

## Solvents and Polarity

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by

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### Abstract

This document describes the concept of polarity in molecules. Polarity is our main tool to predict the extent to which solutes will dissolve in solvents and if two solvents will be miscible, i.e., mix uniformly. The first five sections review molecular structure, electronegativity, and organic nomenclature. The final two sections tabulate common solvent and solution terminology. The purpose of this document is to help students recognize and categorize the different types of molecular species that are used in analytical chemistry methods. This document does not cover ionic compounds and aqueous solutions, which are discussed in the “Soluble Aqueous Salts” document.

The most current version of this document is available online at:

**<http://www.achem.org>.**

This website and associated files are provided by the author to assist users of the text:

B. M. Tissue, *Basics of Analytical Chemistry and Chemical Equilibria*, 2<sup>nd</sup> Ed. (John Wiley: New York, 2023).

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## I. Introduction

Analytical chemists work with many inorganic and organic compounds in solution. A major impediment for students studying analytical chemistry is being unable to recognize the nature of different chemical species. This lack of knowledge makes it difficult to recognize solvents that mix and the nature of solutions. It further makes it difficult to predict when reactions might occur. Let's first define what we mean by chemical species and speciation. IUPAC defines "chemical species of an element" as:<sup>1</sup>

"Specific form of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure."

As an example of isotopic composition, deuterated chloroform,  $\text{CDCl}_3$ , which is used as a solvent for NMR spectrometry, is a different species than chloroform  $\text{CHCl}_3$ . These two species have the same molecular geometry, but they have a different formula weight and different spectroscopic properties. We specify the isotopic composition when an atomic or molecular sample has been enriched or depleted in one or more isotopes compared to the natural abundance of those isotopes. In general, isotopically enriched molecules will have very similar chemical properties to molecules that have the natural abundance of isotopes.

Speciation due to oxidation state is discussed more fully in the "Soluble Aqueous Salts" document. For hydrocarbons, we usually discuss speciation in terms of structure. The "molecular structure" is the arrangement in space of the atoms that make up a molecule. Structural speciation includes many types of isomers, which are molecules with the same constituents but a different arrangement.

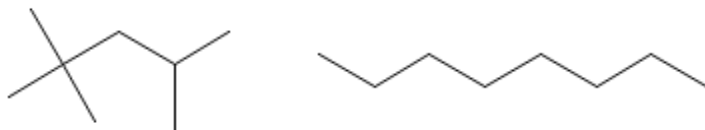
It is not convenient or necessary to draw a three-dimensional structure in every context, so we use different levels of descriptors for molecules. The empirical formula lists only the composition of the molecule. As an example, octane and isooctane (2,2,4-trimethylpentane) both have the molecular formula  $\text{C}_8\text{H}_{18}$  and a formula weight of 114.23 g/mol.

Figure 1 shows the line formulas of octane and isooctane. Each vertex in a line formula represents a carbon atom and the hydrogen atoms are not shown. This representation provides more structural information in that it shows the branching of the carbon backbone. Octane and isooctane are constitutional isomers. They have equivalent empirical formulas but a different structural arrangement. The difference gives these two molecules different chemical and physical properties. For example, the branching in isooctane leads to a much lower boiling point, 99 C versus 125 C for n-octane. While these two molecules will be totally miscible when mixed, they are also easily separated or

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<sup>1</sup> <http://goldbook.iupac.org/CT06859.html>

measured by analytical methods such as gas chromatography. More details of molecular structure can be found in the *Virtual Textbook of Organic Chemistry*.<sup>2</sup>



**Figure 1.** Line formulas of isooctane (left) and octane (right).

Other constitutional isomers can have very similar properties. Most solvents used in analytical methods will consist of a pure compound. There are cases where solvent mixtures are useful, such as xylenes (dimethyl benzene) and hexane. Hexane can be purchased as pure n-hexane or as a mixture that contains n-hexane, 2-methylpentane, 3-methylpentane, etc. There are other types of isomers, such as stereoisomers. These different molecular arrangements are important for analyte determination, but they are not common for typical lab solvents. Numerous other examples can be found in the *Illustrated Glossary of Organic Chemistry*.<sup>3</sup>

## II. Types of Bonding

As a start in recognizing the nature of chemical species, we classify the bonds that hold atoms together as either metallic, ionic, or covalent. Metallic bonds hold metal atoms together in a solid. Solid metals generally need to be oxidized to an ionic form to be dissolved in an aqueous solution or incorporated into a metal complex. Since we are more concerned with liquid solvents and solutions, we will skip discussing this type of bonding.

