Qualitative understanding of partition preferences

Recall information ...

The few aspects discussed above about intermolecular interactions together with the cavity concept for partitioning into a bulk phase enable the derivation of some very useful rules.

Let us start with rules for partitioning of a *given* solute *i* from a given reference phase into *various* bulk phases (e.g., we want to know the best organic solvent for extracting a pollutant from a water sample).

Try to recall the information that we will need here! Now is the time where you will experience that it is not so simple to put together the little information from above into a meaningful picture.

Relevant Information:

- the more energy is required for the cavity formation in a phase the less attractive is this phase for a solute. Obviously, this cavity-energy will depend on the size of the solute. But here we focus on the partitioning of a given chemical into various phases so the size of the solute is not a variable. Thus, the only thing that matters here are the differences in the cohesive energies of various phases.
- The more energy a solute can gain from its interaction with the phase (after it has entered the cavity) the more attractive is this phase for the solute.
- vdW interactions do occur between all kinds of molecules. The vdW interaction energy is proportional to the contact area. The vdW interaction energy per contact area between water and organic compounds is rather similar.
  Here, we focus on the partitioning of a given chemical into various phases. Hence the contact area always is the same. **This means that the vdW interaction energy gained by the solute will be very similar no matter into which phase it partitions.**
- H-bond interactions only occur between molecules that possess complementary H-bond properties.

Combining this information we can conclude that:

- vdW interactions should never cause a large variability in the **cavity energy** in various organic phases or water. Substantial differences in the cavity energy can only occur as a result of H-bonds energies. This can only happen in bipolar phases.
- Substantial differences in the **interaction energy between a solute and a condensed phase** can only arise from H-bond interactions (and not from vdW interactions). These H-bond interactions can only occur for monopolar or bipolar solutes in monopolar (opposite polarity) or bipolar phases. Note though, that the huge difference between partitioning to a gas phase and partitioning into a condensed phase is mainly due to vdW interactions (which do not exist in the gas phase but do exist in any condensed phase).

This leads to the following rules ...