

GREEN CHEMISTRY REAL APPLICATIONS –(c)

Dr. Bina Rani
University Professor of Chemistry
Magadh Mahila College, P.U, Patna

M.Sc 3rd Semester
CC12
Environmental Chemistry and
Green Chemistry

Design and Application of Surfactants for Carbon Dioxide; Making Carbon Dioxide a Better Solvent in an Effort to Replace Solvents that Damage the Environment

Volatile organic compounds (VOCs) and halogenated organic compounds are used by a wide range of industries for various types of cleaning. Some examples of industrial types of cleaning that employ these compounds as solvents are:

- flux removal
- oil and grease removal from metal parts
- garment cleaning

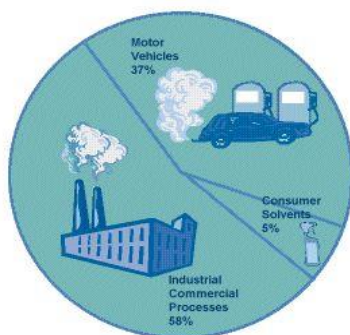
In addition, the individual consumer uses many household products that contain VOCs and halogenated organics. Examples include:

- stains and varnishes
- paint thinner
- fingernail polish remover
- adhesives
- furniture polish
- hair spray

The worldwide use of VOCs and halogenated organics is estimated to be more than 30 billion pounds per year! Many of these solvents pose a threat to our air quality, water supply, the ozone layer, and our personal health. Briefly, let's explore some examples of these solvents, what they are used for, and the effect they have on our environment.

Volatile Organic Compounds (VOCs)

Figure 1. Sources Of VOCs (From [Epa Web Site](#))

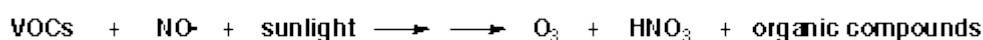


Sources of VOC

VOCs include solvents such as xylene, toluene, benzene, methylene chloride, chloroform, and isopropyl alcohol. They are widely used in industry because they are relatively non-polar and are therefore effective in dissolving oil, wax, and grease. Additionally, the average consumer uses many VOCs on a daily basis. VOCs are also present in gasoline, paints, glues, varnishes, and household cleaning products. VOCs are released from burning fuel (gasoline, oil, wood, coal, natural gas, etc.), and automobiles are a major source of VOCs.

These compounds are called volatile organic compounds because they have a high vapor pressure and thus evaporate readily at room temperature. Their high vapor pressure is generally a result of the weak intermolecular forces between these nonpolar molecules. Because of their volatility, they can be used to clean a delicate item such as electronic components or a wool sweater without the use of heat to evaporate the solvent. Also because of their volatility, they can easily escape into the atmosphere and lower air quality.

VOCs react with nitrogen oxide in the presence of sunlight to form ozone (O₃) and other pollutants (Scheme 1). Ozone is the principal component of photochemical smog and pollution in many of the world's cities. Additional pollutants that are produced from the interaction of sunlight with VOCs and nitrogen oxide, include nitric acid, which leads to acid rain, and aldehydes, ketones and other compounds resulting from partial oxidation of the VOCs.



Scheme 1. Production of Ozone from VOCs

Figure 2. Earth's Atmosphere (from [epa web site](#))



Although there is great concern today about depletion of the stratospheric **ozone** layer (Figure 2), to the contrary, the production of ozone in the troposphere poses a significant health risk. The troposphere comprises the atmosphere we live in and the concern with the presence ozone is that there is too much of it in the air that we breathe. Frequent exposure to ozone can result in permanent damage to the lungs, chest pain, coughing, congestion, and nausea. Tropospheric ozone even damages plant life and makes them more susceptible to insects, disease, and other pollutants.

Halogenated Organic Compounds

Halogenated organics are carbon-based compounds that contain halogen atoms such as fluorine, chlorine, and bromine. Two of the major classes of halogenated organic compounds are the chlorofluorocarbons (CFCs) and the hydrochlorofluorocarbons (HCFCs). These compounds are in general chemically unreactive, nontoxic and non-flammable. These properties have contributed to the popularity of the use of CFCs and HCFCs as solvents for industrial cleaning. In addition, these substances have been widely used as refrigerants, propellants for aerosols and blowing agents. The names and formulas of some common CFCs and HCFCs are shown in the table below.

