

## IMPACT OF SOLVENTS ON ENVIRONMENTAL POLLUTION

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### ABSTRACT

The use of hazardous and toxic solvents in chemical industry is considered as very important problem for the human health and environmental pollution. Organic solvents are very important liquid media for the reactions to take place, and after the synthesis of chemical product for extraction, separation, purification and drying.

Aromatic solvents (benzene, toluene), chlorinated and polychlorinated solvents ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ) and other organic solvents (DMSO, DMF, Petroleum ether, Diethyl ether, Acetone) are used in great quantities in many analytical techniques, can cause environmental problems. Long term exposure to solvents and air pollutants can lead to deleterious effects on respiratory, haematological and thyroid functioning. The aim of the study is to investigate whether chronic exposure to solvents like benzene and pollutants like carbon monoxide in petrol filling workers has adverse effect on blood parameters.

To avoid these hazardous solvents some new solvents called green solvents are prepared. Here we discuss the properties of green solvents and also their applications to other reactions to avoid the environmental pollution.

**Keywords:** organic solvents, hazardous solvents, carbon monoxide, Green solvents.

### 1. INTRODUCTION

Organic solvents are very important as liquid medium for reactions to take place. The majority of solvents are organic chemicals with hazardous and toxic properties, costly (part of the petrochemical industry) and part of the large waste by-products of the chemical industry causing environmental problems. Although most of their toxic potential is known and there are safety rules for their use, prolonged and high concentration exposures can cause occupational diseases.

The subject of toxicology of solvents and their occupational health and safety problems related to their use have been studied extensively. Some solvents were replaced of severely restricted due to their high toxicity or carcinogenicity. Many epidemiological studies with chemists and laboratory technicians in analytical chemical and biochemical laboratories showed that solvent exposure can cause adverse health effects.

Various occupational solvents like benzene and atmospheric polluted air are absorbed into the human body either through the respiratory tract or via epidermal contact. These may cause primary respiratory symptoms and impaired pulmonary and dermatological functions. The haematopoietic system, as the cells recycle continually, is highly sensitive to most of the air pollutants, which are reaching the blood very fast without being biotransformed. The solvents and air pollutants may interfere in the process of red blood cells proliferation. These changes are reflected in the synthesis of heme and the life expectancy of RBCs. Toxic material from air leads to significant damage to red blood cells causing a plastic anemia.

Physical properties of organic solvents

The physical properties of an organic solvent have great bearing on the safe handling procedures for that chemical and play a large role in determining the degree of fire and explosion hazard associated with its use.

### 2. Boiling point

This is an indicator of how readily the chemical becomes a gas (vapourises). The lower the boiling point, the more readily it vapourises. It should be noted that the boiling point for mixtures may be different from those of the components.

### 3. Flash point

The lower the flash point, the greater the flammability. A solvent with a flash point of  $23^\circ\text{C}$  or less is highly flammable.

### 4. Explosive limits

The lower explosive limit (LEL) is the lowest concentration of solvent in air that will ignite. The upper explosive limit (UEL) is the highest concentration of solvent in air that will ignite. As a rule of thumb, the greater the range between the LEL and the UEL, the greater the fire hazard. For example: ether LEL = 1.9% UEL = 36.0% 1,1,1-trichloroethane, which has had stabilisers added LEL = 8.0% UEL = 10.5% Based on these values only, ether presents a greater fire hazard than the 1,1,1-trichloroethane formulation. However, to determine the fire hazard accurately, flash point and vapour pressure would also need to be considered.

### 6. Vapour density

A vapour which is heavier than air (vapour density greater than 1) will tend to collect in pools and spread near ground level and in confined spaces. A vapour which is lighter than air (vapour density less than 1) will tend to rise. However, air movements will increase vapour dispersal in either situation.

### 7. Health Hazards

When considering the hazards associated with any workplace, it is essential to understand the relationship between 'hazard', 'exposure' and 'risk'. Health effects can occur only if a worker is actually exposed to the hazard. The risk of injury or disease usually increases with the duration and frequency of exposure to the agent, and the intensity/concentration and toxicity of the agent.

