this coding is that, the research work will be exposed to and shared with all over the world as we are being abstracted and indexed worldwide.

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1. General,

2. Ethical Guidelines,

3. Submission of Manuscripts,

4. Manuscript’s Category,

5. Structure and Format of Manuscript,

6. After Acceptance.

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*Acknowledgements: Please make these as concise as possible.*

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**22. Never start in last minute:** Always start at right time and give enough time to research work. Leaving everything to the last minute will degrade your paper and spoil your work.

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**28. Make colleagues:** Always try to make colleagues. No matter how sharper or intelligent you are, if you make colleagues you can have several ideas, which will be helpful for your research.

**29. Think technically:** Always think technically. If anything happens, then search its reasons, its benefits, and demerits.

**30. Think and then print:** When you will go to print your paper, notice that tables are not be split, headings are not detached from their descriptions, and page sequence is maintained.

**31. Adding unnecessary information:** Do not add unnecessary information, like, I have used MS Excel to draw graph. Do not add irrelevant and inappropriate material. These all will create superfluous. Foreign terminology and phrases are not apropos. One should NEVER take a broad view. Analogy in script is like feathers on a snake. Not at all use a large word when a very small one would be sufficient. Use words properly, regardless of how others use them. Remove quotations. Puns are for kids, not grunt readers. Amplification is a billion times of inferior quality than sarcasm.

**32. Never oversimplify everything:** To add material in your research paper, never go for oversimplification. This will definitely irritate the evaluator. Be more or less specific. Also too, by no means, ever use rhythmic redundancies. Contractions aren't essential and shouldn't be there used. Comparisons are as terrible as clichés. Give up ampersands and abbreviations, and so on. Remove commas, that are, not necessary. Parenthetical words however should be together with this in commas. Understatement is all the time the complete best way to put onward earth-shaking thoughts. Give a detailed literary review.

**33. Report concluded results:** Use concluded results. From raw data, filter the results and then conclude your studies based on measurements and observations taken. Significant figures and appropriate number of decimal places should be used. Parenthetical remarks are prohibitive. Proofread carefully at final stage. In the end give outline to your arguments. Spot out perspectives of further study of this subject. Justify your conclusion by at the bottom of them with sufficient justifications and examples.

**34. After conclusion:** Once you have concluded your research, the next most important step is to present your findings. Presentation is extremely important as it is the definite medium though which your research is going to be in print to the rest of the crowd. Care should be taken to categorize your thoughts well and present them in a logical and neat manner. A good quality research paper format is essential because it serves to highlight your research paper and bring to light all necessary aspects in your research.

## INFORMAL GUIDELINES OF RESEARCH PAPER WRITING

**Key points to remember:**

- Submit all work in its final form.
- Write your paper in the form, which is presented in the guidelines using the template.
- Please note the criterion for grading the final paper by peer-reviewers.

**Final Points:**

A purpose of organizing a research paper is to let people to interpret your effort selectively. The journal requires the following sections, submitted in the order listed, each section to start on a new page.

The introduction will be compiled from reference matter and will reflect the design processes or outline of basis that direct you to make study. As you will carry out the process of study, the method and process section will be constructed as like that. The result segment will show related statistics in nearly sequential order and will direct the reviewers next to the similar intellectual paths throughout the data that you took to carry out your study. The discussion section will provide understanding of the data and projections as to the implication of the results. The use of good quality references all through the paper will give the effort trustworthiness by representing an alertness of prior workings.

Writing a research paper is not an easy job no matter how trouble-free the actual research or concept. Practice, excellent preparation, and controlled record keeping are the only means to make straightforward the progression.

**General style:**

Specific editorial column necessities for compliance of a manuscript will always take over from directions in these general guidelines.

To make a paper clear

· Adhere to recommended page limits

Mistakes to evade

- Insertion a title at the foot of a page with the subsequent text on the next page
- Separating a table/chart or figure - impound each figure/table to a single page
- Submitting a manuscript with pages out of sequence

In every sections of your document

· Use standard writing style including articles ("a", "the," etc.)

· Keep on paying attention on the research topic of the paper

· Use paragraphs to split each significant point (excluding for the abstract)

· Align the primary line of each section

· Present your points in sound order

· Use present tense to report well accepted

· Use past tense to describe specific results

· Shun familiar wording, don't address the reviewer directly, and don't use slang, slang language, or superlatives

· Shun use of extra pictures - include only those figures essential to presenting results

**Title Page:**

Choose a revealing title. It should be short. It should not have non-standard acronyms or abbreviations. It should not exceed two printed lines. It should include the name(s) and address (es) of all authors.

**Abstract:**

The summary should be two hundred words or less. It should briefly and clearly explain the key findings reported in the manuscript--must have precise statistics. It should not have abnormal acronyms or abbreviations. It should be logical in itself. Shun citing references at this point.

An abstract is a brief distinct paragraph summary of finished work or work in development. In a minute or less a reviewer can be taught the foundation behind the study, common approach to the problem, relevant results, and significant conclusions or new questions.