CFCs
CCl_3F
trichlorofluoromethane
CCl_2F_2
dichlorodifluoromethane

Although CFCs have properties that make them excellent solvents, and useful in many other applications, they are now widely known to decompose in the stratosphere under the influence of high energy UV radiation (UV-C). These decomposition products catalyse reactions that deplete the stratospheric **ozone** layer, resulting in significant increases in the intensity of harmful UV radiation reaching the surface of the earth. In view of this, under the **Clean Air Act** of 1990, CFCs can no longer be produced or imported into the United States. HCFCs are being used as temporary replacements for CFCs because HCFCs do not have as great an ozone layer depleting potential. The carbon hydrogen bond in HCFCs makes them much more reactive than CFCs and the vast majority of the HCFC molecules are destroyed in the troposphere. This prevents most of the HCFC molecules from rising into the stratosphere where they too would act to deplete the ozone layer.

Carbon Dioxide: An Alternative Solvent That Is Environmentally Preferable To VOCs And Halogenated Organic Compounds

Because of the many negative environmental effects of VOCs and halogenated solvents, finding alternatives to these solvents is important. Carbon dioxide presents an option to the VOCs and halogenated solvents and offers many advantages in its use as a solvent. Carbon dioxide is non-flammable, nontoxic, and chemically unreactive and it is also available as a cheaply recovered by-product from the production of ammonia and from natural gas wells.¹ In addition, the used carbon dioxide can easily be recovered, purified, and reused.

Unlike CFCs and HCFCs, carbon dioxide does not contribute to the depletion of the ozone layer, and unlike VOCs, carbon dioxide is not a factor in the creation of tropospheric ozone. However, carbon dioxide has other negative environmental effects. Because carbon dioxide in the atmosphere reflects infrared radiation (heat) back toward the earth, it is a greenhouse gas and it is thus a contributor to **global**

warming. In order for CO₂ to be considered as a green alternative to VOCs and halogenated organic solvents, the used CO₂ should be recycled. After using carbon dioxide as a solvent, it can be recovered and reused by simply allowing the supercritical or liquid carbon dioxide to be converted to a gas, capturing the gaseous carbon dioxide, and leaving the less volatile impurities behind. This recycling process requires very little energy since CO₂ exists as a gas under ambient conditions. Compared with organic solvents or water, its enthalpy of vaporization is considerably lower.

Another consideration when assessing carbon dioxide as a replacement for less environmentally friendly solvents, is the source of the CO₂. As indicated previously, carbon dioxide is produced as a waste product of ammonia production and from natural gas wells and can be recovered from these processes. Thus, no additional carbon dioxide need be produced, and the carbon dioxide that would normally be vented into the atmosphere from these processes, can actually be captured and put to good use. Many of these factors contribute to carbon dioxide being a green alternative to VOCs and halogenated organic compounds.

As indicted above carbon dioxide is a gas at room temperature and atmospheric pressure. In order to use CO₂ as a solvent, it must be converted into a supercritical state or a liquid state. As illustrated in the following phase diagram, carbon dioxide has a supercritical temperature (T_c) of 31 °C and a supercritical pressure (P_c) of 72.8 atm. Supercritical fluids have properties of both a gas and a liquid. Supercritical CO₂ is currently used as a solvent to "naturally" decaffeinate coffee.

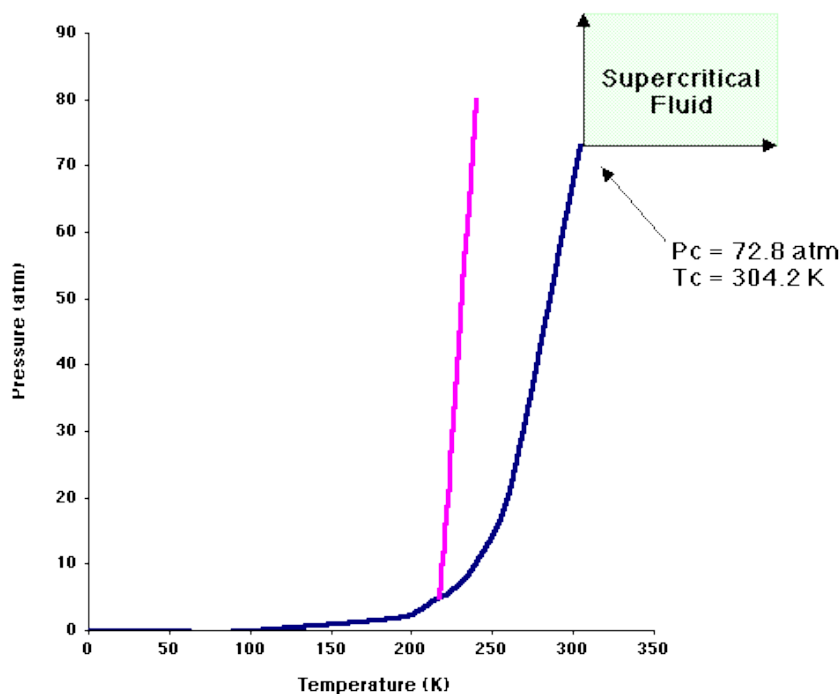
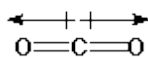