### 8. Exposure routes

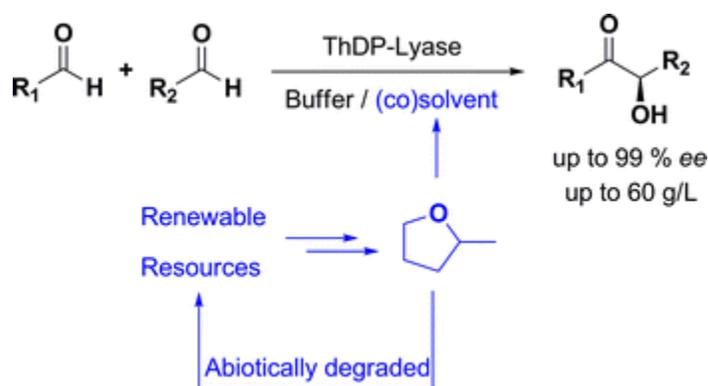
The harmful effects of organic solvents follow inhalation of vapour, eye and skin contact with liquid or vapour, or ingestion, which are described below: □ □

- *Inhalation* is usually the most significant route of entry by which organic solvents enter the human body at work.
- Some organic solvents may be *absorbed* through the skin without any noticeable effect on the skin. Others may cause serious damage to the skin itself.

Toxic atmospheric contaminants may have *local effects* if they harm only the part of the body they come in contact with, or *systemic effects* causing changes to the function of other organs.

## 9. ORGANIC SOLVENTS:

Effect of DMSO used as solvent in copper mediated living radical polymerization The use of DMSO as solvent for transition metal mediated living radical polymerization was investigated using copper (I) bromide/*N*-(*n*-propyl)-2-pyridyl-methanimine catalyst system and ethyl-2-bromoisobutyrate as initiator. The best conditions for polymerization in DMSO of different methacrylates (MMA, BMA, DMAEMA, HEMA) were determined. In all cases, the measured number-average molar mass of the product increased linearly with monomer conversion in agreement with the theoretical  $M_n$  with low polydispersity products ( $1.16 < PDI < 1.4$ ) achieved. Solvent was found to play a crucial role in the process. The effect of the polar solvent has been investigated and it was shown that DMSO could coordinate copper (II), increasing the activation process, or copper (I), changing the nature of the copper catalyst by competitive complexation of ligand and DMSO. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 6299–6308, 2004 Enzyme-catalyzed C–C bond formation using 2-methyltetrahydrofuran(2-MTHF) as (co)solvent: efficient and bio-based alternative to DMSO and MTBE the enzymatic carbonylation of aldehydes (C–C bond formation) catalyzed by benzaldehyde lyase (BAL) affords chiral  $\alpha$ -hydroxy-ketones under mild reaction conditions in aqueous media. To enhance substrate and product availability under aqueous conditions, processes are often set-up using either DMSO as co-solvent, or MTBE as second organic phase. Although efficient, DMSO leads to difficulties in separation during downstream processing, with wastewater formation. MTBE provides a cleaner and straightforward work-up, but its petrochemical origin, together with its poor degradability, gives rise to environmental concerns. Herein it is reported that 2-methyltetrahydrofuran (2-MTHF) is a promising candidate to substitute DMSO or MTBE in lyase-catalyzed reactions. 2-MTHF can be derived from bio-based resources (*e.g.* levulinic acid), and it is abiotically degraded by air. When BAL is added to buffer-2-MTHF (5% v/v) mixtures, enzyme remains stable with a half-life of  $178 \pm 8$  h, with productivities (benzoin synthesis) of  $10 \text{ g benzoin L}^{-1} \text{ h}^{-1}$ . Several BAL-catalyzed aldehyde carbonylations were assessed under those conditions, leading in all cases to high isolated yield (quantitative in majority), and to high enantioselectivity (up to >99%). Furthermore, preliminary results obtained with two phase systems in the BAL-catalyzed benzoin synthesis afforded  $60 \text{ g benzoin L}^{-1}$  in 24 h (*ee* > 99%). Therefore, 2-MTHF may be a valuable (co)solvent, not only to tackle environmental concerns, but also in terms of practical, efficient biocatalysis.



