How does adding hydroxyl groups increase the solubility of a hydrocarbon in water? To understand this, we must return to the two components of the free energy equation: enthalpy and entropy. For a solute to dissolve in a liquid, the solute molecules must be dispersed in that liquid. Solubility depends on how many solute molecules can be present within a volume of solution before they begin to associate preferentially with themselves rather than the solvent molecules. When the solute molecules are dispersed, whatever bonds or attractions holding the particles together in the solute are replaced by interactions between solvent and solute molecules. You might deduce that one reason diamonds are not soluble in water is that the C—C bonds holding a carbon atom within a diamond are much stronger (take more energy to break) than the possible interactions between carbon atoms and water molecules. For a diamond to dissolve in water, a chemical reaction must take place in which multiple covalent bonds are broken. Based on this idea, we can conclude that the stronger the interactions between the solute particles, the less favorable it is for the solute to dissolve in water. At the same time, the stronger the interactions between solute and solvent molecules, the greater the likelihood that solubility will increase.

So do intermolecular interactions explain everything about solubility? Do they explain the differences between the solubility of hexane, hexanol, and hexanediol in water? Hexanediol (HO(CH2)6OH) is readily soluble, and if we consider its structure we can see that interactions between hexanediol molecules include hydrogen bonding (involving the two hydroxyl groups) and van der Waals interactions (LDFs and dipole-dipole). We can also approach this from a more abstract perspective. If we indicate the non-hydroxyl (—O–H) part of a molecule as R, then an alcohol molecule can be represented as R—O—H, and a diol can be represented as H—O—R— O—H. All alcohols have the ability to form hydrogen bonding interactions with each other as well as with water. So when an alcohol dissolves in water, the interactions between the alcohol molecules are replaced by interactions between alcohol and water molecules—an interaction similar to that between water molecules. Like water molecules, alcohols have a dipole (unequal charge distribution), with a small negative charge on the oxygen(s) and small positive charges on the hydrogen (bonded to the oxygen atoms). It makes sense that molecules with similar structures interact in similar ways. Thus, small molecular-weight alcohols can dissolve in water. But if you look again at the previous table, notice that hexanol (a 6-carbon chain with one —O–H group) is much less soluble than hexanediol (a 6-carbon chain with two —O–H groups—one at each end). As the non-polar carbon chain lengthens, the solubility typically decreases. However, if there are more —O–H groups present, there are more possible interactions with the water. This is also why common sugars, which are really polyalcohols with large numbers of —O–H groups (at least 4 or 5 per molecule), are very soluble in water. Their —O–H groups form hydrogen-bonds with water molecules to form stabilizing interactions. As the length of the hydrocarbon chain increases, the non-polar hydrocarbon part of the molecule starts to become more important and the solubility decreases. This phenomenon is responsible for the "like-dissolves-like" statements that are often found in introductory chemistry books (including this one, apparently). So, do intermolecular interactions explain everything about solubility? If only things were so simple!