REVIEW OF GREEN CHEMICAL SOLVENTS AND REVIEV OF WATER AS THE BEST SOLVENT IN CHEMICAL

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ABSTRACAT

Green solvents are a subject that has received attention both in the research community and in the chemical industry due to its effects on pollution, energy consumption, and contributing to air quality and climate change. Most of the organic reactions are carried out in the solvent, so the loss of the solvent represents a major part of the organic pollution. To deal with these issues, a wide range of greener solvents have been proposed and developed over the past three decades. Much of the focus has been on the environmental compatibility of the halal itself, although the type of material the halal is made of and the different conditions can have an impact. In this article, the solvent of water as the best and greenest solvent was specifically examined and various reasons for what causes water to be the greenest and best solvent are discussed. Also, in this review, several aspects of the best green organic solvents used in organic reactions, supercritical water and superheated water and two-solvent system were investigated.

Keywords: Green solvents, Water, Supercritical solvents, Ionic liquids, Green chemistry.

1. INTRODUCTION

Some chemicals pose risks to the environment and living organisms in their production process and consumption cycle. Green chemistry refers to a set of products and processes that are designed to reduce and eliminate the effects of using and producing toxic and harmful compounds for the environment and living organisms. The definition of green chemistry was first presented in the early 1990s. A logical definition of green chemistry can be stated as follows: green chemistry efficiently uses raw materials (preferably renewable), eliminates waste materials, and avoids the use of toxic reagents and solvents or Avoids dangerous in the production and use of chemical products. Green chemistry follows the 12 principles defined by John Werther and Paul Anastas in 1998. These 12 principles are:

1. The best way is to prevent the production of waste, rather than trying to clean or treat it after production.

2. Synthetic methods should be designed in such a way that the continuity and cooperation of all materials to produce the final product will reach the highest possible level. In other words, the atomic economy will reach the highest possible level.

3. Synthesis methods should go in the direction of reducing the use and production of toxic compounds to the lowest possible level.

4. Chemical products should be designed in such a way that they have less risks while maintaining efficiency.

5. The use of auxiliary materials such as solvents should be as minimal as possible.

6. The amount of energy consumed by processes should be considered based on their economic and environmental impact and should be reduced as much as possible. If possible, synthetic processes should be carried out at ambient temperature and pressure.

7. The raw materials used should be selected from renewable compounds if possible.

8. The production of unnecessary derivatives should be minimized because both additional materials are needed for their production and the amount of waste is reduced.

9. The use of catalysts (as much as possible with the ability to choose) should be preferred over the use of stoichiometric compounds.

10. Chemicals should be designed in such a way that they are destroyed after use and do not remain in nature.

11. Analysis methods to monitor and observe the formation of toxic substances should be developed to prevent their formation in advance.

12. The materials and form of them used in the process should be selected in such a way as to minimize possible risks such as leakage, explosion, etc. [1].

Choosing the greenest solvent for a process is a matter of choosing between constraints that are sometimes contradictory. 7 Criteria to be considered are safety (S), occupational health (H), environment (E), quality (danger of impurities in pharmaceuticals), industrial limits (e.g. boiling point, freezing temperature, density, recyclability and cost). In industries, regulations such as REACH (International Certificate of Compliance for Chemical Products) prevent industrial units from using hazardous solvents such as DMF, which were widely used in the past.

Solvents are used in chemical reactions for several reasons. The first and most important reason is crime transfer. In other words, the solvent causes more and more efficient collisions between the raw materials of the reaction. For example, reaction 1, which is the substitution of azide with bromine, is performed both in solvent conditions (both aqueous and organic) and in solvent-free conditions. In the condition without solvent, the contact surface between the two reactants is low, but in the presence of solvent, especially the conditions of two solvents (water and ethanol) because the two reactants become molecular, this contact surface increases greatly and this increase from It can be proven experimentally on the reaction time. In the presence of solvent, the time is reduced to one-twelfth of the condition without solvent.

