

## Solvent-Solute Interactions

It's time to consider a similar classification system for the compounds that dissolve in them, i.e. for solutes. At the risk of oversimplifying, we will divide solutes into 3 groups:

1. ionic
2. polar covalent
3. non-polar covalent

We will use the adage "like dissolves like" as our guide to understanding the forces that enable a solute to dissolve in a solvent. Remember that this adage is really a variation on the statement of Coulomb's Law that says "opposite charges attract". The force of attraction depends upon the nature of the solvent and the nature of the solute. We will look at four types of interactions:

- charge-dipole
- dipole-dipole
- dipole-induced dipole
- induced dipole-induced dipole

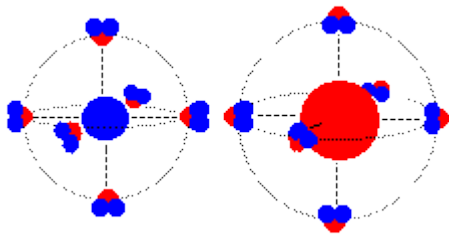
It is important here to distinguish between **intermolecular interactions** and the **intramolecular** interactions that we call covalent bonding. The strengths of covalent sigma bonds range from a low of about 50 kcal/mol to a high of around 125 kcal/mol. The interactive forces described below range from 2-10 kcal/mol. Because they are so much less than typical covalent bonding forces, these interactions are sometimes called **secondary bonding interactions**.

### Charge-Dipole Interactions

This is the classic case of an ionic salt such as sodium chloride dissolving in water. Figure 1 presents a picture of the Coulombic interactions between a positively charged sodium ion and 6 water molecules as well as the corresponding interactions between a negatively charged chloride ion and 6 other water molecules. In the case of the sodium ion, the positive charge attracts the negative end of each water molecule's dipole. The negative charge of the chloride ion attracts the positive end of the O-H bond dipole. The straight dashed lines indicate these charge-dipole interactions. Each ion is encased in a shell of water molecules. The shells insulate the ions from each other, allowing the oppositely charged particles to separate. Molecules that have high dielectric constants are good electrical insulators because of their ability to shield the oppositely charged ions in this way.

Figure 1

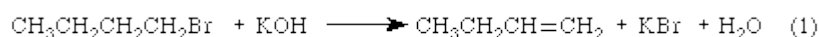
You're All Wet



The image of solutes surrounded by solvents is a useful one to keep in mind. However, it does not lend itself to a compact representation of intermolecular interactions. We'll use an alternative notation to depict dipole-dipole interactions.

## Dipole-Dipole Interactions

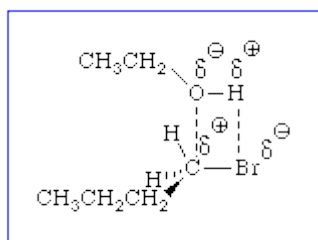
Equation 1 describes the dehydrobromination of 1-bromobutane, a classic example of a 1,2-elimination reaction.



As an experimentalist you would have to select an appropriate solvent for this reaction. Considering only solubility for the moment, you would want a solvent in which both the 1-bromobutane and the KOH would dissolve. While KOH is very soluble in water, 1-bromobutane is not. Conversely, while 1-bromobutane will dissolve in hexane, KOH is completely insoluble. What's needed is a solvent that has just the right balance of polar and non-polar character. In fact, both methanol and ethanol are suitable choices. Figure 2 uses the  $\delta^+ - \delta^-$  notation to focus on the Coulombic attraction between the C-Br bond dipole of 1-bromobutane and the H-O bond dipole of an ethanol molecule. Because the opposite charges that are attracting each other are only partial charges, dipole-dipole interactions are inherently weaker than charge-dipole interactions.

Figure 2

### Dipole-Dipole Interactions



When one of the bonds involved in a dipole-dipole interaction is an O-H bond, the interaction is given the special, but common, designation **hydrogen bonding**.

