



Chemistry Times

A Science Magazine

2022

Department of Chemistry
Krishnagar Women's College,
Krishnagar, Nadia



Message from the Principal

I am glad to know that the Department of Chemistry, Krishnagar Women's College is going to publish an e-magazine titled "Chemistry Time" in the year 2022. The magazine is a collection of academic articles written by the students of the department under the supervision of the departmental faculty. Our young scholars have studied the uses of the "Polymers" in various practical fields and shared their views on the findings.

The department has always supplemented its classroom teaching by arranging seminars, study tours and workshops regularly. Now this e-magazine will provide a platform to our budding scientists to express and exchange their thoughts and views on theoretical and practical aspects of the subject.

I extend my heartiest congratulation to the Faculty and the student of the Department and wish them all success in the new endeavor.

*Dr. Natasa Dasgupta
Principal
Krishnagar Women's College*





Message from the Head of the Department

It is my great pleasure that the department of Chemistry of the college is publishing its first E-Magazine titled "Chemistry Times"-2022-23. This magazine will highlight the project works of the students of 6th semester of the department on matters/issues in the field of different divergent sectors of chemical sciences. In the curriculum of B.Sc (Hons.) syllabus, students are required to take up project works on multiple diversities of modern scientific issues. In line of the above guidelines, the Chemistry department of the college has initiated steps to motivate its students to undertake project works akin to their field of studies warranting immediate attention for solution under the guidance of their faculties. I hope that the noble endeavor of the department of Chemistry will motivate and encourage all students to undertake in innovative studies in different branches of Chemistry and take the society forward. I sincerely apologize for any error, if any, that may creep in the magazine. I also invite suggestions and advice from all to bring about improvement of the E-Magazine. Lastly, I convey my sincere gratitude to Dr. Natasa Dasgupta, Principal, of the college for her unwavering support and encouragement to publish the magazine. I also extend my thanks to our faculty members and students for their untiring efforts and immense contribution in this endeavor. I wish all success of the magazine of the department.

*Dr. Maya Biswas (Sinha)
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Contents

- **Highly Functional Polymeric Hydrogels for Wound Healing Application** Pg. 4-12
Sanjukta Dutta, Dr. Md Moniruzzaman Sk and Dr. Maya Biswas (Sinha), Department of Chemistry, Krishnagar Women's College
- **Polymer Coated Controlled-Release Fertilizer for A Sustainable Agriculture** Pg. 13-17
Arpita Singha, Dr. Maya Biswas (Sinha) and Dr. Md Moniruzzaman Sk, Department of Chemistry, Krishnagar Women's College
- **Weak Interactions** Pg. 18-24
Barna Biswas and Dr. Amit Kumar Guria, Department of Chemistry, Krishnagar Women's College
- **Electrical and Magnetic Properties of Solid** Pg. 25-31
Mausumi Khatun and Smt. Ipsita Pramanik, Department of Chemistry, Krishnagar Women's College
- **Structure-Property Relationship in Polymers** Pg. 32-38
Sonia Debnath and Smt. Nabanita De, Department of Chemistry, Krishnagar Women's College
- **Bonding Theories for Coordination Compounds** Pg. 39-45
Udita Saha and Dr. Amit Kumar Guria, Department of Chemistry, Krishnagar Women's College

Highly Functional Polymeric Hydrogels for Wound Healing Application



*Sanjukta Dutta, Dr. Md Moniruzzaman Sk and Dr. Maya Biswas (Sinha),
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Skin is the largest organ of our body that helps the body from the external environment. Intense hemorrhage is the main cause of fatality in critical situation like accidents, disaster and warfare. Although our skin possesses high skin regeneration potential, some skin defects will not heal itself and need some skin substitutes. Hence, speedy hemostasis and wound healing process have been critical. Although conventional methods of using bandages are used in controlling hemorrhage, they have some limitations like secondary tissue damage, nonbiodegradability, being unfavorable for the irregular shaped wound, etc. Thus, a remarkable progress has been found in the field of skin tissue engineering to develop new skin substitutes. Among them, hydrogels have the most potential candidate to imitate the native skin environment, due to their high porosity, tunable physicochemical characters, good biocompatibility and being favorable for wound dressing. Hydrogels can be applied as temporary or permanent dressing for several wounds to assist the regeneration and healing of the damaged dermis and/or epidermis.

Introduction

Hydrogel is a crosslinked 3D-network with hydrophilic polymers that are able to swell in water without dissolution and hold a huge amount of water and retain their structure due to cross-linking (chemical or physical) of individual polymer chains. Hydrogels are the most iconic class of soft materials. Due to the highly mimic natural extracellular matrix (ECM) properties, hydrogel has been extensively utilized in pharmaceutical and biomedical applications.

Nowadays, traditional dressings like bandages and gauzes are still broadly used in the clinic. Although, they are cost effective, but not much functional to promote hemostasis, adherence and keeping a moisture on wound site. Even, many bandages are harmful when it is being removed from the wound, they may peel off the newly generated tissue or some fibers from the bandage may be left in the wound that cause infection or secondary damage to the patients. A suitable dressing should satisfy the following characteristics:

- Easily fit to a complex wound area and its volume
- Have mechanical protection
- Maintain moisture on wound
- Eligibility for permeability of gases
- Ability of absorbing exudates
- Protect the wound from the infection of bacteria
- Be easily and atraumatically changed and removed
- Be less expensive/commercially acceptable
- Weight must be light
- Be nonallergic, nontoxic, biodegradable, biocompatible, and elastic.

Examples of commercial hydrogels for wound healing applications

Due to the numerous merits of hydrogels, a series of commercial hydrogels as wound dressings are available:

- 3M™ Kerralite Cool™ Moisture Balancing Hydrogel Dressings
- Elasto-Gel™ Wound Dressing
- Kendall™ Hydrogel Dressing
- Suprasorb® G Hydrogel Sheet Dressing
- AquaSite® Hydrogel Sheet



Polymer used in hydrogel wound dressing

The character of hydrogel primarily decided by the polymer from which the hydrogels are made. Plenty of polymers are utilized for wound healing application including natural and synthetic polymers which may include followings:

Collagen

Collagen is a natural structural protein. It has a unique triple-helical structure, which constitutes 25% of the total protein and is rich in ECM proteins and the human body. Significant evidence has mentioned that collagen has the thrombogenic potential to stop bleeding quickly and repair different soft and hard tissues. The sources of collagen to make

hydrogels are mostly avian, bovine or porcine. Collagen-based hydrogel dressings could generate an environment that promote healing and helps in cell migration and skin regeneration.

Although collagen has excellent biological performance, its poor mechanical behavior, high degradation rates, and inability to effectively prevent bacterial growth limits its biomedical applications. Therefore, the production of collagen-based dressing is often accompanied by cross-linkers and other materials.

Chitosan

Chitosan is a cationic polysaccharide polymer in nature with hydrophilic properties, which shows high biodegradability and biocompatibility (see Figure 1). Due to the presence of hydrophilic amino groups, chitosan could utilize the adsorption of fibrinogen so that increasing platelet adhesion and thrombosis. Hence, it is generally used in hemostatic dressing. In addition, the uses of chitosan on the wound surfaces could increase cell proliferation.

However, due to low water solubility and limited mechanical property, chitosan-based hydrogels inhibit the applications of chitosan. To overcome this, chitosan might be modified with different functional groups or synthesize chitosan derivative.

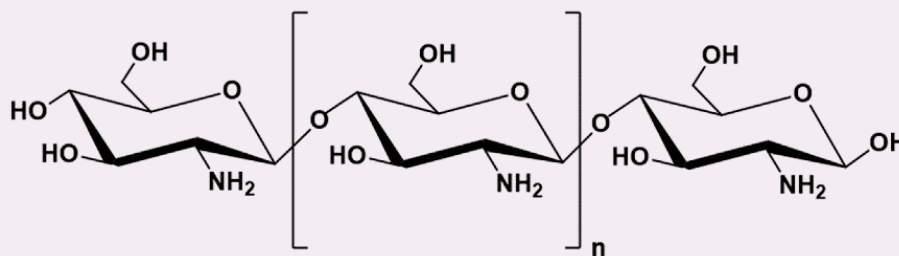


Figure 1: Structure of Chitosan

Alginate

Another natural polysaccharide is alginate with hemostasis and has been broadly used as a hydrogel network substance (Figure 2). Alginate is consisting of D-mannuronic (often called M-block) and L-guluronic acid (often called G-block), wherein G-blocks are distorted or bent while M-blocks extended ribbon-like form. Alginate-based hydrogel dressings are generally prepared through the ionic cross-linking strategy of their solution with divalent cations, such as magnesium, calcium, barium, and zinc ions. Only G-blocks are able to participate in the

gelation processes to prepare hydrogels so that the M/G ratio and the number of repeated G-blocks in a matrix are important factors for physicochemical properties of hydrogel.

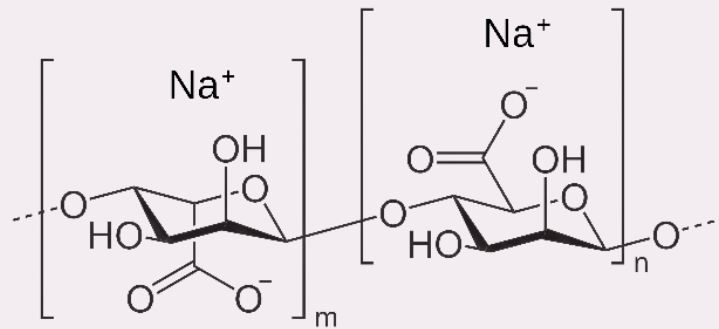


Figure 2: Structure of sodium alginate

Silk fibroin (SF)

Natural fibrous protein is derived from *Bombyx mori*. Silk fibroin is formulated of the tripeptide Arg- Gly-Asp (RGD) sequences, which accommodates one or more long chains of amino acid residues that are soluble in water (Figure 3). SF could participate in different phases of the healing process, and increase cell growth, proliferation, adhesion and migration of different cell types. There are some limitations that hamper the biomedical applications of silk fibroin-based hydrogel, such as irreversible mechanical properties, insufficient adhesion to solid-state interfaces, poor responsiveness to the application environment, etc.

However, in recent years, silk protein hydrogels with different functionalities have emerged. Through the molecular level design and control of the multi-scale structure of silk fibroin, scholars have achieved silk fibroin hydrogels with high strength, injectability, self-healing ability, adhesion property, environmental stimuli-responsiveness, 3D printability, etc.

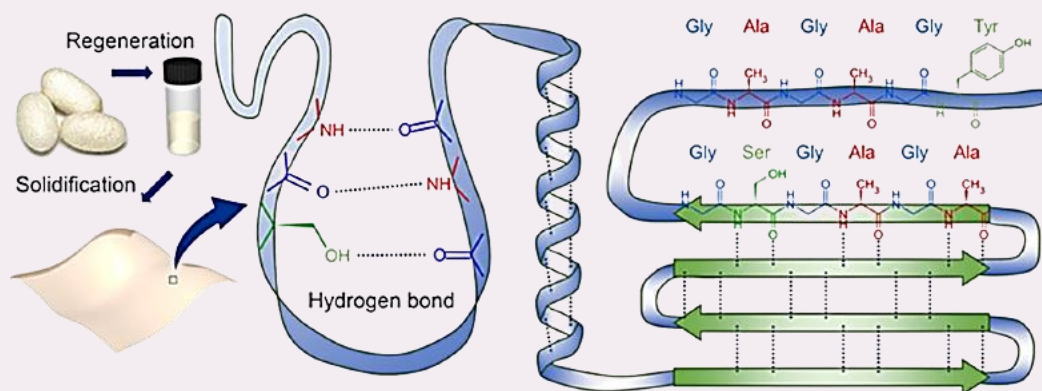


Figure 3: Silk fibroin (SF) and bondings

Polyethylene glycol (PEG)

PEG is a synthetic polymer that possess excellent biocompatibility. In addition, it also has other attractive characteristics including nonimmunogenic, transparent, bioresorbable and nontoxic properties. Even it is a relatively new substance for the wound healing application, it achieved great success till date.