Similarly, ionic bonds hold ions together in solids. An ionic bond occurs due to the electrostatic or Coulombic attraction between a positively charged cation and a negatively charged anion. Ionic solids will dissolve to varying extents in a solvent depending on the energetics of the dissolved ions versus the lattice energy of the solid. We know table salt ( $\text{NaCl}$  or  $\text{Na}^+\text{Cl}^-$ ) is highly soluble in water, whereas limestone ( $\text{CaCO}_3$  or  $\text{Ca}^{2+}\text{CO}_3^{2-}$ ) is only sparingly soluble. We will leave this discussion for the “Soluble Aqueous Salts” help document. Here we will focus on covalent bonding to understand molecules. In general, ionic species do not dissolve in nonpolar solvents, except for some cases of organic ions that exist as ion pairs.

A covalent bond is the sharing of valence electrons between two atoms.<sup>4</sup> These bonds form because the electronic energy of the molecule is less than the total electronic energy of the separated atoms. The simplest case is a diatomic molecule in the gas phase. When two atoms approach each other, they can share their valence electrons to lower

<sup>2</sup> Reusch, W.; <https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/nomen1.htm>.

<sup>3</sup> Hardinger, S. A.; <http://www.chem.ucla.edu/~harding/IGOC/IGOC.html>.

<sup>4</sup> Valence electrons are the electrons in the outermost electron shell of each atom.

the total electronic energy. The shared valence electrons form the bond that holds the atoms together to make a molecule.

There are other weaker types of bonding, such as hydrogen bonding and van der Waals forces. These types of bonding are important to describe material properties, but they are mostly intramolecular interactions. We will neglect them for now in considering the nature of chemical compounds. The key point for our purpose is to be able to recognize the nature of molecular species, and we concentrate here on the intermolecular bonding and polarity of molecules.

### III. Electronegativity

In addition to the number and arrangement of the atoms in a molecule, the specific elements in a molecule will have a large effect on properties. The nature of the bonds in a molecule will determine its chemical properties, including its interactions with solvents and other compounds.

A covalent bond might be polar or nonpolar, depending on how equally the bonding electrons are shared. The atomic characteristic that we use to make this determination is electronegativity. Electronegativity is a relative scale that describes how strongly a given atom will attract electrons from other atoms. Figure 5 shows the Pauling electronegativities for the first three rows of the periodic table.<sup>5</sup> A bond between two atoms of the same element, e.g., molecular hydrogen, H<sub>2</sub>, or the C-C bonds in a hydrocarbon molecule, have equal electronegativity and share the bonding electrons equally. These bonds are completely covalent. Since the electron density of the bond is distributed evenly, these bonds are very “nonpolar.”

H 2.20						He --	
Li 0.98	Be 1.57	B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne --
Na 0.93	Mg 1.31	Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar --

**Figure 2. Pauling electronegativities.**

When the electronegativities of the bonding atoms are not the same, the more electronegative atom will hold the bonding electrons to a greater extent. The result is a partial negative charge on the more electronegative atom and a partial positive charge on the less electronegative atom. The electron density is not shared equally and the bond is polarized. The extent to which a bond is polarized depends on the relative electronegativity of the two atoms.

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<sup>5</sup> This figure is taken from Table 5.1 of the text, which discusses identifying acidic versus non-acidic protons.

Based on their similar electronegativity values, we could slide hydrogen in Figure 2 to be above boron and carbon. Hydrogen atoms bound to atoms with similar electronegativities, such as B or C, are covalent and nonpolar. The bonds of H attached to N, O, and F are also covalent, but with increasing polar character. Unlike ionic compounds, atoms in nonpolar covalent bonds, e.g., C-C, C-H, C-O, C-N, do not dissociate in water.

A hydrogen atom bonded to a very electronegative atom can dissociate in water. Hydrofluoric acid, HF, is a weak acid and dissociates partially when dissolved in water to coexist as HF(aq) and small equilibrium amounts of H<sup>+</sup>(aq) and F<sup>-</sup>(aq). The most common weak acids have an H atom bound to an electronegative atom such as O or S, and we'll see the -COOH group often. The acidity will further be affected by the local chemical structure.