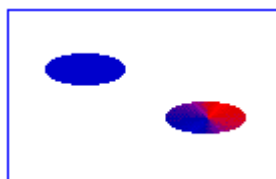
As we'll see shortly, there are additional intermolecular interactions between these two molecules. Before we look at them, however, we're going to consider intermolecular forces that are even weaker than dipole-dipole interactions.

## Dipole-Induced Dipole Interactions

Polar protic and dipolar aprotic molecules both have permanent bond dipoles. Non-polar molecules do not, or if they do, their dipole moments are very small. However, when a molecule with a permanent bond dipole comes close to one with no bond dipole, the electric field associated with the permanent dipole can temporarily distort the electron distribution in the non-polar molecule, thereby inducing a temporary bond dipole. This concept is animated in Figure 3.

Figure 3

Try To See Things My Way



Dipole-induced dipole interactions are invoked when a non-polar molecule dissolves in a polar or a dipolar solvent. The assumption is that the solute dissolves because the forces of attraction between the solvent and the solute are stronger than the intermolecular forces holding the non-polar solute molecule together. The interactions between non-polar molecules are the weakest secondary bonding forces we will consider. They are called **induced dipole-induced dipole interactions** or London forces.

## Induced Dipole-Induced Dipole Interactions

Imagine that you have a camera with macro lens that allows you to see electrons and a shutter speed so fast it can freeze their motion. If you were to take a series of slides of the electrons in dihydrogen, each slide would be different because each picture would catch the electrons at different positions between the hydrogen nuclei. If you superimposed the slides, the composite image would show that electron distribution between the two nuclei was symmetrical, i.e. that dihydrogen is non-polar. However, each individual slide would reveal the electron distribution between the nuclei was not symmetrical. In other words, there is an instantaneous dipole moment induced by the movement of the electrons. Furthermore, the induced dipole in one molecule influences the electron distribution in other, nearby molecules. This is called an induced dipole-induced dipole interaction. Figure 4 simulates this process.

Since these induced dipoles are transient, the intermolecular interactions between them, the London forces, are very weak. Chemists invoke these very weak forces to rationalize the interactions between non-polar molecules. We'll see an example of that when we discuss the relationship between intermolecular interactions and boiling points.

### **Solubility and the Solution Process:**

- The solid dissolves rapidly at first, but as the solution approaches saturation the net rate of dissolution decreases since the process is in dynamic equilibrium.
- Once at equilibrium, the amount of solute does not change with time.
- At equilibrium- rate of dissolution = rate of solution.

### **Solubility Thermodynamics:**

- The Gibbs Free Energy of Mixing-  $\Delta G = \Delta H - T.\Delta S$

Where  $\Delta G$ = Gibbs Free Energy of Mixing,  $\Delta H$  = enthalpy (energy, heat),  $\Delta S$  = entropy (disorder),  $T$  = temperature.

- The entropy of mixing favours complete miscibility of all components.
- Enthalpy- balance of the:
  - o Drug-drug interactions (D-D) (cohesive forces).
  - o Solvent-solvent interactions (S-S) (cohesive forces).
  - o Drug-solvent interactions D-S (adhesive forces).
- 

$\Delta H$  is sometimes negative, and sometimes positive, as it is a sum of the following:

- o S-S – energy required to break weak bonds between solvent molecules.
- o D-D – energy required to break intermolecular bonds between the solute molecules.
- o D-S –  $\Delta H$  is negative since bonds are formed between the species.

Intermolecular forces are important in determining the solubility of a substance as 'like' intermolecular forces for solute and solvent will make the solute soluble in the solvent.

$\Delta G$  must be negative for a solution to form. ( $\Delta G$  - = stable system, + = unstable system)

$\Delta H$  should be minimal.

$\Delta S$  should be maximal (increases stability)

<https://www.youtube.com/watch?v=a5cIccfak84>