Polyvinyl alcohol (PVA)

Polyvinyl alcohol (PVA) has a lot of functions in fabricating hydrogels, mainly hydrogel dressing. It is also biocompatible and capable to keep a moist environment. Specifically, PVA is noted for its anti-protein fouling and biologically inert characters. PVA-based hydrogels are usually physically cross-linked hydrogel, that could be prepared by the freezing/thawing cycle and electron beam irradiation cross-linking strategy so that the usage of conventional chemical cross-linking agents can be avoided. In addition, PVA is usually combined with other materials or pharmaceuticals to produce optimized hydrogel dressing for a quick hemostasis wound healing rate.

Synthesis of hydrogels

Different hydrogel fabrication methods including chemical covalent method, physical noncovalent method or combination of physical and chemical interactions method are followed. In this section, Schiff base reaction, click reaction, and amide bond reaction are discussed to fabricate hydrogels. A summary is provided in Table 1.

Chemical covalent method

Schiff base reaction

The Schiff reaction is involved a dynamic covalent imine bond formation via the crosslinking of amine groups and aldehyde groups (Figure 4). Carbon-nitrogen double bond in a compound is called imine bond. In recent years, this reaction gained significant attention for the formation of self-healing hydrogel. Moreover, with the changes of pH value, the formed imine bonds are reversible, which introduced self-healing ability of the hydrogel.

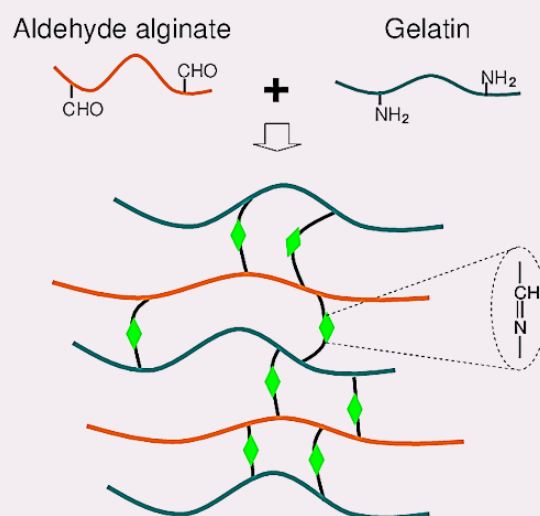


Figure 4: Schiff base reaction

Amidation reaction

Amide bonds are formed by dehydration condensation reaction of amino groups and carboxyl groups; when multiple amide bonds exist at the same time then they are called peptide bonds. They are often used in wound dressing because it can confer hydrogels with temperature sensitivity and adhesive property to tissues.

Esterification reaction

Hydrogels are prepared through the bonding between acid and alcohol groups. Many biomolecules with acid groups may take part in this type of gelation process when the other compound have alcohol groups.

Physical noncovalent cross-linking

The hydrogel which was fabricated by chemical cross-linking reaction generally needs strict reaction conditions and the presence of cross-linking agents, while it is quite easy to form physically conjugated hydrogels through ionic interaction, hydrogen bonding, electrostatic interaction, hydrophobic interaction, etc.

Ionic interaction

Ionic interaction is an attractive force between groups with oppositely charged, or metal-ligand interactions, which can be used as an effective method for making hydrogels with the benefits of fast response to environmental impulse and self-healing ability (Figure 5). Hydrogel which is obtained from ionic interaction tends to contain of two or more oppositely

charged polymers. Polyelectrolytes like gelatin, chitosan and cellulose can effortlessly form hydrogels using this method.

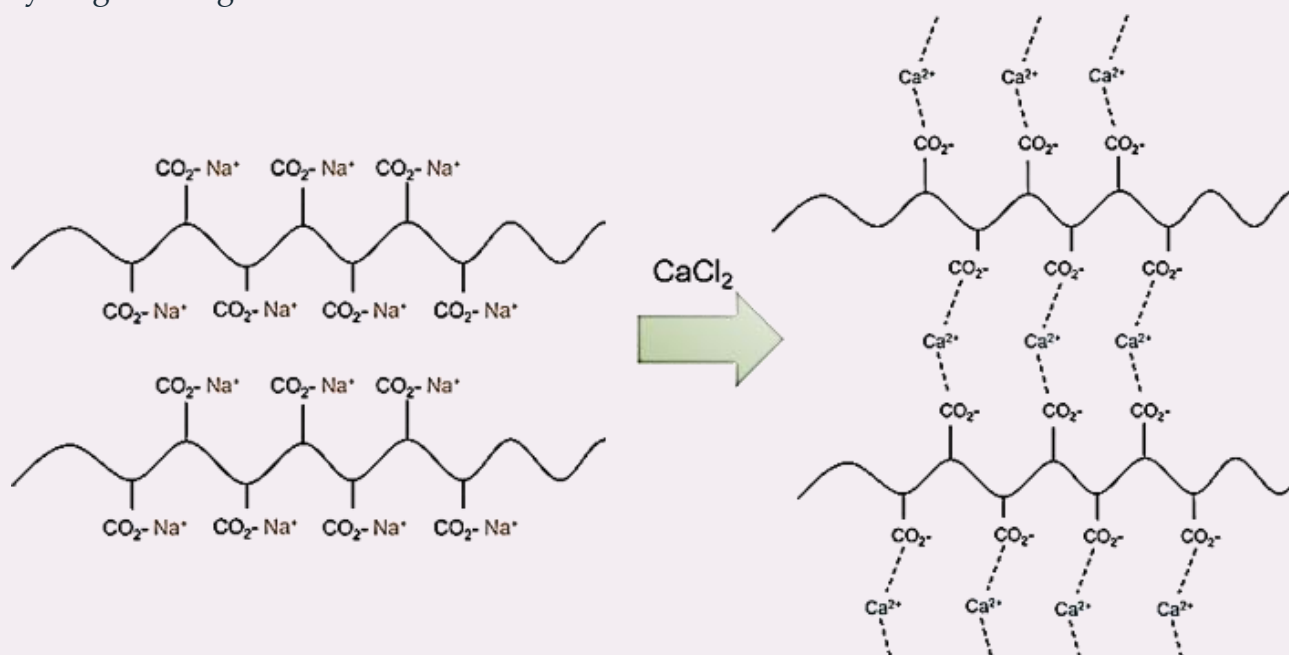


Figure 5: Ionic interaction

Hydrogen bonding

Hydrogen bonding is usually considered as a weak interaction; however, it could be effectively used for the synthesis of hydrogel. In addition, hydrogen bonding would go through dynamic formation and reversion with the change of temperature, solvent or pH. Many of hydrogen donors and acceptors in natural polysaccharides, such as -COOH , -OH and -NH_2 , could generate the conditions for the formation of hydrogen bonding (Figure 6). So, most of natural macromolecules like collagen, agar, gelatin and starch can form hydrogel by hydrogen bonding. Hydrogels that are cross-linked by hydrogen bonding alone are usually formed with some drawbacks, such as weak mechanical strength. Therefore, to obtain hydrogels with desired properties it is sometimes recommended to combine the hydrogen bonding with other type of cross-linking.

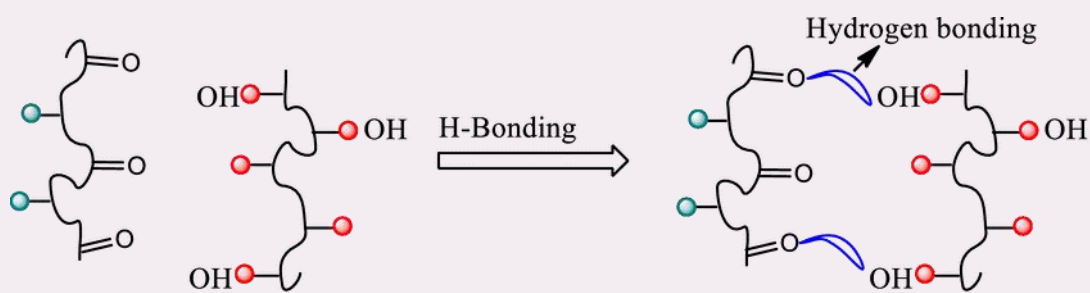


Figure 6: Hydrogen bonding

Hydrophobic interaction

Due to the thermodynamic irreconcilability of hydrophobic and hydrophilic moieties, amphiphilic polymers would self-organize to form hydrogels by hydrophobic interaction in aqueous solutions (Figure 7). The hydrophobic interaction is a new scheme for the preparation of biomedical hydrogels.

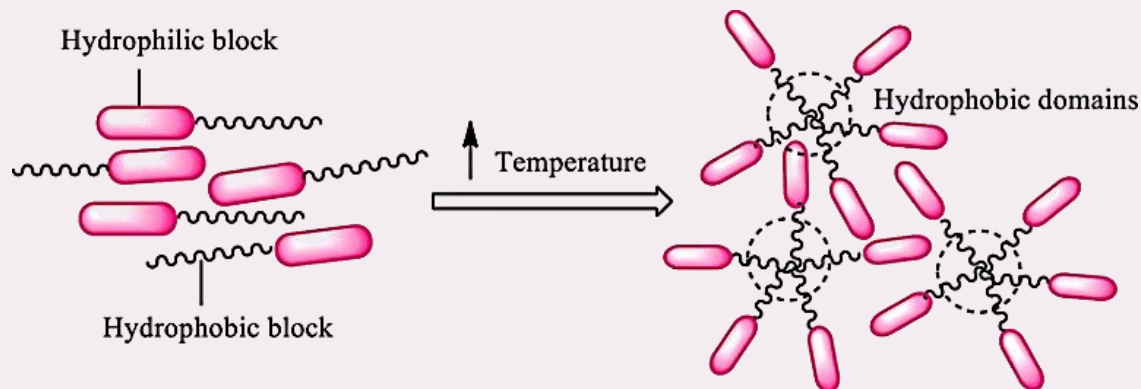


Figure 7: Hydrophobic interaction

Table 1: Advantages and disadvantages of various synthetic strategies of hydrogel based wound dressing.

Cross-linking methods	Bonding type	Advantages	Disadvantages
Chemical covalent cross-linking	<ul style="list-style-type: none"> • Schiff-based reaction • Click reaction • Amidation reaction 	<ul style="list-style-type: none"> • Forming strong bonds 	<ul style="list-style-type: none"> • Almost all need toxic agents • Needs washing to remove residual
Physical noncovalent cross-linking	<ul style="list-style-type: none"> • Ionic interaction • Hydrogen bonding • Hydrophobic interaction 	<ul style="list-style-type: none"> • Safe • Less toxic than chemical agents 	<ul style="list-style-type: none"> • Lower degree of cross-linking • Lower energy of bonds • May alter the properties of the hydrogels • Inability to control the progress of the reaction.

Conclusion and perspective

Bandages, gauzes and sutures are remaining the common wound closure process but they are not efficient for preventing infection and accelerating wound healing. For these issues, researchers give much effort to develop novel and efficient dressings over earlier years. Hydrogels which are crosslinked 3D network polymer have lot of attractive features (i.e. sufficient strength, high moisture content, easy to be modified, superior elasticity) have been widely used as wound dressings. Hydrogels which are based on polysaccharide have inherent characteristics like biodegradability, biocompatibility, and nontoxicity. Nevertheless, synthetic polymer hydrogels are easy to modified and possess better mechanical property.

For future work, fabricating nontoxic and degradable dressing may be the first matter to be concerned, which would depend on the evolution of a new crosslinker, cross-linking methods, etc. To achieve effective prevention from infection or get faster wound repair, specific bioactive species and some antibacterial agents should be added.

Polymer Coated Controlled-release Fertilizer for A Sustainable Agriculture

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Trends in crop production in the last few decades show that nitrogen (N), phosphorous (P) and potassium (K) application rates in agriculture sector increased several times. At the same time nutrient utilization by crops remained relatively low. This showed a potentially alarming situation from environmental, economic and resource conservation points of view and indicates an urgent need for improving efficiency of fertilizer use. Anticipated benefits from controlled release fertilizers (CRFs) are addressed through:

- (a) Nutrient availability in the plant-soil system by plant roots and*
- (b) Matching nutrient release with plant demand.*

Despite the environmental and agronomic benefits offered by CRF, their practical use in agriculture is still very limited. Possible measures which may encourage their use in practice are better assessment of expected benefit, and attainment of improved technologies for producing more efficient and less expensive CRF.