## 10. Benzene

Benzene is a colorless, flammable liquid with a sweet odor. It evaporates quickly when exposed to air. Benzene is formed from natural processes, such as volcanoes and forest fires, but most exposure to benzene results from human activities. Benzene is among the 20 most widely used chemicals in the United States. It is used mainly as a starting material in making other chemicals, including plastics, lubricants, rubbers, dyes, detergents, drugs, and pesticides. In the past it was also commonly used as an industrial solvent (a substance that can dissolve or extract other substances) and as a gasoline additive, but these uses have been greatly reduced in recent decades.

## 11. EFFECTS OF ORGANIC SOLVENTS

**11.1. Health effects:** many occupational diseases caused by chemicals result from breathing air that contains harmful substances.

Exposure to hazardous material may be acute or chronic. *Acute exposures* generally refer to single dose, high concentration exposures over short periods, while *chronic exposures* involve repeated or continuous exposures over long periods. These exposures may have acute, immediate effects or chronic, long term effects. Some examples of health effects are listed below.

**11.2. Respiratory tract:** The vapour of many organic solvents is irritating to the lining of the respiratory tract, affecting the nose, throat and lungs. Asthma-like reactions have been reported with some organic solvents.

**11.3. Skin:** Skin contact often causes drying, cracking, reddening and blistering of the affected area. These signs of inflammation of the skin are called dermatitis and enhance solvent absorption and encourage secondary infection.

**11.4. Eyes:** Direct contact with organic solvent vapour or liquid may cause eye irritation. This is usually reversible and permanent eye damage is rare.

**11.5. Liver:** Many organic solvents are potentially toxic to the liver, either alone or in combination with other solvents. For example, liver damage is associated with exposure to carbon tetrachloride, other chlorinated hydrocarbons and ethanol. Consumption of alcoholic drinks may enhance the effects of many solvents.

**11.6. Kidney:** Both short and long term exposure to certain organic solvents has been found to be harmful to the kidney. Carbon tetrachloride, trichloroethane and petroleum distillates, for example, gasoline, jet fuel and turpentine, are among the most toxic.

**11.7. Cardiovascular system:** Chlorinated hydrocarbon solvents, such as methylene chloride and trichloroethane, may cause harmful effects on the heart. Abnormal heart rhythms have been reported arising from trichloroethylene exposure. Chronic exposure to carbon disulphide is considered to be a contributory factor in coronary heart disease.

**11.8. Nervous system:** Exposure to organic solvents can result in a variety of serious effects in both the central nervous system (CNS - brain and spinal cord) and the peripheral nervous system (PNS - nerves supplying the rest of the body). The acute effects of organic solvent exposure range from an alcohol-like intoxication to narcosis (stupor or insensibility) which may lead to unconsciousness and eventually death from respiratory failure.

Intermediate symptoms include drowsiness, headache, dizziness, dyspepsia (gastric discomfort) and nausea. Long term gross exposure to both n-hexane and methyl n-butyl ketone is associated with degeneration of nerve cells in the PNS, resulting in symptoms such as restless legs, muscle cramps, pains and weakness in limbs and loss of sensation in the limbs. Chronic CNS effects resulting from long term repeated exposures to organic solvents include fatigue, mood disturbance and difficulty in concentrating, memory loss, personality changes and loss of motivation. This damage may eventually become permanent.

**11.9. Organic solvent exposure and cancer:** Benzene is the only organic solvent which has definitively been proven to cause cancer in humans from industrial use. Human evidence shows that extended exposure to levels of benzene may produce leukaemia. A number of other organic solvents cause cancer in laboratory animals exposed to the solvents for much of their life. It is suspected, but not proven, that these solvents may pose a risk to workers who have long term exposure to them.

**11.10. Haematological effect:** exposure to solvents like benzene decreases the RBC count and Hb level causing anemia among workers exposed to >10ppm. But the study conducted by us indicates on the contrary that there is a gradual increase the RBC count and Hb level among the workers exposed to benzene as well as air pollutants like CO.

