ORGANIC SOLVENTS - HEALTH HAZARDS

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ABSTRACT

Mother Nature has always provided humankind with sufficient resources to meet their requirements since eternity. With the advent of modernization rapid changes occurred in lifestyle which resulted in steep increase in demands of humankind. This increase has put immense pressure on the delicate equilibrium of nature, which is constantly adjusting itself to the ever-increasing stress. This adjustment has resulted in serious natural calamities, which have adversely affected humankind. In spite of these adverse effects, humankind is not ready to refrain from putting unnecessary stress on nature. Over the past century, in the name modernization a large number of chemical substances were introduced into the environment in the form of common chemicals used in industries; agriculture; transportation; cosmetics etc. Obviously, most of these chemicals claimed to be useful but they are also very toxic. The harmful effects of these toxins on the environment and human health far outweighs their benefit to the society. One example for such toxic pollutants is Organic solvents, which are very widely used as liquid medium for chemical reactions to take place during synthesis and during work-up processes for extraction, separation, purification and drying.

A vast majority of the organic solvents used in industry and laboratories are volatile, hazardous and toxic organic compounds and they form a portion of the large waste by-products of the industry creating pollution. Given to the wide spread industrial and domestic use of hazardous and toxic solvents, which is considered a very potent problem for the health and safety of workers and a cause of environmental pollution. Although the subject of toxicology of solvents is extensively studied and safety rules for use of solvents is well documented, many epidemiological studies have shown that prolonged exposure to higher concentrations of solvents can cause adverse health effects. As most of the organic solvents are highly volatile, they are readily absorbed through the lungs and skin adversely affecting the functioning of various systems in the body.

Through this article, we will emphasize on the health hazards of commonly used organic solvents used in large volumes to produce goods/products we use in day-to-day life. In addition, we will also take a look at some of the possible alternative eco-friendly solvents or methodologies, which can effectively replace these hazardous organic solvents. The main aim should be to enjoy the natural resources without abusing them, as any stress on the natural equilibrium will backfire on us, “we get what we give”.

Key words: industries; agriculture; transportation; cosmetics, separation, purification.

1. INTRODUCTION

The impact of mankind on the environment is profound and in many cases has been both negative and irreversible. A combination of heavy growth in population and rapid industrialization has created an environmental crisis all over the world. In this era, environmental damage from various sources has become a sacrifice, which seems to be acceptable in the interest of development. However, the effects of wide spread industrial development on the environment has become a major concern in the present century.

In chemical laboratories, organic solvents are used as important liquid medium in syntheses, extractions, separations, purification and drying. Organic solvents also play an important role in analytical methodologies, spectrometric measurements and physicochemical properties' measurements. In chemical industries, Organic solvents are widely used for dissolving and dispersing fats, oils, waxes, pigments, varnishes, rubber etc. They are also used as thinners and solvents in paints, varnishes, inks, waxes, floor and shoe polishes, glues, fuels, antifreeze, degreasing, cleaning and dry cleaning agents. A vast majority of the organic solvents used in industry and laboratories are volatile hazardous and toxic organic compounds. Further, many of these solvents are volatile organic liquids that evaporate easily at normal temperature and pressure, thereby readily producing volatile organic compound (VOC) emissions. For example, Trichloroethylene (TCE) is widely used as a degreasing agent for metal parts in industry. According to a recent international study the use of TCE in work place is linked to a six fold increased risk of developing Parkinson’s disease. A wide range of organic compounds such as Alcohols like Methanol, Ethanol; Ketones like Acetone; Aromatic compounds like Benzene Toluene, Esters, Ethers, Amines, Nitrated and Halogenated Hydrocarbons are widely employed as solvents in laboratories as well as chemical industries.

A few of the very many toxic effects of some of these solvents can be listed as follows:

- Spills and leakages of solvents cause significant air, land and water pollution. Fuel spills that infiltrate the ground can cause significant contamination of drinking water sources. For example, one litre of kerosene can contaminate 100 million litres of drinking water (SEPA); due to their toxic nature, irritant and carcinogenic properties they often land up as the contributory cause to many health issues such as headaches, nausea, dizziness and light-headedness.
- Are highly flammable and require special handling and storage to avoid combustion.

The following characteristics of organic solvents determine the type of hazards they present:

- A majority of organic solvents are volatile. The greater the volatility of a solvent the greater the vapor concentration in the air. Hence, inhalational exposure is an important exposure pathway to be considered when assessing the health hazards of the solvents.