Introduction

Controlled release fertilizers (CRFs) have become increasingly popular and have gathered a great attention from agronomists around the world. It improves the efficiency of nutrient release to the crops and reduce the ecological, environmental, and health hazards. Applying lower amounts of fertilizer is one solution to dealing with new regulations limiting the amount of leached nitrogen. CRFs are fertilizers with one or more primary macro-, meso- or micro-nutrients in a coated granule. There are different types of coating which gradually release the nutrients. Blends are often produced in order to deliver the correct nutrient levels for every crop.

The most important part of a CRF is the coating. The difference in coating materials, percentages and patterns affects the direct availability of nutrients to the plant as well as the leaching during the growth season. The type of polymer coating with a higher initial release are of great concern. Each coating technology has its own specific characteristics. Factors influencing the release of nutrients are moisture content and soil temperature. In resin or sulphate-based polymer coatings, the release mechanism is primarily determined by the thickness of the coating. There are also coated products available in which the microbiology within the soil affects the release pattern.

Limitation in conventional fertilizers

Followings are the limitations with conventional fertilizers:

- The release (and rate and pattern) is not well controlled.
- The beneficial effect is primarily localized.
- They provide only short-term benefits.
- They change the nature of soil, making it either too acidic or too alkaline.
- They reduce soil fertility.
- They get washed away by water easily and cause pollution.

Advantages of CRFs

CRFs have many advantages:

- Better plant growth due to the continuous and uniform availability of the nutrients.
- Reduction in fertilizer application as the risk of leaching is minimal. Of course, even with a CRF, rain will wash away the minerals which are present in the root environment, but thereafter the CRF will immediately release new nutrients.
- The positive effects of CRF application include higher yields, better quality distribution, more uniform grading, and greater plant weight. Because the plant grows evenly and gradually, it is less susceptible to damage and plant diseases.

Coating materials

Coating materials are typically made up of following categories:

- Inorganic material-based coating
Inorganic materials include sulfur, bentonite, and phosphor-gypsum, etc.
- Synthetic polymer-based coating
Synthetic polymer such as polyurethane, polyethylene, alkyd resin, etc.
- Natural polymer-based coating
Natural polymers such as starch, chitosan, cellulose, etc.

- Other organic materials coating

Other organic materials such as biochar, rosin and polyphenol are being utilized.

Different combinations of these materials were also explored to examine the effect on the release rate of urea and to determine their possibility as coating materials for CRFs.

Coating techniques

Various coating techniques are tabulated below:

Coating Techniques	Advantages	Disadvantages
<i>Physical Method</i>		
Rotary Drum	<ul style="list-style-type: none"> • Can be a continuous process, low operating cost, easily scaled 	<ul style="list-style-type: none"> • Requires a large number of materials to achieve a uniform coating
Pan Coating	<ul style="list-style-type: none"> • Can be a continuous process, low operating cost, easily scaled 	<ul style="list-style-type: none"> • High air temperature for drying • Poor maintenance of humidity level results in a defective structure
Fluidized Bed	<ul style="list-style-type: none"> • Can be a continuous process, low operating cost, easily scaled • Can achieve a more uniform coating • A more extensive selection of materials 	<ul style="list-style-type: none"> • Expensive equipment • Long residence time • Prone to filter blocking • Higher chance of solvent explosion • Lower performance with larger granule size
Melting and Extrusion	<ul style="list-style-type: none"> • Solvent-free • Simple and cheap 	<ul style="list-style-type: none"> • Hot melts are involved • Expensive equipment
<i>Chemical Method</i>		
Solution Polymerization/ crosslinking	<ul style="list-style-type: none"> • Solvent reduces viscosity which makes it easier to process. • Crosslinking density can be controlled by varying monomer, initiator and cross-linking agent content 	<ul style="list-style-type: none"> • Lower rate of reaction results in possible loss of compound • Difficult to recover solvent from its final form.
Inverse Suspension Polymerization	<ul style="list-style-type: none"> • Crosslinking density can be controlled by varying monomer, initiator and cross-linking agent content • Higher efficiency due to high reaction rate • The solvent can be recovered which reduces the cost 	<ul style="list-style-type: none"> • Prone to contamination by the suspension • Must perform separation to purify polymer
Microwave Irradiation	<ul style="list-style-type: none"> • Simple and low energy consumption 	<ul style="list-style-type: none"> • Not widely implemented in CRF preparation

Disadvantages of CRFs

Followings are the disadvantages of CRFs:

- Depending on the coating polymer, when temperature is high, the fertilizer may be released too quickly and cause root burn, or dissolve too slowly, causing nutrient deficiencies.
- As plants grow, they require different quantities of fertilizer nutrients depending on their stage of development. A young plant requires less fertilizer than a plant that is more mature and actively growing. However, CRFs are released at a fairly consistent rate, assuming the temperature is stable, and may not supply the correct quantity of nutrients at the time they are required.

Important factors affecting CRFs

The release rate of CRFs is generally affected by the size, coating thickness and uniformity, the selection of material, binder and filler for the formulation. For hydrogels, the temperature, pH, and ionic strength of the environment also affect the nutrient release rate.

Release mechanism of CRFs

In release of CRFs we can see three types of mechanism (Figure 1) -

- *Water adsorption:* Coated materials will absorb soil water and enter into the core of the coated granules.
- *Dissolution of fertilizers (e.g., urea, NPK):* The fertilizers will dissolve in water and form a saturated solution.
- *Leaching:* The saturated fertilizer solution will leach out and accessed by the plant root. This is basically controlled by the nature and pores of the coated materials.

The mechanism is schematically shown as below:

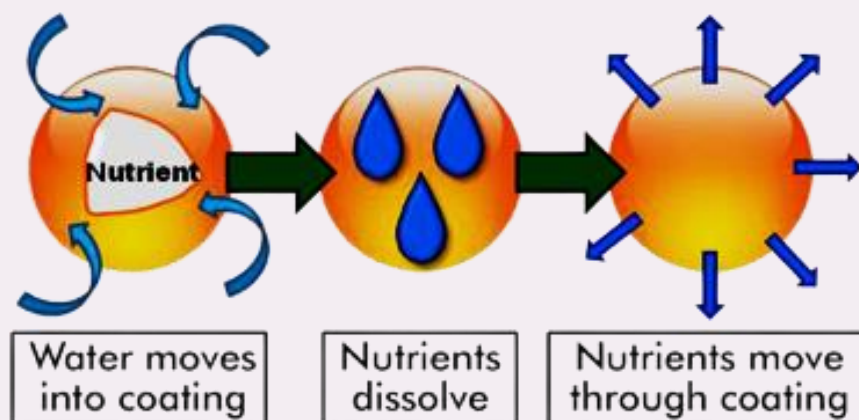


Figure 1: Release mechanism of CRFs

Market insight

The market of CRFs is growing rapidly day-by-day. China has higher consumption of CRFs to their agricultural system. An instance of CRFs used in different countries in 2018 is shown schematically as below in Figure 2:

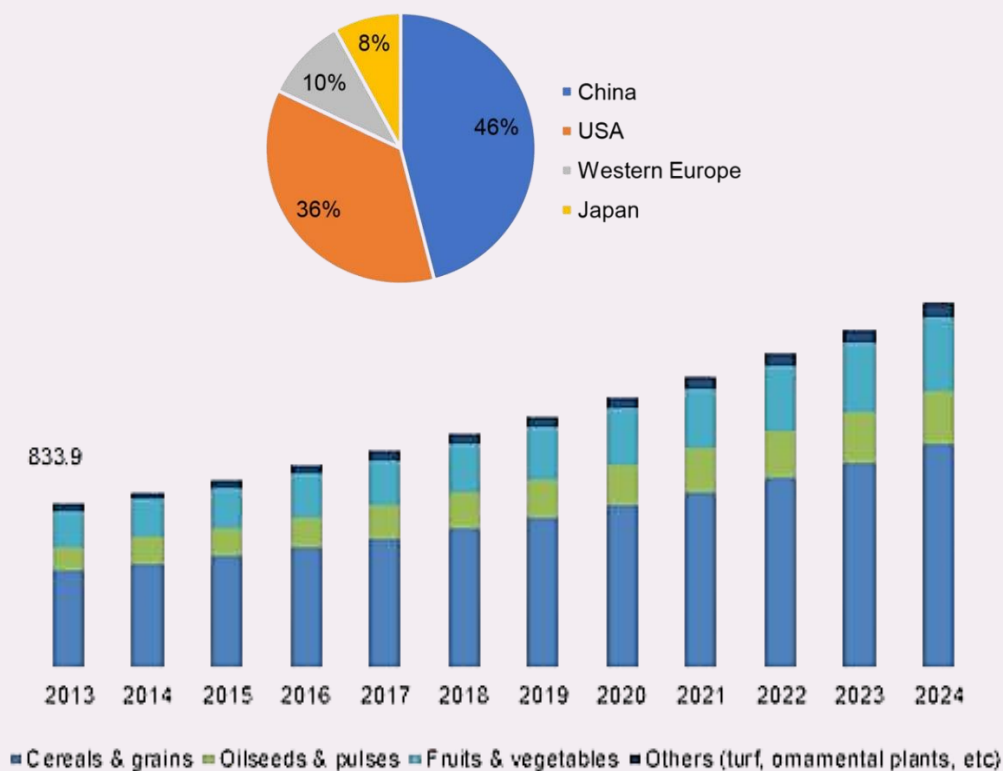


Figure 2: Market insights of CRFs

Conclusions and perspective

The research on CRFs for utilizing coated materials is growing significantly. Binders and fillers play an important role in the release pattern as they can alter the properties of pores and thus interaction with nutrients. The properties of the materials that make CRFs adequately hydrophobic are essential for achieving controlled release without immediate disruption of the coating wall. CRFs can be prepared using physical and chemical methods. Methods of polymerization by microwave irradiation are proven to reduce energy consumption. The temperature, pH, and ionic strength of the environment significantly govern the nutrient release behavior.

In spite of great benefits, it should be mentioned that CRF is a broad field of study that is constantly evolving with multiple aspects yet to be examined and reviewed. Thus, the focus of future works can be narrowed down to the utilization and formulation of low-cost biodegradable materials as a blend or with suitable binders that favor adsorption and provide sufficient hydrophobicity with suitable pores structure. Field testing under different environmental conditions is needed to validate the results.

Weak Interactions

Barna Biswas and Dr. Amit Kumar Guria, Department of Chemistry, Krishnagar Women's College



Weak interactions include hydrogen and halogen bonding, mechanical and cation- π interactions, aromatic-aromatic interactions as well as other types of weak forces. Weak interaction is believed to play a vital role in stabilizing various complex chemical species. Herein, a theoretical study is undertaken to understand the nature, extent and the consequences of weak interactions which include hydrophilic, hydrophobic effect and host-guest complexes. The selected recent examples show that both inter- and intra-molecular non-covalent interactions can influence the formation and stability of coordination compounds.

Introduction

Those forces of attraction which in biological situations, do not take a large amount of energy to break are known as weak chemical bonds. We can take hydrogen bonds for example; hydrogen bonds are broken by energies in the order of 4–5 kcal/mol and van der Waals interactions have energies around 1 kcal/mol. In biological terms, ionic bonds, hydrogen bonds, and van der Waals interactions are considered to be weak bonds. In the biological systems, weak bonds are being continually broken and reformed without the aid of enzymes. Weak bonds might be easily broken, but they are very important because they help to determine and stabilize the shapes of biological molecules. For example, they are very important in stabilizing the secondary structure (alpha helix and beta-pleated sheet) of proteins.