Figure 3. Phase Diagram of CO₂

Solubility Of Substances In CO₂

Although carbon dioxide has polar bonds it is a nonpolar molecule since the dipoles of the two bonds cancel one another.



Because of this nonpolar nature, carbon dioxide will dissolve smaller nonpolar molecules such as hydrocarbons having less than 20 carbon atoms and other organic molecules such as aldehydes, esters, and ketones,² but it will not dissolve larger molecules such as oils, waxes, grease, polymers, and proteins, or polar molecules. However, by using a surfactant, the solubility of many substances in CO₂ can be increased.

Surfactants are substances that increase the solubility of one substance in another. Soaps and detergents are common surfactants that enable nonpolar substances like oil and grease to be emulsified and washed away with the polar solvent water. From our everyday experiences, we know that oil and water do not mix, that is they are insoluble in each other. They are insoluble in each other because oil is nonpolar and water is polar and the rule of thumb for solubility is "like dissolves like". In other words, polar solvents dissolve polar solutes, and nonpolar solvents dissolve nonpolar solutes. A surfactant is a molecule that contains a polar portion and a nonpolar portion. By having both polar and nonpolar groups within the same molecule, a surfactant can interact with both polar and nonpolar molecules, thereby increasing the solubility of two otherwise insoluble substances.

In water, surfactant molecules tend to cluster into a spherical geometry with their nonpolar ends on the inside of the sphere and their polar ends on the outside. The polar ends are on the outside so they can interact with the polar solvent water. These clusters are called micelles and an example is shown in Figure 4.

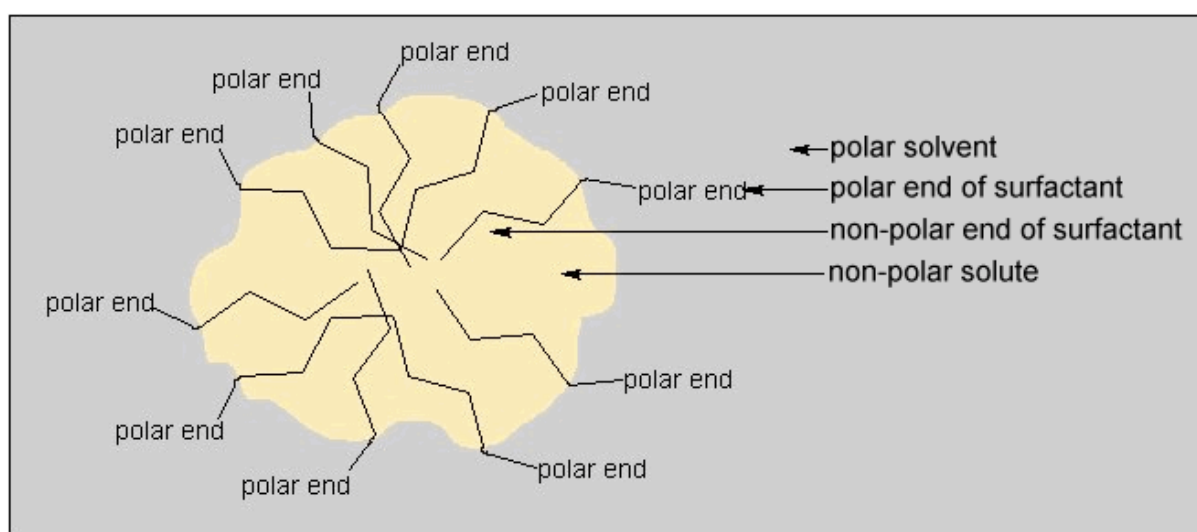


Figure 4. Micelle Structure of a Surfactant in a Polar Solvent
(reprinted with permission from the American Chemical Society)

A surfactant for liquid or supercritical fluid CO₂ will have to have both CO₂-philic (CO₂ loving) and CO₂-phobic functionality. In 1994, Joseph M. DeSimone of the University of North Carolina and North Carolina State University published his discovery that polymers such as those shown in Figure 5 are soluble in liquid or supercritical fluid CO₂³. This fluoropolymer is soluble in CO₂ because of the weak van der Waals attractive forces that are present between CO₂ and the fluorocarbon tail of the polymer.

