PART

3

Separation and Purification Techniques

Essay — Intermolecular Forces in Organic Chemistry

The structures of organic molecules and the making and breaking of covalent bonds in chemical reactions are the major focus of classroom work in organic chemistry. After a discussion of intermolecular forces, mainly in the context of boiling points, the emphasis is on covalent bond chemistry. Except for hydrogen bonds, weak intermolecular forces may seem largely unimportant. However, many experimental techniques of organic chemistry—for example, the separation and purification of organic compounds—depend almost entirely on the weak forces between molecules.

Several categories of weak intermolecular interactions are listed here from strongest to weakest:

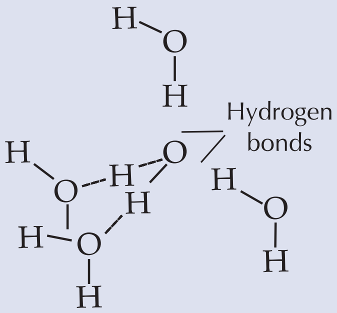
- Hydrogen bonding
- Dipole-dipole interactions
- Dipole-induced dipole interactions
- Induced dipole-induced dipole interactions

These electrostatic intermolecular forces are all concerned with favorable enthalpy changes that occur when molecules attract one another.

Hydrogen Bonding

Hydrogen bonding, often called H-bonding, occurs when hydrogen atoms are covalently attached to highly electronegative elements. Hydrogen atoms attached to atoms of these elements—most important are oxygen and nitrogen—can have reasonably strong electrostatic interactions, as well as weak orbital overlap, with electronegative atoms in nearby molecules. These interactions form intermolecular hydrogen bonds, whose energies are on the order of 15–20 kJ/mol (3.5–5 kcal/mol). This range of energies is only about 5% of the energy associated with covalent bonds, but it is enough to make hydrogen bonds the strongest of the weak intermolecular forces.

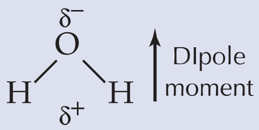
Perhaps the most dramatic example of intermolecular interactions by hydrogen bonding occurs between molecules of water. The high boiling point of water is an indication of the substantial intermolecular forces between water molecules. H_2O boils at 100ºC whereas CH_4, which is approximately the same size, boils at −162ºC. H_2O also boils over 160º higher than H_2S, which has a higher molecular weight and surface area. An intermolecular H-bonding network gives ice an open tetrahedral structure, which makes ice a very unusual solid: it floats because it is less dense than the liquid phase of water. Planet Earth would be a very different place without liquid water and floating ice.



Organic molecules that have hydrogen atoms covalently bonded to oxygen or nitrogen can also form H-bonds with water molecules or with other organic molecules that have oxygen or nitrogen atoms in them.

Dipole-Dipole and Dipole-Induced Dipole Interactions

Water is also distinguished by its polarity due to the relatively large charge separation in the polar O—H covalent bonds in water molecules. Just as bonds can be polar, entire molecules can be polar, depending on their shape and the nature of their bonds. Water has a large permanent dipole moment as well as a high dielectric constant, which gives it the ability to dissolve many inorganic and organic salts but not the ability to dissolve most organic molecules. Organic molecules that dissolve in water are usually those that can also hydrogen bond, particularly low molecular-weight alcohols, carboxylic acids, and amines.



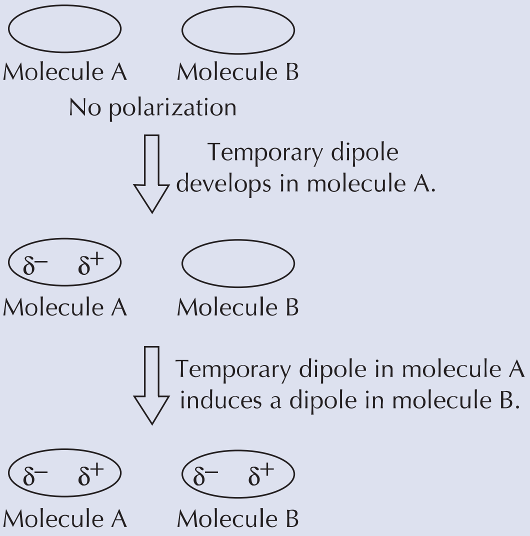
Molecules that have dipole moments can attract one another when their dipoles align so that there is an electrostatic attraction between them.

Some molecules, such as dimethyl sulfoxide (CH_3SOCH_3) and acetonitrile (CH_3CN), even though they have no hydrogen atoms that can H-bond with other molecules, have significant dipoles, which makes them polar solvents and miscible with water. In addition, each of them is able to accept an H-bond from a molecule of water.