Hydrogen Bond

Although it is stronger than most other inter-molecular forces, the typical hydrogen bond is much weaker than both the ionic bond and the covalent bond. As the name “hydrogen bond” suggests, one part of the bond involves a hydrogen atom. The hydrogen atom must be attached to one of the elements like O, N or F, all of which are strongly electronegative heteroatoms. These bonding elements called the hydrogen-bond donor. Hydrogen bonds can differ in strength from very weak (1-2 kJ/mol) to extremely strong (40 kJ/mol), so strong as to be identical from a covalent bond. The prototypical length of a hydrogen bond in water is 1.97 Å.

Intra-molecular hydrogen bonds are those which occur inside one single molecule. This takes place when two functional groups of a molecule can form hydrogen bonds with each other. For this to happen, both a hydrogen donor and a hydrogen acceptor should be present within one molecule, and they must be in close proximity of each other in the molecule. When hydrogen bonding takes place between different molecules of the same or different compounds, it is termed as inter-molecular hydrogen bonding. They can occur between any numbers of like or unlike molecules because hydrogen donors and acceptors are present in positions where they can interact with one another. For instance, intermolecular hydrogen bonds can happen between NH_3 molecules alone, between H_2O molecules singly, or between NH_3 and H_2O molecules (Figure 1).

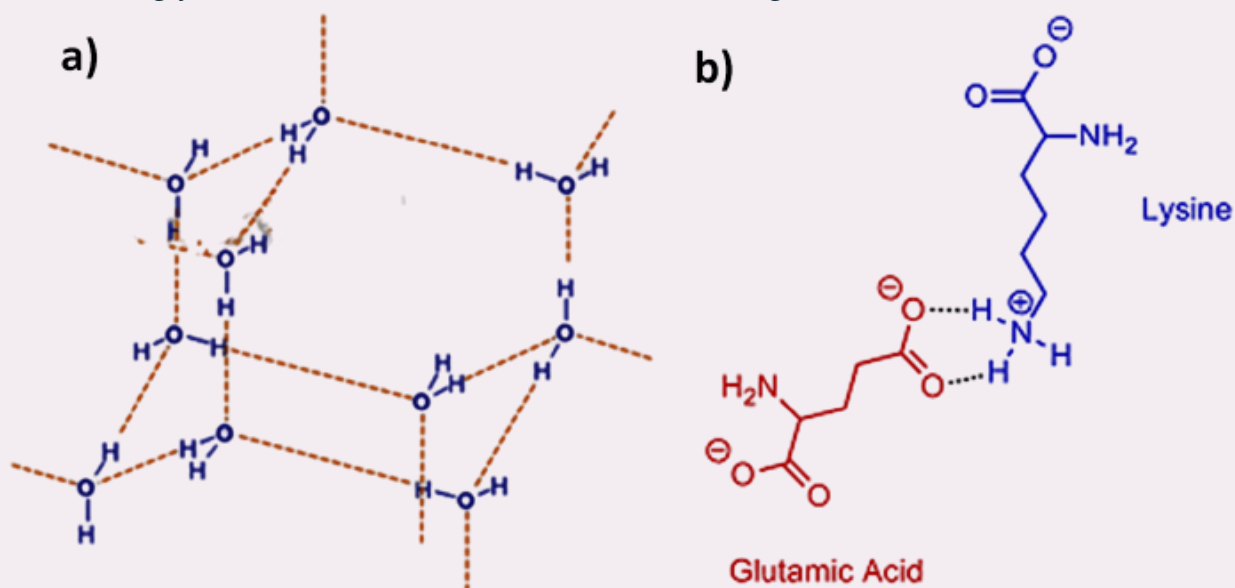


Figure 1: a) Intermolecular hydrogen bonding in water and ice. b) Example of salt bridge between amino acids glutamic acid & lysine demonstrating electrostatic interaction & hydrogen bonding.

H-bonds have considerable importance in biological chemistry. The recurrent occurrence of OH and NH gr. to donate hydrogen, and C=O groups to act as sources of electrons, means many H- bonds can form. These H-bonds helps in determining the shape shown by nucleic acids and proteins.

Salt bridges

A non-covalent interaction between two ionized sites is termed as a salt bridge. It consists of two components - one is a hydrogen bond and another is an electrostatic interaction. In the salt bridge, a proton migrates from a carboxylic acid group to a primary amine or to the guanidine group in Arg. Typical salt bridges includes Lys or Arg as the base and Asp or Glu as the acid. Of all the non-covalent interactions, salt bridges are amid the strongest. Ion pairing is one of the most crucial non-covalent forces in chemistry, in biological systems, in different materials and also in many applications such as ion pair chromatography. Salt bridges are not only found in proteins, but they can also be found in supra-molecular chemistry.

The cation-pi interaction

A stabilizing electrostatic interaction of a cation with the polarizable pi electron cloud of an aromatic ring is termed as the cation-pi interaction (Figure 2a). One p atomic orbital on each of the aromatic carbon overlaps in a pi fashion with its two neighbors to form a conjugated pi (π) orbital system. The pi electrons of aromatic rings contain delocalized annular clouds above and below the ring plane. Closeness of a positive charge to one face of the ring attracts and polarizes the pi electron cloud.

Cation-pi interactions make an important contribution to the total stability of most proteins. Gallivant and Dougherty (1999) deduced that "cation-pi interactions should be considered alongside the more conventional hydrogen bonds, salt bridges, and hydrophobic effects in any analysis of protein structure". Cationic moieties that are within 6.0 Å of the face of an aromatic ring of phenylalanine, tyrosine, or tryptophan amino-acids may take part in polar interactions.

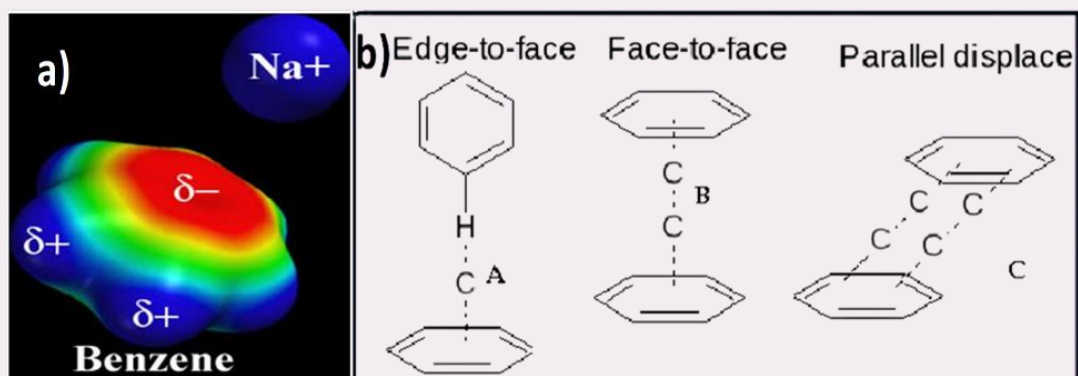


Figure 2: a) Cation- π interaction. Surfaces colored by electrostatic potential. b) Schematic representation of the three types of orientation found in the Ar-Ar interactions

Aromatic-Aromatic (Ar-Ar) interaction

Aromatic-aromatic interactions are those interactions that take place between the side chains of the aromatic amino acid residues (Figure 2b). Simply, aromatic-aromatic interactions are explained as pairs of interacting aromatic residues following the criteria-

- The centres of the aromatic rings of the two interacting residues are separated by a distance between 4.5 Å to 7 Å.
- The dihedral angle must fall between 30° to 90°.
- Free energies of formation when such interactions take place should be between -0.6 and -1.3 kcal/mol.

The aromatic interactions are comparably non-polar in nature. They play an important role in maintaining the overall structure of the protein molecules and the protein-DNA complexes. These interactions induce three different types of geometries, namely, edge-to-face or T-shaped, face-to face and parallel displaced or offset stacked interactions.

Van der Waals Interaction

Van der Waals forces come under weak intermolecular forces that are dependent on the distance between atoms or molecules. These forces arise from the interactions between uncharged atoms or molecules. For instance, van der Waals forces can appear from the fluctuation in the polarizations of two particles that are close to each other. In the group of forces van der Waals forces are the weakest under the category of '**weak chemical forces**'. This force rapidly vanishes when the distance between the interacting molecules are increases. The strength of van der Waals forces ranges from 0.4 kJ/mol to 4 kJ/mol.

The first contribution to van der Waals forces is because of the electrostatic interactions between two polar molecules when they came together, they arranged themselves in a way so that the partial positive charge become toward the partial negative charge. This **Keesom interaction** can only take place among molecules that possess permanent dipole moments. Also, Keesom interactions do not occur in aqueous solutions that contain electrolytes and are very weak van der Waals interactions. **Debye forces** are caused due to the interactions between permanent dipoles and other atoms or molecules which results in the formation of induced dipoles. These induced dipoles take place when one molecule with a permanent dipole repels another molecules electron. A molecule with permanent dipole might induce a dipole in a similar neighbouring molecule and cause mutual attraction. **London force or dispersion** (fluctuating dipole–induced dipole) arises due to the non-zero instantaneous dipole moments of all atoms and molecules (Figure 3). Such polarization is induced either by a polar molecule or by the repulsion of negatively charged electron clouds in non-polar molecules. The London interaction is universal and also present in atom-atom interactions.

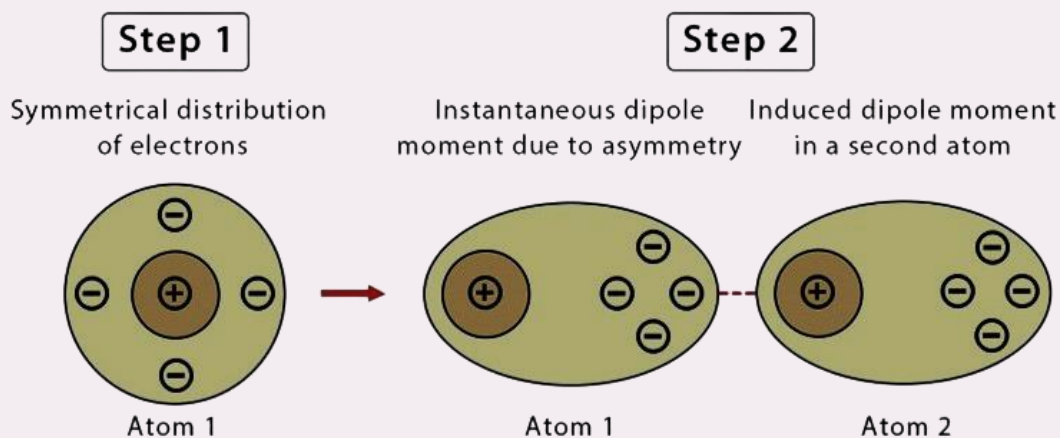


Figure 3: London dispersion forces.

Van der Waals interaction is an important bonding type that assists in stabilizing the protein structure, graphene layers, etc. (Figure 4). Gecko lizard makes use of these forces to climb on the walls. Some other animals use these forces to walk on water.

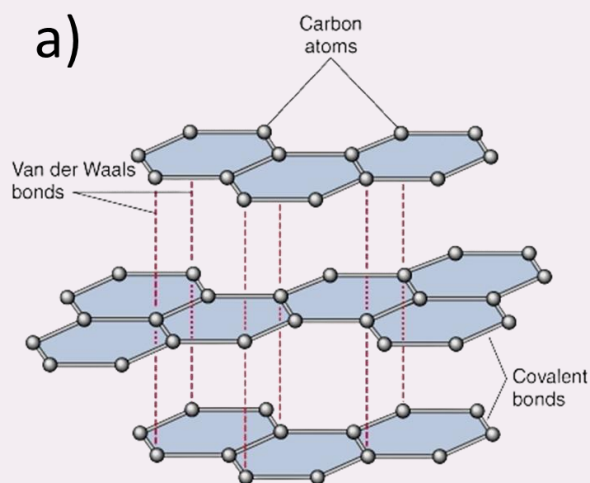


Figure 4: a) Graphene's bonding forces in graphite and b) Gecko lizard.