#### IV. Classifying a molecule as polar or nonpolar

Determining the polarity of a bond is straightforward. The extent to which the bond is polarized depends on the relative electronegativity of the atoms. Classifying a molecule as polar or nonpolar is more variable. The overall polarity of a molecule depends on the geometry and presence of heteroatoms. Molecules that contain only carbon and hydrogen atoms, i.e., hydrocarbons, will always be nonpolar. Nonpolar molecules are generally miscible with each other and will have limited solubility in water. Molecules that contain heteroatoms, e.g., N, O, and S, will have polar regions. The degree of polar character in a covalent bond depends on how different the electronegativities of the constituent atoms. The overall polarity of molecules will depend on the relative number of heteroatoms versus the size of the hydrocarbon chains. Ethanol, CH<sub>3</sub>CH<sub>2</sub>OH is very polar and miscible with water, whereas octanol, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH is nonpolar and has limited solubility in water.

Covalent compounds can range from polar to nonpolar. Some polar compounds can be converted to ionic forms. For example, acetic acid, CH<sub>3</sub>COOH, can be neutralized with NaOH to form sodium acetate, CH<sub>3</sub>COO<sup>-</sup>Na<sup>+</sup>, and water. Most of the bonds in the acetate ion are covalent, but the negative charge makes it an ionic species. Octadecanoic acid or stearic acid, C<sub>17</sub>H<sub>35</sub>COOH, is a naturally occurring fatty acid with eighteen carbons. Because of the long alkyl chain, it has low solubility in water (<1 g/L) and higher solubility in organic solvents.

#### V. Organic Nomenclature

Before discussing specific examples, we need some background on naming molecules correctly. The following paragraphs provide the basics of naming simple organic compounds that are used as solvents. Many resources are available online for more complicated molecules.

Organic compounds are named based on the carbon backbone, i.e., methane, ethane, propane, butane, pentane for  $\text{CH}_4$  to  $\text{C}_5\text{H}_{12}$ . Larger hydrocarbons use the Greek numerical prefix for the number of carbons in the chain. A compound with a functional group gets a suffix to identify the group. For example, an alcohol name ends on -ol. A number is added before the backbone name to specify the location of the functional group. Iso-propanol The number is not always needed for small molecules, for example, 2-propanol is also called isopropanol.

Table 1 gives a general classification of different solvents based on the relative polarity of their functional groups. A functional group is a heteroatom or a portion of the molecule that has multiple bonds or different atoms that give it distinct characteristics. The “R” symbol in some examples, known as an “R-group” represents a heteroatom or a hydrocarbon subgroup. Any hydrocarbon with a functional group consists of the alkane chain (or ring), which can itself be thought of as a nonpolar functional group. The overall degree to which a molecule will be nonpolar varies with the length and branching of the hydrocarbon chain. Longer alkyl chains contribute more nonpolar character to a given molecule. For example, ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , dissolves in water completely, but octanol,  $\text{C}_8\text{H}_{17}\text{OH}$ , is only slightly soluble at 0.5 g/L. Both molecules are alcohols, but they differ in polarity due to the length of the alkane chain. Similarly, a linear chain will be more nonpolar than a molecule of the same size that has a branched structure.

**Table 1. Relative Polarity of Solvents**

relative polarity	compound class	common examples
very nonpolar	alkanes	hexane, $\text{C}_6\text{H}_{14}$
nonpolar	alkenes	1-hexene, $\text{C}_6\text{H}_{12}$ or $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
	aromatic hydrocarbons	benzene, $\text{C}_6\text{H}_6$
moderate polarity	ethers	diethyl ether, $\text{C}_4\text{H}_{10}\text{O}$ or $(\text{C}_2\text{H}_5)_2\text{O}$
	esters	ethyl acetate, $\text{C}_4\text{H}_8\text{O}_2$ or $\text{CH}_3\text{COOCH}_2\text{CH}_3$
	ketones	acetone, $(\text{CH}_3)_2\text{C}=\text{O}$
	aldehydes	acetaldehyde, $\text{C}_2\text{H}_4\text{O}$ or $\text{CH}_3\text{CH}=\text{O}$
polar	nitrile	acetonitrile, $\text{CH}_3\text{C}\equiv\text{N}$
	alcohols	ethanol, $\text{C}_2\text{H}_5\text{OH}$
	amines	$\text{R-NH}_2$
	organic acids	$\text{R-COOH}$
very polar	water	$\text{H-O-H}$

The solubility of organic compounds in water depends on their size and functional groups. The very nonpolar and nonpolar examples in Table 1 have little solubility in water. The polar examples can be miscible or immiscible with water, depending on the size of the hydrocarbon backbone.