Write your summary when your paper is completed because how can you write the summary of anything which is not yet written? Wealth of terminology is very essential in abstract. Yet, use comprehensive sentences and do not let go readability for briefness. You can maintain it succinct by phrasing sentences so that they provide more than lone rationale. The author can at this moment go straight to shortening the outcome. Sum up the study, with the subsequent elements in any summary. Try to maintain the initial two items to no more than one ruling each.

- Reason of the study - theory, overall issue, purpose
- Fundamental goal
- To the point depiction of the research
- Consequences, including definite statistics - if the consequences are quantitative in nature, account quantitative data; results of any numerical analysis should be reported
- Significant conclusions or questions that track from the research(es)

Approach:

- Single section, and succinct
- As a outline of job done, it is always written in past tense
- A conceptual should situate on its own, and not submit to any other part of the paper such as a form or table
- Center on shortening results - bound background information to a verdict or two, if completely necessary
- What you account in an conceptual must be regular with what you reported in the manuscript
- Exact spelling, clearness of sentences and phrases, and appropriate reporting of quantities (proper units, important statistics) are just as significant in an abstract as they are anywhere else

**Introduction:**

The **Introduction** should "introduce" the manuscript. The reviewer should be presented with sufficient background information to be capable to comprehend and calculate the purpose of your study without having to submit to other works. The basis for the study should be offered. Give most important references but shun difficult to make a comprehensive appraisal of the topic. In the introduction, describe the problem visibly. If the problem is not acknowledged in a logical, reasonable way, the reviewer will have no attention in your result. Speak in common terms about techniques used to explain the problem, if needed, but do not present any particulars about the protocols here. Following approach can create a valuable beginning:

- Explain the value (significance) of the study
- Shield the model - why did you employ this particular system or method? What is its compensation? You strength remark on its appropriateness from a abstract point of vision as well as point out sensible reasons for using it.
- Present a justification. Status your particular theory (es) or aim(s), and describe the logic that led you to choose them.
- Very for a short time explain the tentative propose and how it skilled the declared objectives.

Approach:

- Use past tense except for when referring to recognized facts. After all, the manuscript will be submitted after the entire job is done.
- Sort out your thoughts; manufacture one key point with every section. If you make the four points listed above, you will need a least of four paragraphs.

- Present surroundings information only as desirable in order hold up a situation. The reviewer does not desire to read the whole thing you know about a topic.
- Shape the theory/purpose specifically - do not take a broad view.
- As always, give awareness to spelling, simplicity and correctness of sentences and phrases.

**Procedures (Methods and Materials):**

This part is supposed to be the easiest to carve if you have good skills. A sound written Procedures segment allows a capable scientist to replacement your results. Present precise information about your supplies. The suppliers and clarity of reagents can be helpful bits of information. Present methods in sequential order but linked methodologies can be grouped as a segment. Be concise when relating the protocols. Attempt for the least amount of information that would permit another capable scientist to spare your outcome but be cautious that vital information is integrated. The use of subheadings is suggested and ought to be synchronized with the results section. When a technique is used that has been well described in another object, mention the specific item describing a way but draw the basic principle while stating the situation. The purpose is to text all particular resources and broad procedures, so that another person may use some or all of the methods in one more study or referee the scientific value of your work. It is not to be a step by step report of the whole thing you did, nor is a methods section a set of orders.

Materials:

- Explain materials individually only if the study is so complex that it saves liberty this way.
- Embrace particular materials, and any tools or provisions that are not frequently found in laboratories.
- Do not take in frequently found.
- If use of a definite type of tools.
- Materials may be reported in a part section or else they may be recognized along with your measures.

Methods:

- Report the method (not particulars of each process that engaged the same methodology)
- Describe the method entirely
- To be succinct, present methods under headings dedicated to specific dealings or groups of measures
- Simplify - details how procedures were completed not how they were exclusively performed on a particular day.
- If well known procedures were used, account the procedure by name, possibly with reference, and that's all.

Approach:

- It is embarrassed or not possible to use vigorous voice when documenting methods with no using first person, which would focus the reviewer's interest on the researcher rather than the job. As a result when script up the methods most authors use third person passive voice.
- Use standard style in this and in every other part of the paper - avoid familiar lists, and use full sentences.

What to keep away from

- Resources and methods are not a set of information.
- Skip all descriptive information and surroundings - save it for the argument.
- Leave out information that is immaterial to a third party.

**Results:**

The principle of a results segment is to present and demonstrate your conclusion. Create this part a entirely objective details of the outcome, and save all understanding for the discussion.

The page length of this segment is set by the sum and types of data to be reported. Carry on to be to the point, by means of statistics and tables, if suitable, to present consequences most efficiently.You must obviously differentiate material that would usually be incorporated in a study editorial from any unprocessed data or additional appendix matter that would not be available. In fact, such matter should not be submitted at all except requested by the instructor.

Content

- Sum up your conclusion in text and demonstrate them, if suitable, with figures and tables.
- In manuscript, explain each of your consequences, point the reader to remarks that are most appropriate.
- Present a background, such as by describing the question that was addressed by creation an exacting study.
- Explain results of control experiments and comprise remarks that are not accessible in a prescribed figure or table, if appropriate.
- Examine your data, then prepare the analyzed (transformed) data in the form of a figure (graph), table, or in manuscript form.