Mechanical bonding

Mechanical bonding is a type of chemical bond that is normally found in rotaxanes and catenanes or other molecular structures that are mechanically interlocked. In this kind of adhesive bonding, the adhesive material locks physically. In the study and determination of strength of industrial steel, such as cobalt and titanium as well as other materials mechanical bonding and is very useful. The type of mechanical bonding is an indication as to whether a certain surface or material has gone through the correct preparation to achieve a strength level that can fight off the harmful effects of corrosion. Mechanical bonding also involves a mechanical constraint that prevents two parts of a molecule from separating, rather than a chemical bond, which is based on the transfer or sharing of electrons.

Halogen bonding

"A halogen bond occurs when there is evidence of a net attractive interaction between an electrophonic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity."- IUPAC (2013). Halogens participating in halogen bonding are: iodine (I), bromine (Br), chlorine (Cl), and sometimes fluorine (F). All four halogens are capable of acting as XB donors (as proven through theoretical and experimental data) and also follow the general trend: $F < Cl < Br < I$, with iodine normally forming the strongest interactions.

Some consequences of weak interaction

Hydrophobic effect

The hydrophobic effect is the entropy-driven aggregation of non-polar molecules in aqueous solution that occurs to minimize the ordering of water molecules with which they are in contact. This is not an attractive force but a thermodynamically driven process. The hydrophobic effect guides the formation of membranes and contributes to the folding of proteins and the formation of double helical DNA.

Host-guest complexes

In supra-molecular chemistry, host-guest chemistry describes complexes which are composed of two or more molecules or ions that are held together in unique structural relationships by forces other than those of full covalent bonds. Host-guest chemistry incorporates the idea of molecular recognition and interactions through non-covalent bonding. Non-covalent bonding is critical in maintaining the 3D structure of large molecules, such as proteins and is involved in many biological processes in which we can see large molecules bind specifically but transiently to one another

Summary and Outlook

In conclusion, non-covalent interactions have a unique signature and their presence can be revealed solely from the electron density. Non-covalent bonds determine the shape of many large biological molecules and stabilize complexes composed of two or more different molecules. One of the most exciting features of non-covalent interactions is that they are responsible for the structure and dynamics and, consequently, also the function of biological macromolecules such as DNA and proteins. The immense complexity of this field requires a more and more cross-disciplinary approach, inclusive of the life sciences and materials sciences, design element in the construction of coordination polymers and crystal engineering.

The roles of non-covalent interactions as discussed above prove the versatile function of those weak forces in the synthesis of coordination compounds and we expect a marked expansion of the field in the near future, namely resulting from the further use of the recently recognized icosagen, tetrel, pnictogen and chalcogen bonds in synthetic transformations, which are still very little explored.

Electrical and Magnetic Properties of Solid

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The condition of the matter is one of the distinct forms that the various phases of the matter take. Four states of matter can be found in daily life: solid, liquid, gas, and plasma. Many other states, such as Bose-Einstein condensate and neutron degenerate matter, are considered to occur only in extreme conditions such as ultra-cold or ultra-dense matter. Other states, such as quark-gluon plasmas, are thought to be possible but remain theoretical for the time being. The states within the device are in a gaseous, liquid or solid state. Solids are distinguished by a tight atomic bond and a high viscosity, resulting in a rigid form. Most solids are crystalline, in as much as they have a three-dimensional periodic atomic structure; certain solids (such as glass) lack this periodic arrangement and are non-crystalline or amorphous.

Introduction:

The particles (ions, atoms or molecules) are tightly packed together in the solid. The forces between the particles are intense in such a way that the particles can't move freely but can only vibrate. As a result, the solid has a stable, definite shape and a certain volume. Solids can only change their shape by force, as if they were broken or cut. A solid is a sample of matter that retains its shape and density when not confined.

Types of solid

Solid can be classified as follows -

- *Crystalline Solid:* The solids featuring highly ordered arrangements of their particles (atoms, ions, and molecules) in microscopic structures are called crystalline solids

(Figure 1). These ordered microscopic structures make up a crystal lattice that accounts for the structure of the solid at any given point. Examples of crystalline solids include salt (sodium chloride), diamond, and sodium nitrate.

- *Amorphous Solid*: The solids in which the particles are not arranged in any specific order or the solids that lack the overall order of a crystal lattice are called amorphous solids (Figure 1). The term ‘amorphous’, when broken down into its Greek roots, can be roughly translated to “without form”. Many polymers are amorphous solids. Other examples of such solids include rubber, glass, pitch, tar, fused silica, plastics, gels, and nanostructured materials. polymers of high molecular mass, etc.

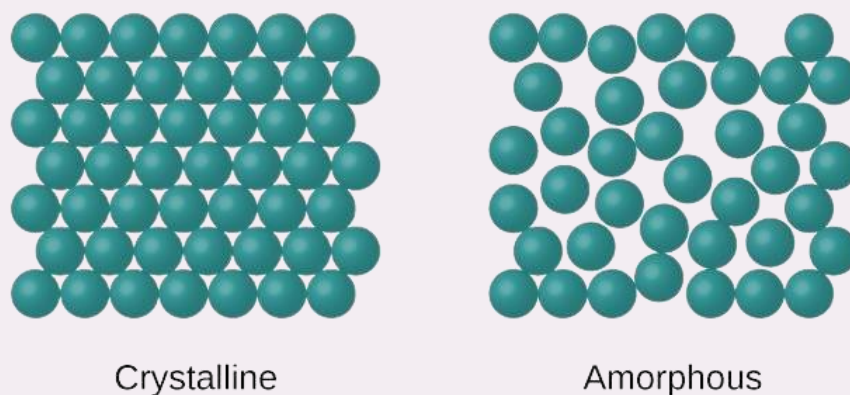


Figure 1: Molecular arrangement of crystalline solid (left) and amorphous solid (right).

Electrical properties of solids

Electrical properties of solids are measured in terms of conductivity. Conductivity may be defined as the ease with which electric current can pass through a given substance. All solids do not conduct electricity in equal amounts. Some of them have high conductivity, whereas some of them do not conduct electricity at all. On the basis of the conduction of electricity, solids can be broadly divided into three categories:

- Conductors**: Conductors are the solids that allow easy passage of electric current through them. Metals are generally good conductors of electricity. Electrical conductivity in metals is due to the presence of mobile electrons. The conductivity of metals is of the order of $10^7 (\Omega\text{m})^{-1}$. There is no gap between the conduction band and the valence band. Thus, electrons can easily flow from the valence band to the conduction band under the influence of an electric field, making them good conductors of electricity. Few examples are given in Figure 2.



Figure 2: Different types of conductors

b) **Semiconductors:** Semiconductors are the materials which have a conductivity between conductors (generally metals) and non-conductors or insulators (such as ceramics). Semiconductors can be compounds such as gallium arsenide or pure elements, such as germanium or silicon. Physics explains the theories, properties and mathematical approach governing semiconductors. There are two types of semiconductors (Figure 3):

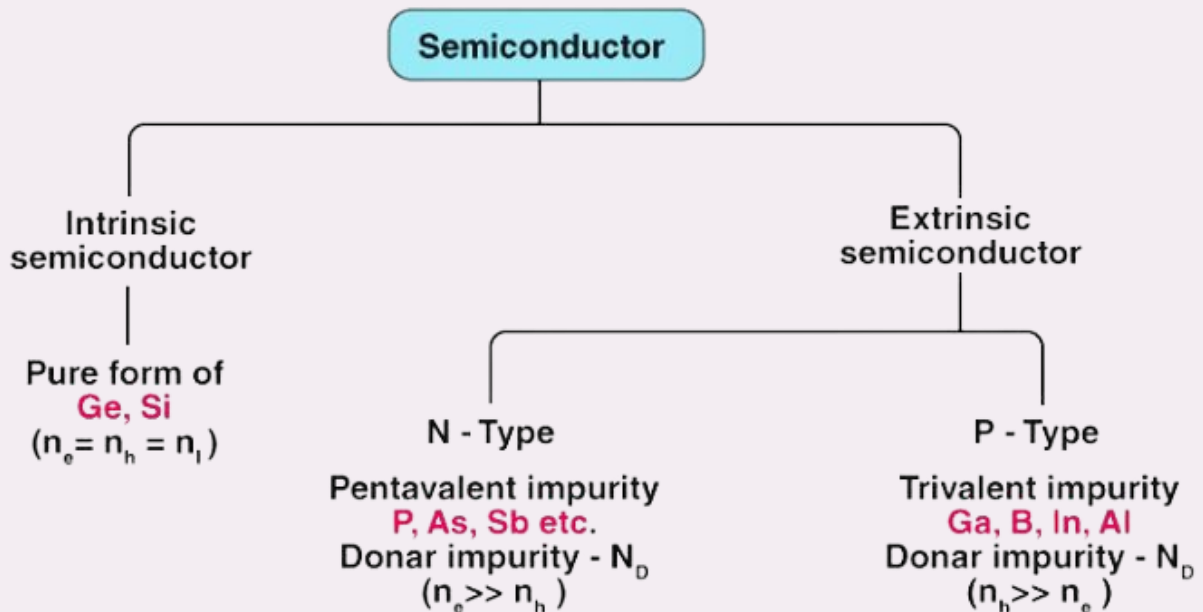
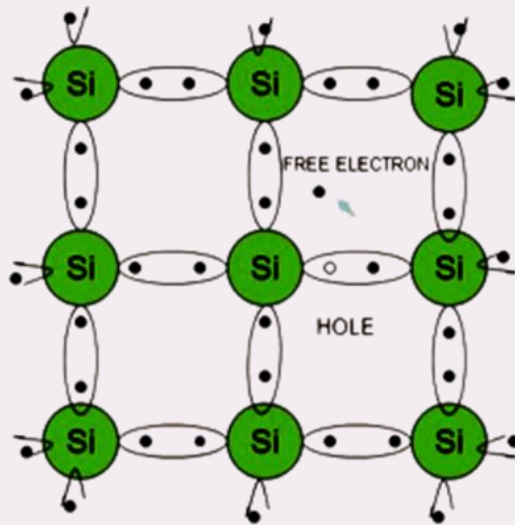


Figure 3: Classification of semiconductors

i. **Intrinsic semiconductor:** When heat is provided to the semiconductors, sometimes they eject electrons from their position leaving a positive hole behind them. These

types of materials are known as undoped or intrinsic semiconductors (Figure 4). Example: Silicon, Germanium.



Semiconductor in pure form is known as Intrinsic Semiconductor.

Ex. Pure Germanium, Pure Silicon.

At room temp. no of electrons equal to no. of holes.

Figure 4: Mechanism of intrinsic semiconductors

ii. **Extrinsic semiconductor:** Silicon and germanium generally have a low conductivity in their pure state. To increase the conductivity of the semiconductors small amount of impurity is added to the semiconductor. This process of adding the impurities to improve the conductivity of semiconductors is known as doping and the semiconductors are referred to as extrinsic semiconductors or doped semiconductors (Figure 5).

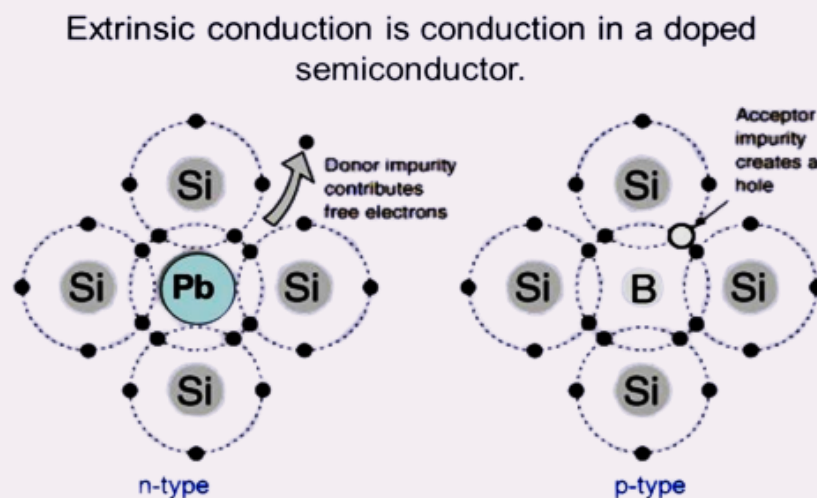


Figure 5: Mechanism of extrinsic semiconductors

c) **Insulators:** These materials do not conduct electricity. The band gap between the valence band and conduction band is very large. Even if a large amount of energy is provided to these solids, they do not conduct electricity. Example: Wood, plastics, etc. (Figure 6).