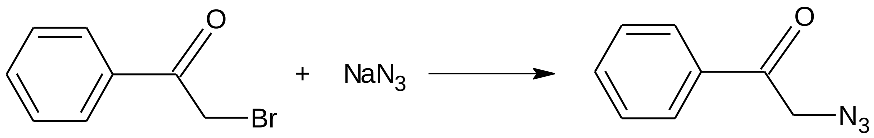

Figure 1 - Substitution reaction of azide with bromine

Another reason for using solvent is energy control. In reaction 2, when the condition is without solvent, when the third component is added to the reaction, intense heat and explosion occur, but in the condition with solvent, the solvent plays the role of controlling the energy and prevents this from happening. Other factors of the use of solvent include uniform and homogeneous heating of the reaction, easier mixing of materials in the reaction container, and the ability to add solid compounds in the reaction.

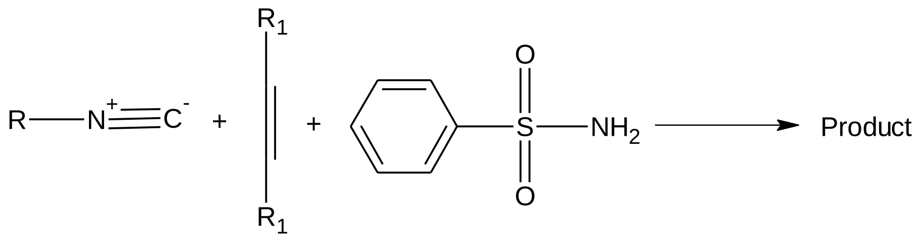

Figure 2. Explosive three-component reaction in the absence of solvent

Water is the best solvent in organic chemistry and was used as a solvent for the first time in 1828 in the synthesis reaction of urea and Heller. In 1912, Victor Grignard stated in his Nobel Prize speech for the preparation of Grignard's reagent that water and even water vapor will destroy Grignard's reagent. This caused the researchers to use conditions without water and dry solvent in their reactions. In 1980, two scientists named Breslow and Rideout were able to perform the Diels-Alder reaction in water solvent, the remarkable thing being that this reaction was performed in less time and in a specific direction. This reaction started the use of water solvent in organic reactions [2].

2. DISCUSSION AND CONCLUSIN

Solvents are classified into three categories in green chemistry: green solvents, suitable solvents, and hazardous solvents. Green solvents include water, ethanol, acetone and 1-propanol. This category is divided based on three factors known as HSE, which includes health, safety and environment. In Table No. 1, some solvents are ranked according to this category, based on HSE factors out of 10, each factor is given a score. Solvents that are displayed in green color are green solvents whose total score is higher than 15. Solvents that are displayed in yellow color are suitable solvents with a total score between 10 and 15 points. and also red solvents are dangerous solvents that have scores lower than 10. For example, water, which is known as the greenest and best solvent, has scored 10 in the safety and health section, but it has received a score of 4 in the environmental section. The reason for the score of 4 in the environmental section is because water can dissolve a wide range of substances in itself, so it can easily introduce dangerous substances into the environment.

Table number 1. Classification of solvents based on HSE parameters

Halal Name	Health	Safety	Environmental	Total
Water	10	10	4	**24**
Methanol	5	5	4	**14**
Yinzen	3	1	5	**9**
Xylene	5	6	2	**13**
Ethanol	6	8	3	**17**
Toluene	4	4	3	**11**
DMSO	2	7	5	**14**
Chlorobenzene	8	4	6	**18**
Nitro methane	2	4	3	**9**
Benzyl alcohol	7	7	6	**20**
Anisole	6	7	5	**18**
Acetonitrile	6	6	2	**14**

In another comparison, ethanol and methanol have been investigated. Ethanol has obtained a higher score in the safety and health section because methanol is a toxic substance and even its vapors are dangerous, but in the environmental section, methanol is more biodegradable than ethanol and is removed from the environment more easily than ethanol[3].

Table 2 can be mentioned in another category of solvents.