- A very majority of organic solvents show the tendency to evaporate at ambient temperatures and are easily absorbed through the skin. The two most important exposure pathways for organic solvents in the workplace are through lungs and skin.
- Many organic solvents have low flash points and will burn if ignited. The flammability and explosiveness of a solvent are clearly important determinants of hazard associated with its use. Some solvents may also be explosive Ex. Nitrocellulose. There may also be a risk of exothermic reactions of some solvents with other materials, which may lead to fire or explosion. The following classification is used to qualify the flammability hazard associated with a solvent:

  HIGHLY FLAMMABLE: flashpoint <23°C
  FLAMMABLE: flashpoint23-61°C
  COMBUSTIBLE: flashpoint 61-150°C
- Solvents such as DiMethylsulfoxide and glycol ethers, which have both water and lipid solubility are well absorbed through the skin.

2. Health effects:

2.1. Skin: The skin contains high levels of fats and upon contact with solvents can cause defatting. As a result, the skin becomes dry, scaly and eventually cracked. A dry, cracked skin tissue further allows greater absorption of solvent upon direct contact. Solvents like Toluene, Xylene, Butanol & Styrene cause skin irritation and irritant dermatitis. Wood Turpentine, Formaldehyde and Epoxy resins may cause allergic contact dermatitis.

2.2. Respiratory tract: All organic solvents irritate the upper respiratory tract to some degree. Long-term exposure to the stronger irritants(Ex. Aldehydes) may lead to chronic or persisting cough and increased sputum production.

2.3. Liver: Liver acts as a central organ for detoxification of harmful substances and is particularly prone to damage. Detoxification by liver enzymes usually involves converting a substance into a more hydrophilic metabolite to accelerate its excretion. The enzymatic activity of certain liver enzymes (Ex: Cytochrome-c-oxidase) is used as a biomarker to determine Xenobiotic exposure in fish and in some invertebrates (Sarkar et al. 2006).Chloroform, Carbon tetrachloride, Vinyl chloride, Bromobenzene (Zurita et al. 2007), microcystins (from blue- green algal-blooms) and numerous pharmaceutical drugs such as Acetaminophen, Diclofenac, Aspirin, Ketoprofen, anabolic steroids, contraceptive pills, Tetracycline and Penicillin can be cited as examples of Hepatotoxins at high doses.

2.4. Kidneys: A number of chemicals including chlorothalonil, diphenylamine, Lead and aircraft- deicers have been shown to damage or adversely affect kidney histology or function (Caux et al. 1996, Drzyzga 2003, Hartell et al. 1995, Johnson, F.M. 1998). Glycol ethers and some chlorinated solvents also show considerable toxicity towards the kidneys.

2.5. Heart: Chlorinated organic solvents, such as Methylene chloride and Trichloro ethane are known for their harmful effects on the heart. Chronic exposure to Carbon disulphide is considered as a contributory factor in coronary heart disease. Repeated exposure to some solvents can cause cardiac sensitization, which can produce life-threatening irregularities in the rhythm of the heart, which can be considered as a possible cause of sudden death in otherwise healthy individuals exposed to high levels of organic solvents

2.6. Mutagenicity/Carcinogenicity: A number of chemicals can bind to DNA, forming “adducts”, or produce reactive hydroxyls or radical species, which can increase the frequency of mutation or lead to changes in gene regulation and gene repair. Examples of known (human) carcinogens (Group 1, as classified by the International Agency for Research on Cancer, IARC) are Benzene, Formaldehyde, Asbestos, Cr(VI) compounds, Aflatoxins, Diethylstilbestrol (a synthetic Oestrogen), Vinyl chloride & Coal tar.

As is evident from the descriptions above, potential adverse biological responses to environmental chemicals may vary greatly in their mechanisms and time and size scales, with acute toxicity representing only a small (albeit most severe) response scenario. In contrast to priority organic pollutants (POPs), many chemicals of potential or emerging concern (CPECs) currently occur in the environment at concentrations presumed to be below the threshold for acute toxicity. Thus, any biological response to them, if occurring at all, would be assumed to occur at the sub lethal, chronic level.

The International Agency for Research on Cancer has classified a number of solvents in regards to their carcinogenicity. According to this classification, BenzenehasbeenclassifiedasaGroup1 (recognized human carcinogen) carcinogen as it has been associated with certain forms of Leukemia in heavily exposed workers. However, it has not been associated with carcinogenic effects in any circumstances other than heavy occupational exposure.