Figure 6: Different types of insulators

Band structure in solids

A useful way to visualize the difference between conductors, insulators and semiconductors is to plot the available energies for electrons in the materials. In insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap (Figure 7).

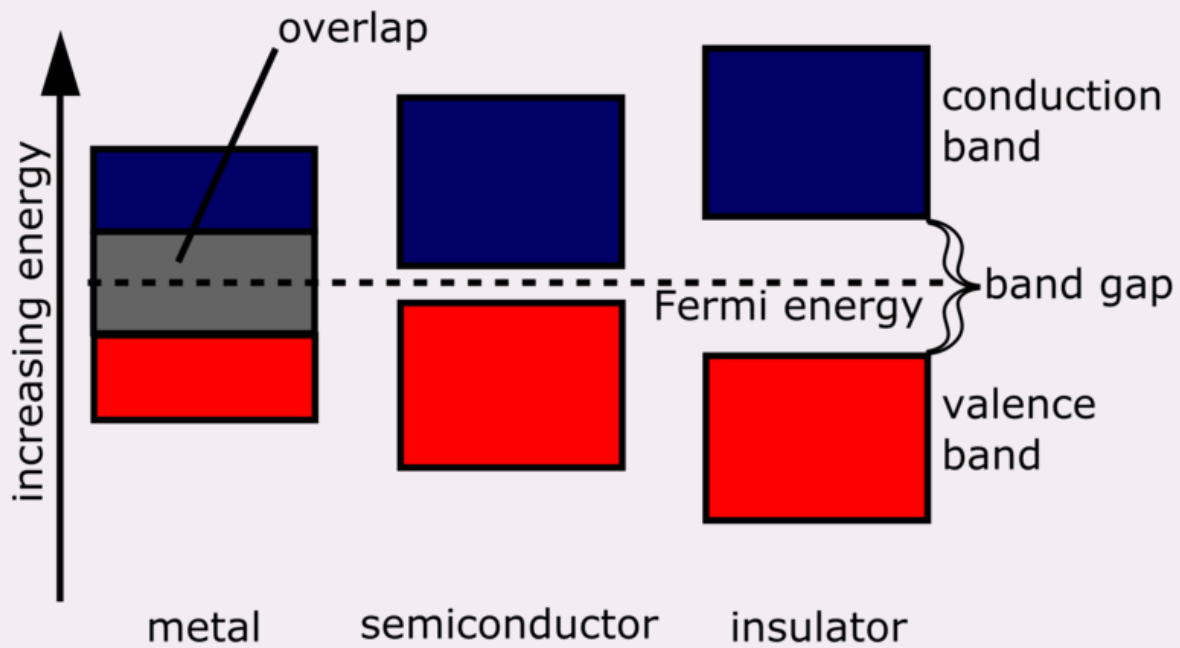


Figure 7: Band structure of conductors(metal), semiconductors and insulators.

Magnetic properties of solids

The magnetic properties of the solids are the results of the magnetic property of the atoms or ions of the solid within them. i.e. the magnetization and magnetism will depend on the movement of electrons within the atom or ion of the solid. According to the magnetic behaviors of the solids the most materials are classified into diamagnetic, paramagnetic and ferromagnetic.

Classification of magnetic materials

There are three classes into which all the magnetic materials may be grouped according to their magnetic behaviors, although there is some overlap among groups:

a) Diamagnetic substances

The materials with diamagnetic behaviors are slightly repelled in the magnetic field and those materials do not retain magnetic properties when an external field is removed (Figure 8). They have weak and negative susceptibility to magnetic fields. In diamagnetic materials all the electrons in the atom or ion are in paired condition, so there is no permanent net magnetic moment per atom. Diamagnetic materials contain most elements from periodic tables including copper, silver and gold.

b) Paramagnetic substances

These types of materials are slightly attracted by a magnetic field and the material does not retain the magnetic behaviour after the removal of the external magnetic field (Figure 8). Paramagnetic properties are due to the presence of some unpaired electrons. They have small and positive susceptibility to external magnetic fields. Paramagnetic materials contain magnesium, molybdenum, lithium and tantalum.

c) Ferromagnetic substances

They possess a strong attraction to magnetic fields and retain the magnetic behaviors after the removal of the external magnetic field (Figure 8). Ferromagnetic substances have some unpaired electrons, so their atoms have net magnetic moment. They have strong magnetic behaviors due the presence of magnetic moments. Iron, cobalt and nickel are the examples of the ferromagnetic material.

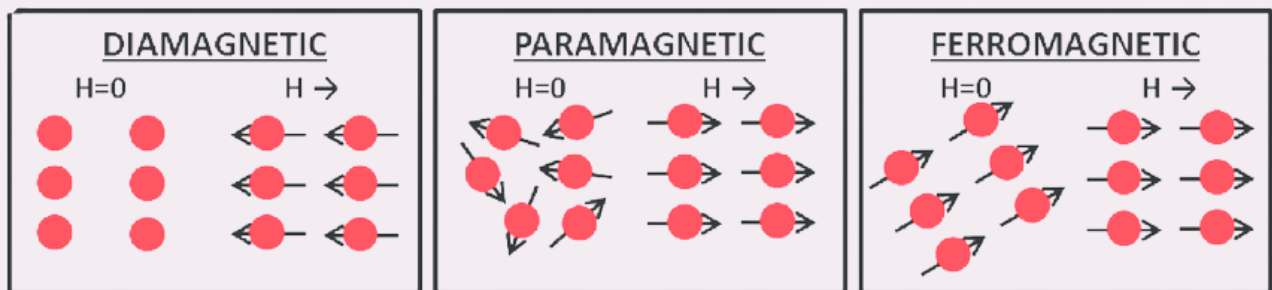


Figure 8: Diamagnetic, Paramagnetic and Ferromagnetic substances

Conclusion

Solid-state batteries, as their name suggests, are batteries that have both solid electrodes and solid electrolytes. These kinds of batteries are a rapidly developing and emerging tech touted by many as the next generation in battery technology. Solid state batteries have comparatively low flammability, higher electrochemical stability, higher potential cathodes, and higher energy density as compared to liquid electrolyte batteries.

Solid-state batteries are capable of holding much more energy per unit of mass than today's lithium-ion batteries, which means an electric vehicle (EV) could go for much longer before needing to be recharged. Even though the electrolyte is solid, it is porous on a microscopic level, allowing electrons to pass through it.

Structure-Property Relationship in Polymers

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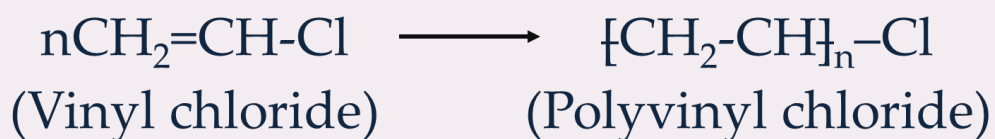


The modern plastic industry began with utilization of natural rubber for erasers and in rubberized fabrics a few years before Goodyear's discovery of vulcanization in 1893. Natural rubber is polyisoprene in which monomer units are isoprene i.e 2- methyl-1,3- butadiene. This is actually polymeric substance. Natural polymers have been utilized throughout the ages. Since his beginning man has been dependent on animal and vegetable matter for sustenance, shelter, warmth and other requirements. Gradually the study of polymer properties began. The physical properties of polymer are dependent on molecular weight, polarity, crystallinity, linearity, temperature, degree of polymerization, etc.

Introduction

Polymer:

A polymer is a molecule built up by the repetition of small, simple chemical units. In some cases the repetition is linear and in some cases the chains are branched or interconnected to form three-dimensional networks. The repeat unit of the polymer is usually equivalent or nearly equivalent to the monomer, or starting material from which the polymer is formed. Thus polyvinyl chloride, $[-CH_2-CH-]_n-Cl$ is made of its monomeric unit vinyl chloride, $CH_2=CH-Cl$



Molecular Structure

Molecular structure may be classified as a) linear structure b) branched structure and c) cross linked structure.

a) Linear Structure

They are formed by long chains without any type of excess attachments. The repeating units of that molecule join together and form a long chain. The long chains are typically held together by the weaker van der Waals or hydrogen bonding. Since these bonding types are relatively easy to break with heat, linear polymers are typically thermoplastic. Examples: Polyethene (Figure 1), PVC.

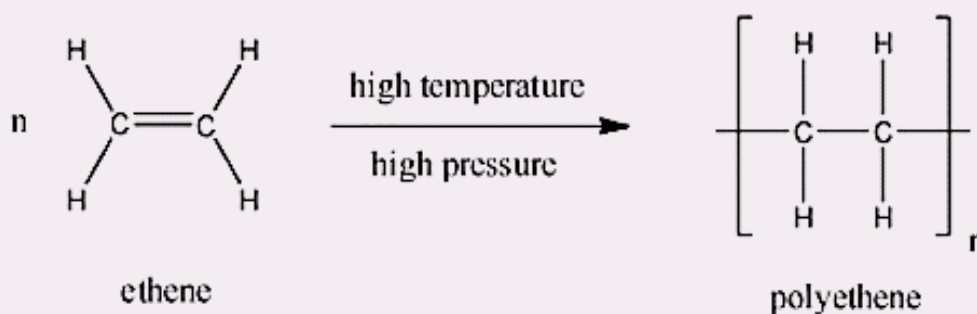


Figure 1: Formation of polyethyne

Properties:

- Tightly packed, high density.
- Melting point and boiling point are higher.

b) Branch Structure

This kind of polymer is also a chain structure having a main chain including smaller chains by side as branches of the main chain. Since the short chains do not bridge from one longer backbone to another, heat will typically break the bonds between the branched polymer chains and allow the polymer to be a thermoplastic. Example: Low density polyethylene (LDPE).

Properties:

- Loosely packed.
- Low-density.
- Melting point and boiling point are lower.

c) Cross-linked structure

Cross-linked polymers are those polymers that are obtained when a cross-link bond is formed between the monomeric units (Figure 2). The cross-linked polymer leads to the formation of long chains which can be either branched or linear, that can create covalent bonds between the polymeric molecules. Example: Epoxy-resin.

Properties:

- Network like Structure.
- Don't melt at high temperature tend to become a soft like material.
- Degree of cross-linking is a positive value.

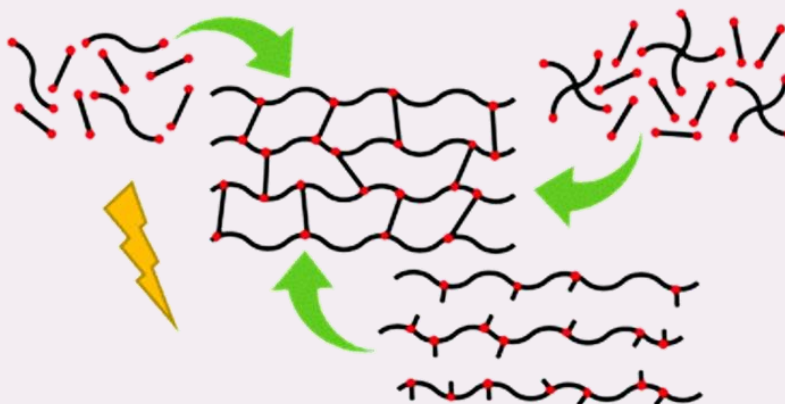


Figure 2: Formation of cross-linked polymer

Molecular forces and chemical bonding

Polymers are held together by primary forces (covalent bonds) and secondary forces (van der Waals and hydrogen bonds). In covalent bonding there is a sharing of valence electrons (the s and p shells) to complete an octet (a group of eight electrons) around atoms. The formation of covalent bonds (primary forces) between monomers makes polymer molecules. Atoms of polymer attached together by covalent bonds with bonding energies about 320-370 kJ/mol. Polymer molecules also bind through secondary forces. Secondary forces are also called van der Waals forces.