In Table 2, solvents are divided into six categories:

1) Green solvents

2) Suitable solvents
3) Solvents with problems
4) Problematic and somewhat toxic solvents
5) Toxic solvents
6) Hazardous solvents

This classification for solvents is more accurate and suitable for conducting research work and is a better and more practical guide for conducting tests and selecting solvents according to health, safety and environmental parameters. The first category, which is specific to green solvents, are the solvents that are suggested for use and are the best and greenest solvents in organic chemistry. In the sixth category, which are dangerous solvents such as: benzene, chloroform and diethyl ether, there are solvents whose use is prohibited.

When a compound is dissolved in even a small amount of water, the solvent is coated and the molecules are pressed.

Table number 2. Classification based on HSE

Green solvents	**Water, Ethanol, Anisole, Butanol, Sulfolane, Isopropanol, Ethyl acetate, Isopropyl acetate, Butyl acetate**
Suitable solvents	**Methanol, Tertiobutanol, Benzyl alcohol, Ethylene glycol, Acetone, Cyclohexanone, Methyl acetate, Acetic acid, Acetic anhydride.**
Solvents with problems	**Hethane, Methylcyclohexane, Toluene, Xylene, Chlorobenzene, Acetonitrile, dimethyl sulfoxide**
Problematic and somewhat toxic solvents	**Cyclohexane, Formic acid, Pyridine, Tetrahydrofuran, Methyl tert-butyl, dichloromethane**
Toxic solvents	**Pentane, Hexane, Diisopropyl ether, 1.4-dioxane, Methoxyethanol, dimethylformamide**
Hazardous solvents	**Diethyl ether, Benzene, Chloroform, Nitro methane**

When water plays the role of a solvent, it coats the primary materials with solvent, and if it has two primary materials, both materials are repelled by water. Water brings these two substances closer to each other, and these two substances, which tend to react with each other, react with each other. This effect is called cavity effect. For example, in reaction number 1, the product is formed as a precipitate and the product is extracted by filtration [3].

Water can be used as a solvent in several ways: water at room temperature or boiling temperature, superheated water, supercritical water and two solvent systems.

Superheated water is pressurized water at temperatures between the normal boiling point, 100°C (212°F) and the critical temperature, 374°C (705°F). Also known as "subcritical water" or "hot water under pressure". Superheated water is produced by excessive pressure that raises the boiling point or by heating water in a sealed container with an enclosed space, where liquid water is in equilibrium with saturated vapor pressure. Many of the unusual properties of water are due to very strong hydrogen bonding.

In the range of superheated temperature, hydrogen bonds are broken and with the increase of temperature alone, the properties change more than usual. Water becomes less polar and behaves more like an organic solvent such as methanol or ethanol. The solubility of organic substances and gases increases several times and water itself can act as a solvent, reagent and catalyst in industrial and analytical applications, including extraction, chemical reactions and cleaning [4].

Superheated water has been used to oxidize dangerous substances in the wet oxidation process. Some organic matter oxidizes in the environment, so when oxygen levels are low, organic compounds can be stable in superheated water. For example, the concentration of hydronium and hydroxide ions in superheated water is 100 times greater than that of water at 25°C, so superheated water can act as a stronger acid and a stronger base and cause different types of reactions. It can be done [5].

Supercritical fluid refers to any substance that is higher than its pressure and temperature at the critical point. where the gas and liquid phases are not distinct from each other. These types of fluids can disperse between solids like gases or dissolve substances in themselves like liquids. Near the critical point, any small change in pressure or temperature causes a huge change in density. Supercritical fluids are very suitable for replacing organic solvents in industrial and laboratory processes. Carbon dioxide and water are among the most used supercritical fluids, which are used in decaffeination and power generation (power plants). fluid under conditions of temperature and pressure above the critical point. These fluids have high permeability and low viscosity in terms of transfer properties like gases, and in terms of solubility, they are similar to liquid solvents. In the region above the critical point where the fluid is called supercritical. This is the stage where there is no distinction between the gas and liquid phases and the density of the liquid is equal to the density of the gas. Since in extraction processes with supercritical fluid the pressure is higher than the critical pressure, unlike the operations performed in the liquid phase, variable pressure is effective in controlling the process. It should be noted that near the critical point, small changes in pressure and temperature can cause large changes in density. Due to the very suitable characteristics of these types of fluids, they are used for a wide range of materials in purification, extraction and separation [6].