What to stay away from

- Do not discuss or infer your outcome, report surroundings information, or try to explain anything.
- Not at all, take in raw data or intermediate calculations in a research manuscript.
- Do not present the similar data more than once.
- Manuscript should complement any figures or tables, not duplicate the identical information.
- Never confuse figures with tables - there is a difference.

Approach

- As forever, use past tense when you submit to your results, and put the whole thing in a reasonable order.
- Put figures and tables, appropriately numbered, in order at the end of the report
- If you desire, you may place your figures and tables properly within the text of your results part.

Figures and tables

- If you put figures and tables at the end of the details, make certain that they are visibly distinguished from any attach appendix materials, such as raw facts
- Despite of position, each figure must be numbered one after the other and complete with subtitle
- In spite of position, each table must be titled, numbered one after the other and complete with heading
- All figure and table must be adequately complete that it could situate on its own, divide from text

**Discussion:**

The Discussion is expected the trickiest segment to write and describe. A lot of papers submitted for journal are discarded based on problems with the Discussion. There is no head of state for how long a argument should be. Position your understanding of the outcome visibly to lead the reviewer through your conclusions, and then finish the paper with a summing up of the implication of the study. The purpose here is to offer an understanding of your results and hold up for all of your conclusions, using facts from your research and generally accepted information, if suitable. The implication of result should be visibly described. Infer your data in the conversation in suitable depth. This means that when you clarify an observable fact you must explain mechanisms that may account for the observation. If your results vary from your prospect, make clear why that may have happened. If your results agree, then explain the theory that the proof supported. It is never suitable to just state that the data approved with prospect, and let it drop at that.

- Make a decision if each premise is supported, discarded, or if you cannot make a conclusion with assurance. Do not just dismiss a study or part of a study as "uncertain."
- Research papers are not acknowledged if the work is imperfect. Draw what conclusions you can based upon the results that you have, and take care of the study as a finished work
- You may propose future guidelines, such as how the experiment might be personalized to accomplish a new idea.
- Give details all of your remarks as much as possible, focus on mechanisms.
- Make a decision if the tentative design sufficiently addressed the theory, and whether or not it was correctly restricted.
- Try to present substitute explanations if sensible alternatives be present.
- One research will not counter an overall question, so maintain the large picture in mind, where do you go next? The best studies unlock new avenues of study. What questions remain?
- Recommendations for detailed papers will offer supplementary suggestions.

Approach:

- When you refer to information, differentiate data generated by your own studies from available information
- Submit to work done by specific persons (including you) in past tense.
- Submit to generally acknowledged facts and main beliefs in present tense.

## THE ADMINISTRATION RULES

Please carefully note down following rules and regulation before submitting your Research Paper to Global Journals Inc. (US):

**Segment Draft and Final Research Paper:** You have to strictly follow the template of research paper. If it is not done your paper may get rejected.

- The **major constraint** is that you must independently make all content, tables, graphs, and facts that are offered in the paper. You must write each part of the paper wholly on your own. The Peer-reviewers need to identify your own perceptive of the concepts in your own terms. NEVER extract straight from any foundation, and never rephrase someone else's analysis.
- Do not give permission to anyone else to "PROOFREAD" your manuscript.
- Methods to avoid Plagiarism is applied by us on every paper, if found guilty, you will be blacklisted by all of our collaborated research groups, your institution will be informed for this and strict legal actions will be taken immediately.)
- To guard yourself and others from possible illegal use please do not permit anyone right to use to your paper and files.

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| Topics | Grades | | |
|---|---|---|---|
| | **A-B** | **C-D** | **E-F** |
| ***Abstract*** | Clear and concise with appropriate content, Correct format. 200 words or below | Unclear summary and no specific data, Incorrect form<br>Above 200 words | No specific data with ambiguous information<br>Above 250 words |
| ***Introduction*** | Containing all background details with clear goal and appropriate details, flow specification, no grammar and spelling mistake, well organized sentence and paragraph, reference cited | Unclear and confusing data, appropriate format, grammar and spelling errors with unorganized matter | Out of place depth and content, hazy format |
| ***Methods and Procedures*** | Clear and to the point with well arranged paragraph, precision and accuracy of facts and figures, well organized subheads | Difficult to comprehend with embarrassed text, too much explanation but completed | Incorrect and unorganized structure with hazy meaning |
| ***Result*** | Well organized, Clear and specific, Correct units with precision, correct data, well structuring of paragraph, no grammar and spelling mistake | Complete and embarrassed text, difficult to comprehend | Irregular format with wrong facts and figures |
| ***Discussion*** | Well organized, meaningful specification, sound conclusion, logical and concise explanation, highly structured paragraph reference cited | Wordy, unclear conclusion, spurious | Conclusion is not cited, unorganized, difficult to comprehend |
| ***References*** | Complete and correct format, well organized | Beside the point, Incomplete | Wrong format and structuring |

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