## 12. THYROID GLAND

The decrease in the TSH level could be either due to the toxic effect of the solvents like benzene present in the petrol vapor and polluted air. We believe that the low level of TSH is probably associated with central pituitary dysfunction due to solvent and polluted air exposure [21]. The increase in the T4F and T4 may be due to the fact that when a person is exposed to the environmental pollutants may lead to negative effect on selenium metabolism [22]. Even if the selenium is sufficient, it will be replaced by the solvents present in the petrol vapor or polluted air. This may be the reason for decrease in the T3 and T4F levels. The studies conducted by Goldman and Dillon showed that selenium supplementation does protect against the toxic effect of the environmental pollutant on thyroid function

### Environmental contamination

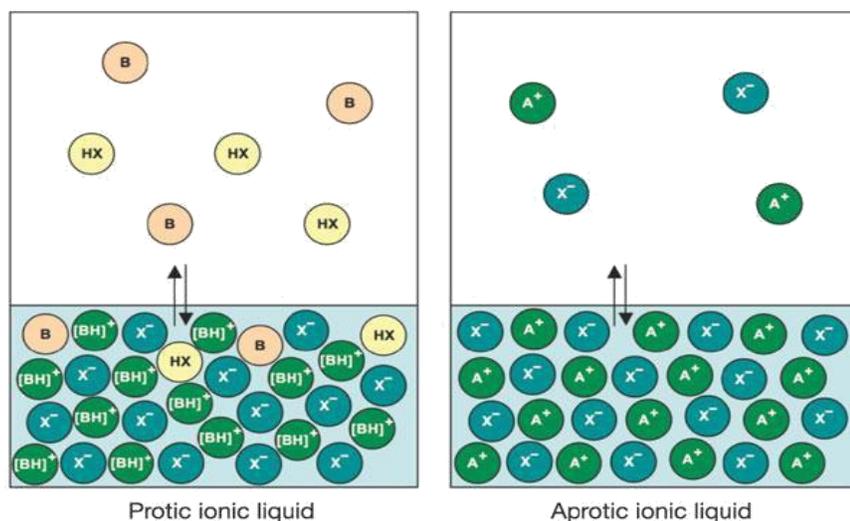
A major pathway to induce health effects arises from spills or leaks of solvents that reach the underlying soil. Since solvents readily migrate substantial distances, the creation of widespread soil contamination is not uncommon; there may be about 5000 sites worldwide that have major subsurface solvent contamination; this is particularly a health risk if aquifers are affected. Green Chemistry, Green Solvents. Alternative Techniques in Organic Synthesis Green Chemistry aims for less toxic solvents but in recent years new methods have been developed where organic synthesis can be performed without solvents, mild conditions and low energy consumption. 10 New conferences and symposia have promoted the use of alternative methods or "green" solvents.<sup>12,13</sup> The new field of "green" solvents in organic synthesis has been extended by research papers and publications.<sup>14</sup>

Some of these methods are presented below with a brief explanation of how they work and some references.

Ionic Liquids in Organic Synthesis. Are they Green Chemistry?

Ionic liquids are mixtures of anions and cations, molten salts, with melting point around 100° C, which can be used as alternative solvents in organic synthesis. Although the ionic liquids do not comply full with green chemistry principles, they are very promising as alternatives to organic solvents.<sup>15</sup>

In the scientific literature there are a large number of research papers for the use of ionic liquids in synthetic routes and various applications.



### 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 because some reagents are not soluble and provides selectivity. The low solubility of Oxygen is also an advantage for some reactions where metal catalysts are used.

### Techniques for Organic Synthesis in Perfluorinated Phases

In some new methodologies chemists use perfluorinated diphasic solvents to dissolve a catalyst with very long perfluorinated chain. These catalysts can be very effective and provide high yields in some types of reactions where the catalysts play an important part. Another advantage is that after the reaction the catalyst can be separated and recycled.<sup>26</sup>

### Supercritical carbon dioxide and supercritical water

A supercritical liquid is at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. The supercritical liquid can effuse through solids like a gas, and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of a supercritical fluid to be "fine-tuned". Supercritical liquids are suitable as a substitute for organic solvents in a range of industrial and laboratory

## 13. CONCLUSION

Physiological dysfunctioning effects are constantly observed in the occupationally exposed petrol workers. The data suggests that background benzene and air pollutants could account for substantial part of respiratory, hematological and thyroid dysfunctioning. In order to prevent these among petrol filling workers, we suggest that medical observation, including pre employment and periodic medical Checkups, should be performed which include pulmonary function tests. Control strategies should be adopted to reduce the benzene concentration in the ambient air and evaporation control. Thus medical screening and screening of benzene and CO in air may protect workers from developing chronic respiratory disorders.

## 14. REFERENCES

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