Dichloromethane, Ethyl acrylate, Tetrachloroethylene and Styrene are classified as Group 2B (possible human carcinogens). Other solvents including Methyl acrylate, Methyl chloride, Methylmethacrylate monomer, petroleum solvents, Toluene, 1,1,1-trichloroethane, 1,1,2-trichloroethane and Xylene are in Group 3 (not classifiable as to their carcinogenicity to humans). The American Conference of Governmental Industrial Hygienists has recommended Biological Exposure Indices for the following solvents: n-Hexane, Benzene, Toluene, Xylene, Ethyl benzene, Styrene, Phenol, Methyl ethyl ketone, Perchloroethylene, Trichloroethane, Trichloroethylene, Dimethylformamide, & Carbon disulfide. For many solvents, significant levels may be present only in exhaled air. For solvents with relatively slow excretion, such as Perchloroethylene and Trichloroethane, analysis of blood is a reasonable alternative to exhaled air. Organic solvents should be stored separately from other classes of chemicals and should be labelled to show the contents, hazards and storage precautions.

3. Alternative Techniques in Organic Synthesis: Green Chemistry - Green Solvents: The new field of "green" solvents in organic synthesis has been extended by research papers and publications. Some of these methods are presented below with a brief explanation of how they work and some references.

4. Ionic Liquids in Organic Synthesis: Ionic liquids are mixtures of Anions and Cations, molten salts, with melting point around 100^{o}C, which can be used as alternative solvents in organic synthesis. Although the ionic liquids do not comply fully with green chemistry principles, they are very promising as alternatives to organic solvents. In the scientific literature, there are a large number of research papers for the use of ionic liquids in synthetic routes and various applications.

5. Organic Synthesis in Water: Although water is considered a problem for organic synthesis and the purification processes and drying in final products is very cumbersome, in recent years water is considered a good solvent for organic reactions. A good example is the synthetic routes of the Diels-Alder reactions in which the hydrophobic properties of some reagents makes water an ideal solvent. Water as a solvent accelerates some reactions and because some reagents are not soluble, provides selectivity. The low solubility of Oxygen is also an advantage for some reactions where metal catalysts are used.

6. Supercritical carbon dioxide and supercritical water: Supercritical liquids are suitable as a substitute for organic solvents in a range of industrial and laboratory processes. Carbon dioxide and water are the most commonly used supercritical fluids. Supercritical CO_2 and water are considered "green" solvents in many industrial processes, providing high yields in many reactions, and there are many examples of their use in the scientific literature.

7. Organic Synthesis with Carbonic esters: Carbonic esters, such as DMC, dimethyl carbonate ($CH_3OCOOCH_3$) can replace Methychlorides and dimethylsulphate esters, which are toxic and hazardous. DMC can be used in methylation reactions of Phenols, Anilines and Carboxylic acids. DBU is an alternative solvent that can be used for methylation reactions of Phenols, Indoles and Benzimidazoles.

8. Replacement of Toxic Solvents with Less Toxic Ones: Replacement of Benzene with Toluene, Cyclohexane instead of Carbon tetrachloride, dichloromethane instead of Chloroform etc can be cited as the classic examples of this approach. The scientific literature contains many examples and practices with replacement of the most toxic and hazardous solvents. In recent years, new methods have been developed for solvent-free synthesis under mild conditions and with low energy consumption.

9. Microwave synthesis: Organic reactions can be performed in microwave furnaces under solvent-free conditions. These techniques are considered "greener" than the conventional methods. The wide range of applications of microwave chemistry has been extended recently to many aspects of organic synthesis.

10. Sonochemistry in Synthesis: Sonochemistry is also considered as a solvent-free reaction methodology. High yields, low energy requirements, low waste, no use of solvents are some of the fundamental advantages of these sonochemical techniques.

11. Green Solvents from Plants: Plants are not only considered as a renewable source of energy but also a resource for various materials. Unlike petroleum, which is the main source of chemicals in the petrochemical industry, plant oils or vegetable oils derived from plant sources are renewable sources. Vegetable oils can replace petroleum derived organic solvents with better properties and more eco-friendly conditions as waste. Chemists have advanced and recent techniques where vegetable oils can be effectively used as replacement for hazardous organic solvents [Spear SK, Griffin ST, Granger KS, et al. "Renewable plant-based soybean oil methyl esters as alternatives to organic solvents". Green Chemistry 9:1008-1015, 2007].

In the last decade, tremendous research is going on in the field of use of "green" solvents in polymerization methods. There have been some successful uses of alternative solvents in polymerization under the principles of Green Chemistry [Erdmenger T, Guerrero-Sanchez C, Vitz J, et al. Recent developments in the utilization of green solvents in polymer chemistry. Chemical Society Reviews 39:3317-3333, 2010].

All these techniques aim at replacing toxic and hazardous solvents in many chemical processes in the synthetic laboratory and in the chemical industry.

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