A. Primary bonding forces

a) Ionic bond

The most stable electric configuration for most atoms important in polymers is a complete outer shell of 8 electrons called an octet (Figure 3). In inorganic system this structure may be obtained by the donation of an electron by one atom to another to form ionic bond. This bonds

not generally found in macromolecular substances except in the use of divalent ions to provide cross-links between carbonyl groups in natural resins and in ionomers.

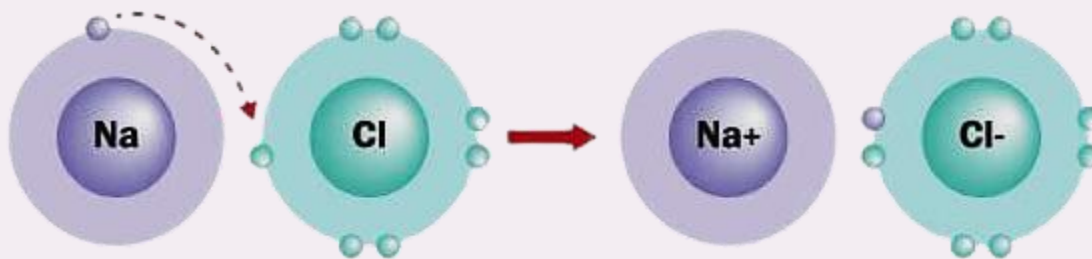


Figure 3: bonding of NaCl

b) Covalent bond

This type of bonding is formed when one or more pairs of valence electron are shared between two atoms again resulting stable electronic shell (Figure 4). Covalent bond is most common primary bonding forces in polymer.

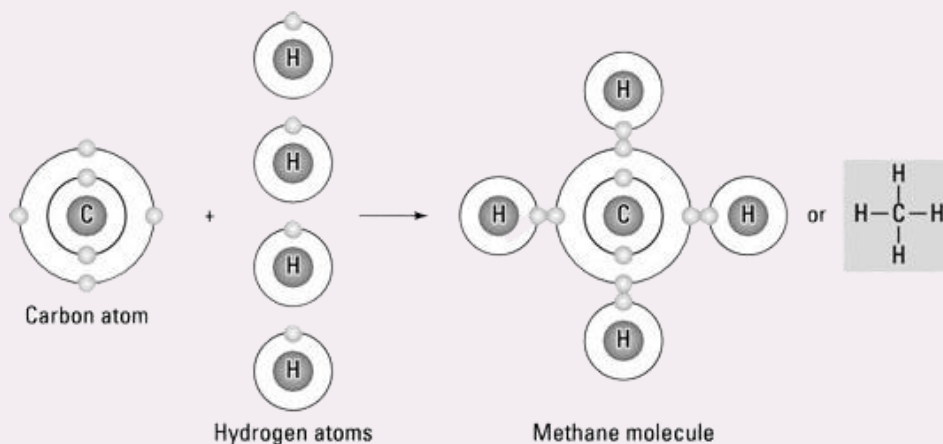
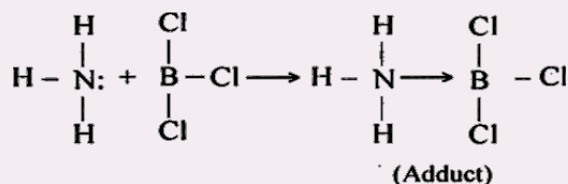


Figure 4: Covalent bonding in Methane molecule

c) Coordinate bond

This kind of bond is similar to covalent bond. Electrons are shared to produce stable octet in case of this bond but in this the both shared electrons belong to one atom. Example: Addition compound of BCl₃. The coordinate or semipolar bond has properties between those of the ionic and covalent bond.



d) *Metallic bond*

In metallic bond the number of valence electrons is far too small to provide complete outer shell for all the atoms. The resulting bonds involve the concept of positively charged atom embedded in a permitting gas of free electrons (Figure 5).

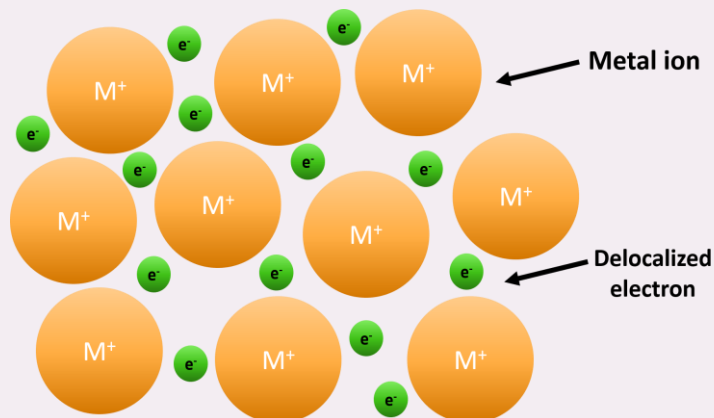


Figure 5: Metal ions and free electrons in metal cluster

B. Secondary bonding Forces

a) *Dipole-dipole interaction*

In a molecule different type of atoms moves with equal and opposite charges. This molecule is said to be polar, or in a large distance have a permanent dipole moment. Such molecule acts like electrically neutral system. But at molecular distance the separation of charge becomes remarkable and generate a net intermolecular force of attraction. Interaction energies magnitude bank on mutual alignment of dipole. For changes of temperature the value of dipole forces changes (Figure 6).

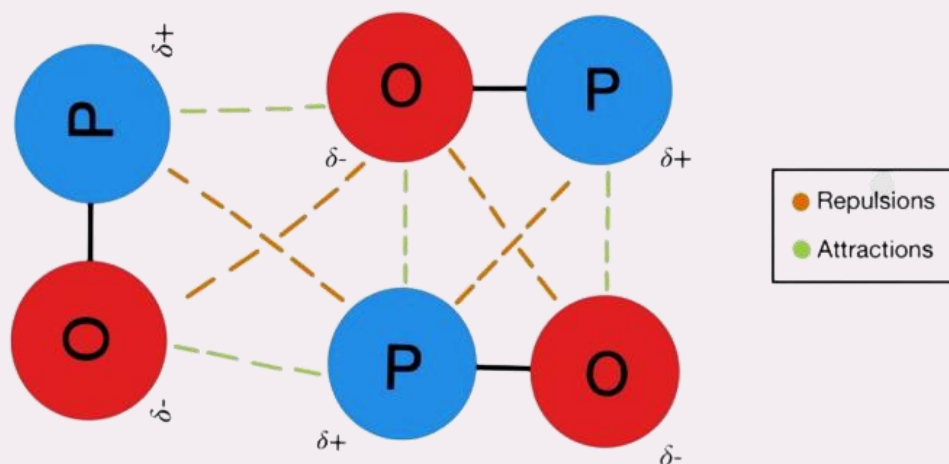


Figure 6: Dipole-Dipole interaction

b. Induction forces

The neighboring molecules which don't have permanent dipole moment are affected by a polar molecule. Electrons and nuclei of the neighboring molecule which generate induced dipole shift slightly. The intermolecular forces between the permanent and induced dipole are called the induction force.

c. Dispersion forces

The intra-molecular forces of attraction are covalent bond, ionic bond and coordinate bond which form within molecule. Between molecules the forces of attraction which clutch them are called the intermolecular forces of attraction. The liquids, solids and solution states are the result of dispersion forces of molecules of any compound. The London dispersion forces are the weakest intermolecular forces. London dispersion forces can be described as provisional attractive forces because of the development of temporary dipoles in a nonpolar molecule (Figure 7). When the electrons in two contiguous atoms are moved and almost get some temporary dipoles, these electrons pull them through London dispersion forces.

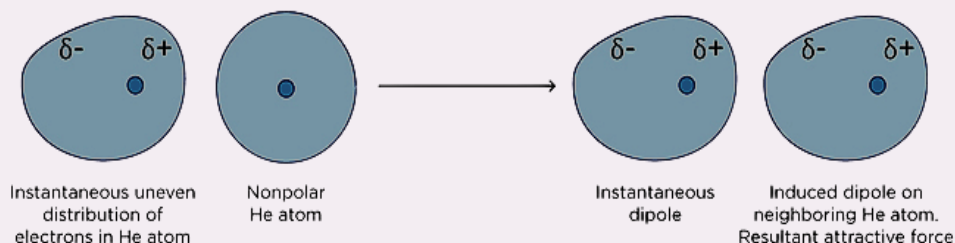


Figure 7: Pictorial description of London dispersion force

Physical properties guided by bonding

a) Molecular weight

The molecular weight is important to determine the properties of the polymer. The sum of atomic weight of the atoms present in the molecule, is called molecular weight. Higher the molecular weight, the higher will be the average length of the bulk chain of the polymer. All polymer molecules don't have same molecular weight.

b) Polarity and crystallinity

If the atoms are dissimilar, they may not share equal electrons. One of the atoms will have more density than other one. This would make the end more negative than the other and generate a negative pole and positive pole. This bond is called polar bond and the molecule is said to be polar molecule. The attraction between the molecular chain affected by the

polarity of a polymer, which effects the structure of polymer. The polarity affects Solubility which effects permeability.

The degree of long chain order in a material is defined as crystallinity. It strongly affects it's properties. The more crystallinity of a polymer, more continuous it's chains aligned. With increase of crystallinity, the hardness and density of that polymer increases.

c) Effect of temperature

Cross linked and other polymer modulus with the temperature. If the temperature increases from the lower point of Tg the polymer changes its state from frozen to rubbery state and modulus may decrease. In frozen state polymer molecule exhibit only slow vibration and have broad modulus. As the temperature increases the kinetic energy increases which leads the polymer to show rubbery state and further increase in temperature modulus reduces till the polymer melts.

d. Degree of polymerization

Degree of polymerization is important to determine the physical properties of polymer. A polymer has same or different types of molecules in it. It is calculated as molar mass of the polymer divided by molar mass of Monomer of that polymer.

Mathematically,

$$\text{Degree of Polymerization (DP)} = M_w/M$$

M_w = molar mass of polymer, and M =molar mass of Monomer.

Conclusion

The physical properties of the polymers related to the structure and bonding. The geometrical arrangements of atoms in polymers or polymer chains. In fiber state, the polymers melt and burn easily. The polymers have disadvantages as well as like joint brittleness, limited gap curing. Hereby structure can't be made by polymer as the structural rigidity is very less. The findings presented in this report may help to increase the other chances of finding different materials.

Bonding Theories for Coordination Compounds

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Werner forwarded his theory of complex compounds at a time when the structure of atoms was not clearly understood. Pauling applied the idea of orbital hybridization to explain the geometry and magnetic properties of many complexes (VBT). However, the valence bond theory had many drawbacks; particularly it could not explain the spectral properties of coordination compounds. The crystal field theory (CFT) first framed around 1933-36 by H. Bethe and van Vleck to account for certain physical properties of transition metal salts. With some allowance for covalence, the theory works much better; it is then often called the adjusted crystal field theory (ACFT) or sometimes the ligand field theory (LFT). The molecular orbital theory (MOT) of bonding in complex compounds gives a more systematic understanding of the bonding but quantitative work becomes more complicated than the other theories.

Introduction

In 1869 Wilhelm Blomstrand discovered the complex ion and proposed bonding is known as Complex ion chain theory. The theory of coordination chemistry was based on the work of Alfred Werner (1866-1919). He got Nobel Prize in 1913, for his careful experiments were carried out in the late 1880 and 1890s. His experiment was based on the different properties of different series metal halide complexes with ammonia. He is known as the father of coordination chemistry. Coordination compounds are used in hydrometallurgical processes for the extraction of metals like nickel, cobalt from their ores and is important catalytic processes to bring about polymerization of organic compounds such as polyethylene and

polypropylene. Coordination compounds are also used in the analysis. To fulfil these requirement more scientific theories like VBT, CFT and LFT are proposed.