Molecules that have dipole moments can also induce dipoles in other nearby molecules that do not have dipole moments of their own. This process provides an attractive force, although it is usually not as great as the one provided by dipole-dipole interactions.

Induced Dipole-Induced Dipole Interactions

The weakest intermolecular interactions are induced dipole-induced dipole interactions, often called London dispersion forces. These intermolecular forces result from temporary charges on molecules due to fluctuations in the electron distribution within them. Because all covalent molecules have electrons, they exhibit this induced dipole-induced dipole polarization. The magnitude of these dispersion forces depends on how easily the electrons in a molecule can move in response to a temporary dipole in a nearby molecule, called *polarizibility*.



London dispersion forces are the only intermolecular interactions that attract alkane molecules to their neighbors. They play a major role in the structure of lipid bilayer membranes, where fatty acids having linear alkane chains of 11–19 CH_2 groups closely pack together to form the membrane.

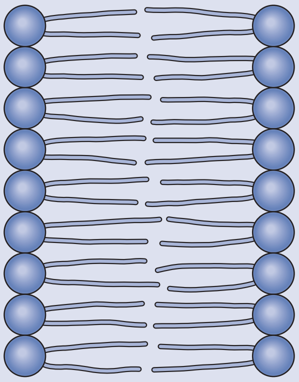


Diagram of a bilayer membrane. The fatty acid chains are attached as esters to molecules of glycerol, which also have ionic phosphates attached, shown as blue circles.

Van der Waals Forces

All weak intermolecular forces, with the exception of hydrogen bonds, are often referred to as van der Waals forces. The magnitude of van der Waals interactions depends on the surface areas of the interacting molecules. Thus, larger molecular-weight compounds have higher boiling points, and isomers whose shapes lead to larger surface area also have higher boiling points.

When very large molecules interact, a combination of many hydrogen bonds and van der Waals electrostatic forces can produce a large cumulative effect with strong association between the molecules. These intermolecular forces can also occur between different portions of very large molecules. For example, they determine the three-dimensional shapes of proteins and nucleic acids (DNA and RNA).

Solubility

Water and an organic solvent, such as hexane, do not dissolve in one another because water has extensive hydrogen bonding as well as dipole-dipole forces. To dissolve hexane in water would involve breaking apart these favorable electrostatic interactions between water molecules. In addition, the alkane molecules have their own attractive van der Waals forces which would be disrupted by foreign water molecules. Thus, water is not soluble in hexane.

The insolubility of organic and inorganic salts in hexane can be understood by recognizing that for salts to dissolve, the positive and negative ions in the salt crystals must be separated from each other. The electrostatic ion-ion attraction is strong, and the weak interactions between the ions and hexane molecules cannot begin to compensate for the energy required to separate the ions from one another. However, water has quite strong ion-dipole forces with both positive and negative ions, which can often compensate for the energy required to separate the ions from one another. Thus, ionic salts are much more soluble in water than in hexane.

The solubility of many organic compounds in relatively nonpolar organic solvents can be understood by the compensating intermolecular forces that produce a favorable enthalpy and often more so by the favorable entropy of mixing, which is related to the greater disorder that results when a solid dissolves in a liquid or two liquids dissolve in one another.

Intermolecular Forces in Separation and Purification

Part 3 is concerned mainly with the techniques that organic chemists use to separate liquids from other liquids by extraction and distillation and to separate solids from liquids by crystallization and filtration. Understanding the techniques of separation and purification of organic compounds depends on understanding the weak intermolecular interactions of liquids and solids.

Extraction is a technique for separating a water-insoluble organic compound from water-soluble salts and polar organic compounds by mixing an organic solvent with an aqueous mixture. Carrying out two or three extractions of a water mixture with an organic solvent usually serves to separate and purify a desired organic compound.

We have already briefly discussed the importance of intermolecular forces in determining the boiling points of organic compounds. The stronger the intermolecular forces, the more energy it takes to pull the molecules away from each other and the higher the boiling point. The technique of distillation utilizes the difference in boiling points of compounds in a mixture to effect their separation.

Crystallization is often carried out by adding water to an organic reaction mixture to decrease the solubility of a solid organic product, which can then be filtered from the aqueous mixture. The technique of recrystallization uses differential solubility to purify a solid. In general, organic compounds become more soluble at higher temperatures. A recrystallization solvent of the right polarity is chosen so that the solid dissolves in hot solvent but is largely insoluble in cold solvent. Impurities remain dissolved in the cold solution when the recrystallized solid is filtered.