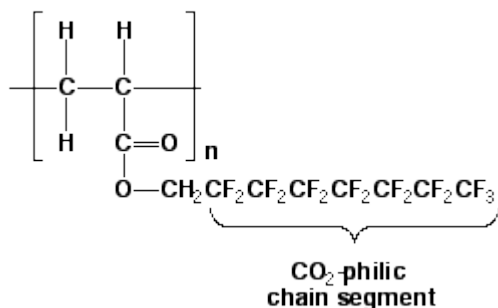


Figure 5. Polymer with CO₂-philic Fluorocarbon Tail

Polymers are molecules with very high molar masses. Water has a molar mass of 18 amu, but polymers typically have molar masses of 10,000 up to several million amu. Polystyrene is a very common polymer and has the repeat unit:

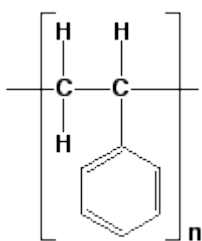


Figure 6. Polystyrene

This means that the unit contained within the brackets repeats over and over again. More specifically, it repeats *n* times and we would call *n* the degree of polymerization. For most polymers, *n* > 1000.

Polystyrene is used for a variety of packaging applications, such as plastic drinking cups, plastic cup lids, packaging for small produce items such as berries or cherry tomatoes. As a foam, it is commonly known as Styrofoam and is used as a drinking cup for hot beverages, foam insulation, and the familiar 'peanuts' used to protect delicate items in shipping.

Polystyrene is a brittle polymer and is most often combined with other polymers to improve its properties. One way to modify the properties of a polymer is to make a copolymer. A copolymer contains two different types of repeat units within the same polymer chain. A copolymer is not a blend of two different polymers, but instead the two monomers are covalently bonded along the length of the chain. A copolymer of

styrene and acrylonitrile is used to make automobile parts, appliances (refrigerator shelves), medical supplies, and battery cases.

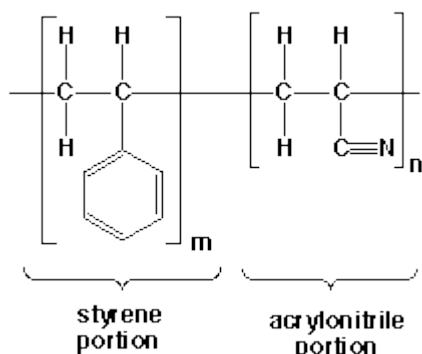


Figure 7. Styrene Acrylonitrile Copolymer

Copolymers can exist in a variety of arrangements. Three possible copolymer sequencing arrangements are shown below. In these structures, **S** represents the styrene monomers and **A** represents the acrylonitrile monomers.

Random **SASASAASSAS**
 Block **SSSSSAAAAAA**
 Alternating **SASASASASASA**

The polymer shown in Figure 5 is unusual because most polymers are not soluble in CO₂. In fact, the polymer in Figure 5 is one of the only two CO₂ soluble high molar mass polymers⁴. So, to make a CO₂ surfactant, DeSimone synthesized copolymers using polystyrene as the CO₂-phobic portion and the polymer shown in Figure 5 as the CO₂-philic portion². Figure 8 shows the structure of this block copolymer. The copolymer shown in Figure 8 can be schematically represented as SSSSSSSAAAAAA, where S=styrene units and A=Fluor acrylate units.