Werner's theory [1823]

The important postulates of Werner's theory are as follows:

- In coordination compounds a central metal atom shows two types of valency: primary valency and secondary valency.
- Oxidation state is related to the primary valency and coordinate number is related to secondary valency.
- For every metal atom of secondary valency is fixed, that is the coordination number is fixed.
- Primary valency and secondary valency are satisfied by the work of metal atom. Primary valency is satisfied by negative ion secondary valency is satisfied by negative ion or neutral molecules.
- The geometry of the coordination compounds for definite structure the secondary valency is fixed in a position in space. For example, a metal ion having secondary valency and these arranged octahedral around the central metal ion, on the other hand when the metal ion has four secondary valency, it is arranged in tetrahedral or square planar geometry around the central metal ion. So, stereochemistry of the complex ion is determined by the secondary valency. Also, the primary valences are non-directional.

Limitations of Werner's theory: The drawbacks of this theory are listed below:

- This theory fails to explain the magnetic properties, coloured and optical properties, which are shown by coordination compounds.
- It fails to explain the reason why all elements could not form coordination compounds.
- The directional properties of bonds in the coordination compounds are failed to explain in this theory.
- The stability of the complex is not explained by this theory.
- It fails to explain the nature of complex.

Valence Bond Theory (VBT)

The valence Bond Theory was invented by the American scientist Linus Pauling and John C. Slater. This Theory is based on the Lewis concept of the electron pair bond. According to this theory in a molecule the electrons occupy the atomic orbitals rather than molecular orbitals.

At first Linus Pauling suggests the VBT theory and was supported by Slater. In this theory we know how molecules formed covalent bonds between their atoms. By the overlapping of valence orbitals, a covalent bond is formed and restricted unpaired electrons, which has antiparallel spin. The strength of bonding between the atoms in the molecule is determined by strength of overlap. The overlapped orbitals are regularly directional. A sigma bond is formed by the axial overlapping of orbitals. The axial overlapping of orbitals a pi bond is also formed.

Limitations of Valence Bond Theory (VBT): The drawbacks of VBT are listed below:

- Although it provides a satisfactory pictorial representation of the complex qualitatively, it does not provide a quantitative interpretation of the stability of complexes.
- It does not explain the spectra (colour) of the complexes.
- It does not predict any distortion in symmetrical complexes, whereas all the copper (II) and titanium (III) complexes are distorted.
- It does not give any detailed information about the magnetic properties of the complexes. In particular, it cannot explain the temperature-dependent Paramagnetism of the complexes.
- It does not explain why at one time, the electrons must be arranged against Hund's rule while at other times the electronic configuration is not disturbed.
- It does not provide any satisfactory explanation for the existence of inner orbital and outer orbital complexes.
- Sometimes the theory requires the transfer of electrons from a lower energy level (Example: 3d) to the higher energy level (4p), which is very much unrealistic in the absence of an energy supplier.
- Electron spin resonance shows that in Cu(II) complexes, the electron is not in the 4p level, and the complex is planar.
- It cannot explain why certain complexes are more labile than others. Labile complexes are those in which one ligand can be easily displaced by another ligand. On the other hand, inert complexes are those in which displacement of ligands is slow.

Crystal Field Theory (CFT)

In Crystal Field Theory, it is assumed that the ions are simple point charges (a simplification). When applied to alkali metal ions containing a symmetric sphere of charge, calculations of bond energies are generally quite successful. The approach taken uses classical potential

energy equations that take into account the attractive and repulsive interactions between charged particles. The shapes and occupations of d-orbitals become important in building an accurate description of the bond energy and properties of the transition metal compound (Figure 1). Let us consider a molecule with octahedral geometry. Ligands approach the metal ion along the x, y, and z axes. The electrons in the d_{z^2} and $d_{x^2-y^2}$ orbitals experience greater repulsion. It requires more energy to have an electron in these orbitals than it would to put an electron in one of the other orbitals. This causes a splitting in the energy levels of the d-orbitals. This is known as crystal field splitting.

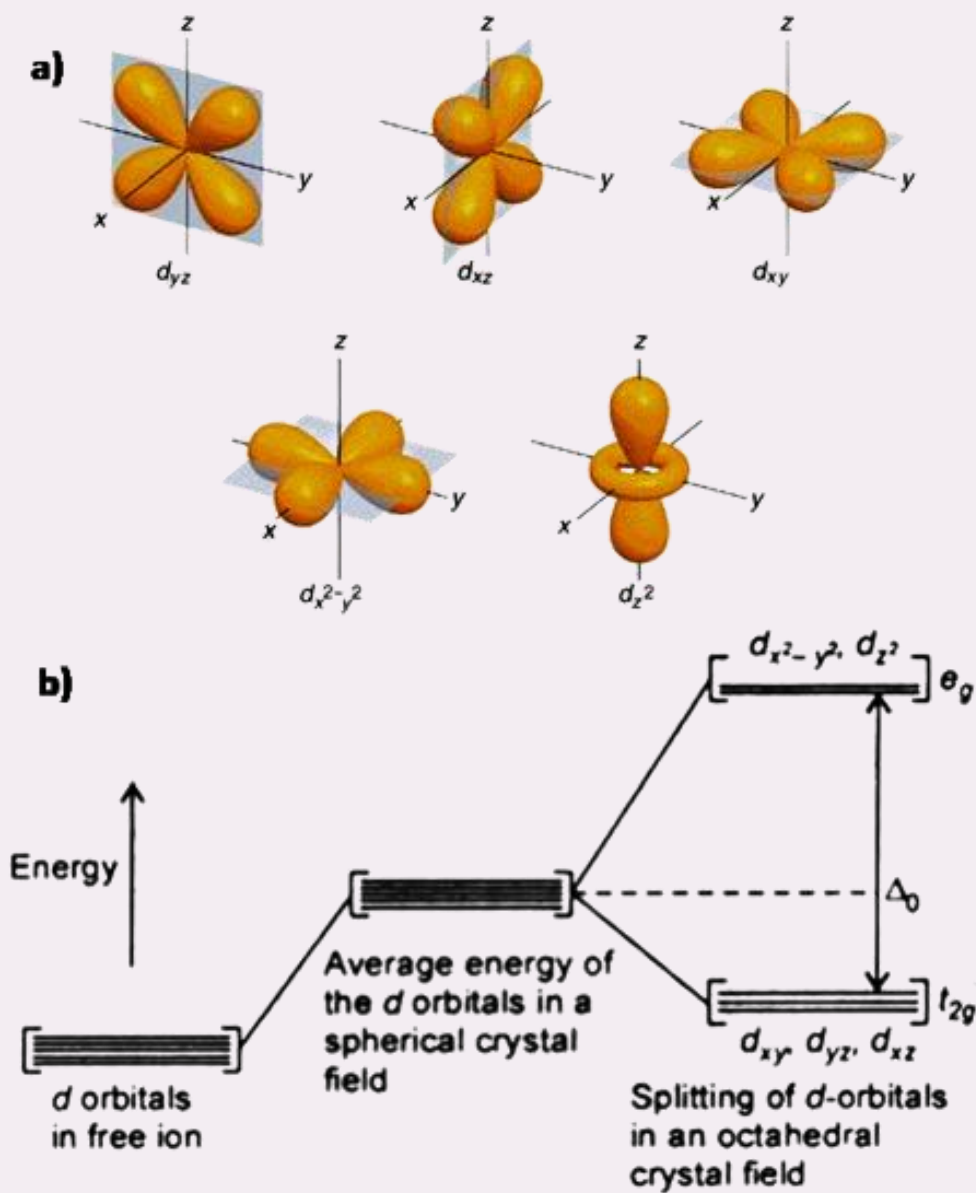


Figure 1: a) Shape and orientations of d orbitals. b) Crystal field splitting in octahedral complex.

Factors affecting the magnitude of crystal field splitting energy (Δ):

- For a given ligand, octahedral crystal field splitting energy (Δ_o) does not vary much along the metal ions in first transition series in the same oxidation state.
- For a given ligand, Δ_o increases with the oxidation state of the metal.
- For a given ligand and same stereochemistry, the magnitude of, Δ increases by about 30% to 50% on passing from the 1st transition series to the 2nd transition series and again by about the same amount from the 2nd transition series to the 3rd transition series.

Limitations of CFT: Some drawbacks of CFT are as follow:

- The interaction between metal-ligand is purely electrostatic cannot be said to be very realistic.
- Only takes d-orbitals of central atom in to account. The s and p orbitals are not considered
- It failed to explain the behaviour of certain metals which cause large splitting while others show small splitting.
- This theory does not explain the possibility of having pi bonding.
- This theory gives no significance to the orbitals of the ligands. Hence, it cannot explain any properties related to ligand orbitals and their interaction with metal orbitals.

Ligand Field Theory (LFT)

Ligand field theory is an example of effective operator theory and can be employed to construct multiplet states arising from dn configurations. It is only applicable for the system where the ground state and lower energy excited state are controlled by d orbital contributions. Ligand field theory (LFT) describes the bonding, orbital arrangement, and other characteristics of coordination complexes. It represents an application of molecular orbital theory to transition metal complexes. A transition metal ion has nine valence atomic orbitals: five nd, one (n+1)s, and three (n+1)p orbitals. These orbitals are of appropriate energy to form bonding interaction with ligands. The LFT analysis is highly dependent on the geometry of the complex, but most explanations begin by describing octahedral complexes, where six ligands coordinate to the metal. Ligand Field Theory can be considered an extension of Crystal Field Theory such that all levels of covalent interactions can be incorporated into the model. Treatment of the bonding in LFT is generally done using Molecular Orbital Theory.

In molecular symmetry terms, the six lone-pair orbitals from the ligands (one from each ligand) form six symmetry adapted linear combinations (SALCs) of orbitals, also sometimes called ligand group orbitals (LGOs).

Molecular Orbital Theory (MOT)

The MOT is a theory on chemical bonding developed in the beginning of the twentieth century by F. Hund and R. S. Mulliken to describe the structure and properties of different molecules.

- ***Octahedral complexes involving σ bonding only:*** For the transition metals, most usual order of energies of metal orbitals is $nd < (n+1)s < (n+1)p$; that is, $3d < 4s < 4p$ for first row transition metals. For most ligands, for example H_2O , NH_3 or F^- , the ligand σ orbitals are lower in energy than the metal valence orbitals. Again, for each combination of metal and ligand orbitals, there will be a lower energy bonding molecular orbital and a higher energy antibonding molecular orbital. To a first approximation, the bonding and antibonding MOs lie equidistant from the mean of the energies of the combining orbitals. The t_{2g} orbitals on the metal (d_{xy} , d_{yz} , d_{zx}) remain unchanged in energy as they are non-bonding in an σ only bonding description.
- ***Octahedral complexes involving π interaction:*** Some ligands have empty π orbitals with the correct symmetry to enter pi interaction with the metal t_{2g} orbitals. These are sigma Lewis base and pi Lewis acid ligands. Carbon monoxide is an example of such pi acceptor ligands. For example, in forming a metal carbonyl, the HOMO of CO, localized near the carbon atomic orbitals in energy, will first form a C-M sigma bond. The LUMO on CO π^* -MOs are fully vacant and possess the correct symmetry for π -interaction with metal t_{2g} orbitals. Since the ligand π^* MO level is vacant, the electrons in the metal t_{2g} (nb) orbital are assigned to the t_{2g} (π) MO, whereby they get somewhat stabilized. Such π bonding helps to remove electron density accumulated on the metal and thus stabilizes lower oxidation states of metals. However, the net effect is always the result of a competition between sigma donation and pi acceptance in the metal ligand interaction.

Summary and Outlook

In conclusion, Werner's theory predicted stereoisomerism among inorganic complex compounds and verified his theory by actually preparing a large number of geometrical and

optical isomers. According to VBT, a coordination entity is formed as a result of coordinate covalent bond formation by electron pairs from ligands through overlap of appropriate atomic orbitals of the bonded atoms. In CFT, considers the ligands as point negative charges while the metal electrons are associated with their usual atomic orbitals. The theory now considers only the electrostatic interaction between the metal and ligands. The MOT provides a better rationalization of the observed spectral and magnetic properties of complexes, besides being able to justify the relative positions of the ligands in the spectrochemical series.

New complexes are discovered and prepared everyday basis. Some of these have special/peculiar type of bonding/interactions (detected with the improved scientific instruments/devices). Therefore, new bonding theories may be proposed to illustrate those interactions.