## VI. Solvents

We can usually purchase a pure chemical as a solid, liquid, or gas, depending on its melting and boiling points. An analyte of interest is often a small component in a sample, which might be in any one of these three phases. For analysis, we must often capture or convert the analyte in a sample of air, liquid, or solid into a liquid mixture that is compatible with the method or instrument we are using for analysis. Similarly, the sample might consist of a complex matrix, and the analyte must be segregated from interfering species.

Table 2 summarizes the language that we use for solvents, solutes, and solutions. The following discussion is quite broad, but it is meant to provide the context to clarify the smaller subset of cases that we discuss in more depth. This section mostly describes organic compounds.

**Table 2. Solvent Terminology**

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Mixture	A general term for any gas, solid, liquid, slurry, or gel that contains multiple components. A mixture can be homogeneous or heterogeneous.
Solvent	A liquid consisting of one pure substance or of multiple miscible liquids. The term implies that it will be used to dissolve solutes.
Miscible	An adjective to describe liquids that form a homogeneous single phase when mixed in any ratio.
Immiscible	An adjective to describe liquids that phase separate on mixing.
Solute	A chemical species that dissolves in a solvent. Solute may be neutral or charged.
Solution	A solvent that contains dissolved solutes. We sometimes refer to pure solvent as a blank solution, although that is not consistent with this definition.
Organic solvent	A solvent composed of one or more hydrocarbons that is used to dissolve nonpolar solutes.
Aqueous solution	A liquid water solution that contains solutes.

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Solvents are classified broadly as being nonpolar or polar. This classification results from the types of functional groups in the molecular structure of the solvent. A functional group is a sub-part of the structure with certain types of atoms and bonding. Polar solvents have functional groups with polar bonds and nonpolar solvents have structures that consist primarily of nonpolar bonds. The section on electronegativity provides a foundation for understanding polarity in a molecule, but the two broad classes nonpolar and polar are sufficient to discuss solvents. If a finer degree of classification is needed, there are a number of empirical scales to rank the polarity of solvents that can be found through online searches. Likewise, tables of miscible solvents and solubility data can be found online for most common solvents.

Two solvents will be miscible if they have similar polarity. They will be immiscible if they have very different polarities. A nonpolar liquid, such as olive oil, is not miscible with a polar solvent such as water. We can shake a container of olive oil and vinegar to mix them as a vinaigrette, but these two solvents will separate in two separate phases over time.

Immiscible liquids will dissolve in each other to some extent. Even though benzene and water are immiscible, some concentration of benzene will dissolve in water before the addition of more benzene separates to a separate layer from the water solution. (1.8 g/L at room temperature). Adding more than 1.8 g of benzene to 1 L of water will lead to a separate phase of liquid benzene forming in contact with the water. Since benzene is less dense than water, the excess benzene will exist as a layer of solvent resting on top of the water. To summarize, “like dissolves like” is always a useful guide. Hopefully this document has helped to recognize when molecular species will be alike and when they will be different.

## VII. Solution Terminology

A major use for solvents in analytical applications is to dissolve other substances. We use the following terms to describe solutions and the components in solutions. Note that the quantitative aspects in this table are temperature dependent.

**Table 3. Solution Terminology**

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Soluble	An imprecise term indicating that a given species will dissolve in a given solvent.
Slightly soluble	An imprecise term indicating that a given species will dissolve to a small extent in a given solvent.
Insoluble	An imprecise term indicating that a given species will not dissolve to any appreciable extent in a given solvent.
Saturated	Refers to a solution that is in equilibrium with another phase, solid, liquid, or gas, and no further species will dissolve.
Solubility, <i>s</i>	The concentration at which a solute is saturated in a given solvent.
Electrolyte	A species that makes a solution electrically conductive when added to the solvent.
Weak electrolyte	A species that makes a solution slightly conductive when added.
Strong electrolyte	A species that makes a solution very conductive when added.
Spectator ion	An ion in solution that does not take part in a particular reaction or equilibrium.

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