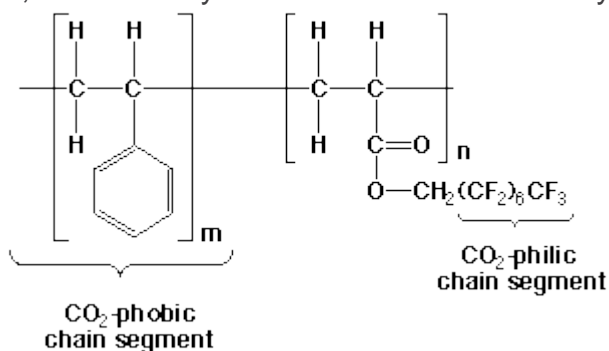


Figure 8. Copolymer Containing CO₂-phobic and CO₂-philic Units

Just as surfactants for water form micelle structures, so do surfactants for CO₂. Figure 9 shows this micelle structure for a CO₂ surfactant, with the CO₂-philic portion on the outside of the micelle. As with detergents that act as surfactants for cleaning using the solvent water, a CO₂ surfactant can increase the solubility of greases, waxes, and oils in the solvent CO₂.

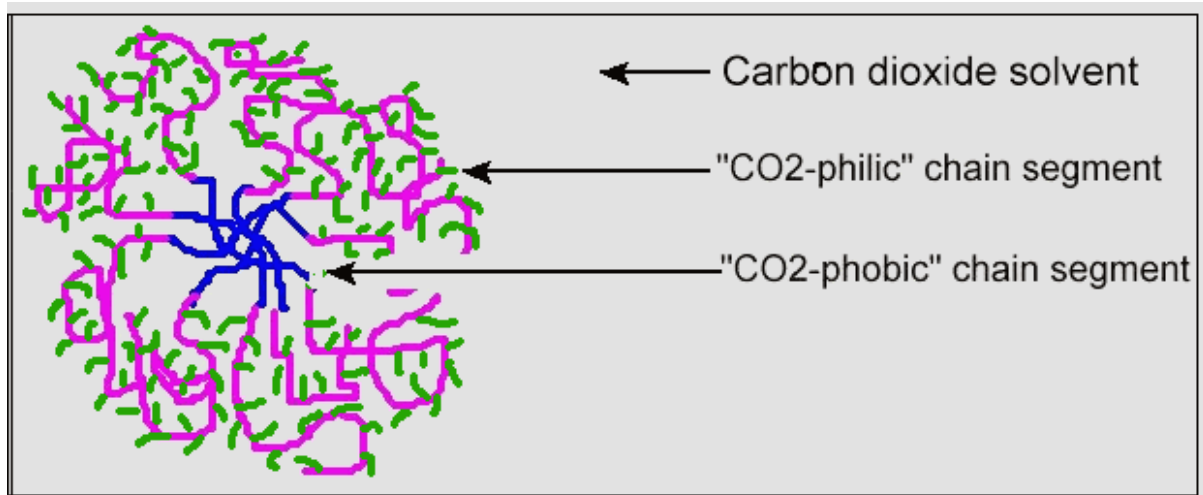


Figure 9. Micelle Structure for CO₂ Surfactant
 (reprinted with permission from the American Chemical Society)

Current Use Of CO₂ Surfactants

The dry-cleaning industry typically uses the solvent perchloroethylene (PERC), as the cleaning agent. Because clothes are cleaned in a liquid solution that is mostly PERC, and very little if any water is used, the term "dry cleaning" is used.

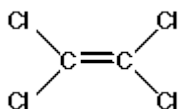


Figure 10. Tetrachloroethylene or Perchloroethylene (common name)

It is estimated that 344 million lb of PERC were produced in the United States in 1998. The dry-cleaning industry uses approximately 50% of the PERC produced each year, which amounts to 172 million pounds of the solvent. The EPA has classified PERC as a groundwater contaminant and a potential human health hazard. PERC is a suspected human carcinogen and a known rodent carcinogen. Breathing PERC for short periods of time can adversely affect the central nervous system. Effects include dizziness, fatigue, headaches, sweating, and possibly loss of coordination and unconsciousness. These effects are not likely to occur though at levels of PERC that are normally found in the environment, but people who work in the dry-cleaning industry have the greatest risk for exposure.

The use of PERC in the dry-cleaning industry began in the late 1930's. Prior to PERC, petroleum-based products such as kerosene were the dry-cleaning solvent of choice, but because of their high flammability, they were hazardous to work with and fires were common. PERC however, is not flammable and thus offers a significant advantage over petroleum-based cleaners. Because of the double bond in PERC, it is destroyed in the troposphere preventing it from rising to the stratosphere. Thus, unlike many other halogenated organic compounds, PERC does not contribute to the destruction of the ozone layer. However, PERC can contribute to the formation of photochemical smog, when it reacts with other VOCs, nitrogen oxide, and sunlight (Scheme 1).