Carbon dioxide and water are the most commonly used supercritical fluids. By changing the temperature and pressure, the fluid can be moved to more liquid or gaseous properties. The most important property of these fluids is their solubility, which has a direct relationship with their density at a constant temperature, and with the increase in density, the amount of this ability also increases, and since density has a direct relationship with pressure, it can be said that their solubility increases with an increase in pressure. find The relationship between solubility and temperature is a bit more complicated. At constant density, solubility increases with increasing temperature, while near the critical point, with a slight change in temperature, many changes in density are seen. Therefore, near the critical point, the solubility of these fluids usually decreases with increasing temperature and then increases again. The use of supercritical fluids in chemical industries. Supercritical fluids are used in chemical industries in two forms, solvent and environment, to carry out reactions. Among the applications of supercritical fluids as a solvent, we can mention the extraction of bitumen from oil-bearing rocks, the extraction of paint base materials, and the extraction of nitrophenol derivatives using supercritical carbon dioxide. In addition, many hydrogenation reactions can be performed in supercritical water environment. In the following, several other applications for supercritical fluids in the chemical industry are described. Energy production by oxidation of coal in supercritical water is one of the methods of energy production, burning coal in supercritical water. Oxidation with supercritical water In 2003, Bermojo proposed two new methods for producing energy by burning coal in supercritical water, one is the pulverized coal method and the other is the compressed fluid bed method. To compare the efficiency of the oxidation process in different methods, the effect of pressure and temperature on the produced energy (Wp) and consumed energy (Wc) and axial work should be investigated. Barmjo's research shows that the central work in the oxidation process in supercritical water is 5% more than other energy production processes, but instead, no additional air is needed to complete the complete oxidation process; As a result, thermal efficiency increases in this method. The results of the experiments showed that the oxidation efficiency in supercritical water has a direct relationship with the increase in temperature. up to 30 MPa, the efficiency of the process increases very quickly;

But when the flow pressure is much higher than 30 MPa, the efficiency of the oxidation process decreases [7].

Another category is the reaction in two-solvent systems. Water and ethanol are among the most famous of these solvents, water and ethanol dissolve in each other in any amount, but when an organic compound is added to it, the system becomes a two-phase system, one phase of water and alcohol and one phase of the compound. Organic and alcohol. It is mostly used when an organic and inorganic compound react with each other, but it can be used in other cases as well. In reaction number 3, which is a Friedel-Crafts chelation reaction, there is no need to use a catalyst in a two-phase solvent. Research has shown that the efficiency of this reaction is 66% in hexafluoroisopropyl alcohol solvent, and it was not done in pure water. But the best efficiency is when it is 20% hexafluoroisopropyl alcohol and 80% water. This is because in this ratio hexafluoroisopropyl alcohol has the highest strength of hydrogen bonding that it can do in this ratio [8].

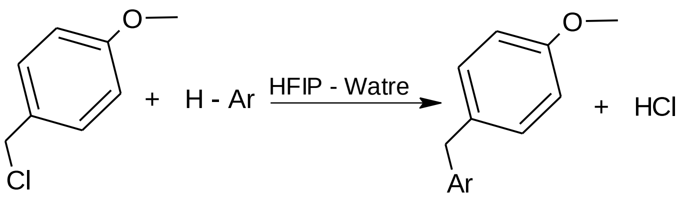

Figure 3. Friedel-Crafts reaction

3. CONCLUSION

The chemical composition of water and its physical properties make it an excellent solvent. Water molecules have a polar arrangement of oxygen and hydrogen atoms. One side (hydrogen) has a positive electrical charge and the other side (oxygen) has a negative charge. This causes the water molecule to attract many different types of other molecules. Water can be strongly attracted to a different compound such as salt (NaCl), so that it can disrupt the forces of attraction that hold the sodium and chloride in the salt compound together, thereby dissolving it. From the point of view of green chemistry, it was investigated and proven in this article that water is the best and greenest solvent available in nature.

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