Qualitative understanding of partition preferences

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Frequently asked questions

1) In the literature (especially in chemical engineering) one often finds the so-called Hansen and Hildebrand solubility parameters to be used for estimating partitioning. e.g. http://aic.stanford.edu/sg/bpg/annual/v03/bp03-04.html and Hansen.pdf. Why are these concepts not covered in this chapter?

Answer: The mentioned approaches do not work properly because they are build on an incomplete representation of the cavity model. Hildebrand solubility parameter describes the cohesive energy of solvents thus reducing the whole free energy of transfer to the cavity energy. It is thus only suitable for comparing the partitioning of solutes that do not form H-bonds with the solvent (or for solutes that do all form the same H-bonds with the solvents). The Hansen parameters try to consider the H-bonds between solute and solvent in addition to the cavity energy but they also stay short of a correct description because they do not use separate descriptors for the H-bond acceptor and H-bond donor properties of the solutes and solvents (see also Fowkes and Mostafa (Ind. Eng. Chem. Prod. Res. Dev. 1978, 17, 3-7). As a consequence it ignores, for example, that compounds which do not have H-bonds within their own pure phase might still form (strong) H-bonds when entering other phases. According to the Hansen approach no organic compound should show a higher affinity to any other organic phase than to its own pure phase. However, this statement is only correct if all interactions are solely of the van der Waals type. It often fails if H-bonds play a role as shown by the first two examples in the Table below.

Besides, the model also fails at the other end of the scale, i.e. in predicting high activity coefficients as is demonstrated by the last two examples in Table 1.

Table 1: Experimental and calculated (according to the Hansen approach eq. (18) from ref. (1)) activity coefficients, g∞ , at infinite dilution.

Solute	Solvent	g ∞ (exper.)	g ∞ (calc.)
1,4 dioxane	chloroform	0.21	1.06
butylacetate	phenol	0.18	1.83

octane	anilin	37	5.10
octane	nitromethan	111	4.96

(1) Jang, M.; Kamens, R.M.; Leach, K.B.; Strommen, M.R. *Environ. Sci. Technol.* **1997** , *31* , 2805-2811 .

2) Often van der Waals forces are qualified as weak (for example compared to H-bonds). How weak or strong are they?

Answer: The reason for this misconception probably has historic reasons. If two molecules hit each other in the gas phase then they will interact and this can be measured as a deviation of the ideal gas law (i.e. a pressure reduction). And, of course, if two molecules (think of spheres) meet then their contact area is rather small and so are their (dispersive) van der Waals interactions. However, the two molecules may be able to fully engage in H-bonds. In this case the H-bond may be stronger than the vdW interaction. But that is not the case that we are interested in. Our atmosphere is so dilute that we can safely neglect any interactions. And in liquids and solids the molecules are completely surrounded by neighbors so that there vdW interaction energy is much higher than in the gas phase.

Water is the liquid with by far the strongest H-bond network. But even in water ca. 30% of the cohesive energy comes from van der Waals interactions. For organic molecules in organic phases, van der Waals interactions dominate in strength over hydrogen bonds. Be aware that this is not in contradiction to our previous conclusion that liquid-liquid partitioning is mostly determined by Hydrogen-bonds. For partitioning, only the difference in the interactions matter and not their absolute strength. Since van der Waals interactions are rather similar in different phases they have much less influence on liquid-liquid partitioning then the H-bonds that are weaker but can exhibit larger differences between two liquids. Link for the animation in "The cavity model in quantitative terms"

3) Van der Waals interactions can be subdivided into dispersive, London, (induced dipole - induced dipole) interactions, Debye (dipole - induced dipole) interactions and Keesom (dipole - dipole) interactions. It seems that in almost all textbooks (e.g. http://www.800mainstreet.com/08/0008-0012-interforce.html) it is stated that dipole-dipole forces are stronger than the dispersive (London) interactions. Should it then not be more important to find out the dipole moment of a molecule in order to assess its capability for van der Waals

interactions rather than it´s size or contact area which determines the dispersive van der Waals interactions?

Answer: Again, in the gas phase this would be true. Two molecules can orient each other such that they ideally exploit their dipole interactions (i.e. bringing together a positive and a negative charge) while the dispersive interactions stay small. But in a condensed phase each molecule has 9 to 12 neighbors and when orientation towards one of these neighbours is ideal for dipole interactions then it will be disadvantageous for dipole interactions with all other neighbours. In condensed phases, dispersive interactions are therefore the dominating part of the van der Waals forces and for their quantification contact area is important.

The following table shows partition constants of three isomers of dichlorobenzene. They differ substantially in their dipole moments (0 -2.6 debye) while their dispersive interactions should be similar and H-bonds do not occur. Their partitioning to phases with a strong dipole moment (water, their own pure phase and a mineral surface) is very similar which should not be the case if dipole moments were important.

Importance of dipole moments for partitioning

	dipole moment (debye)	$K_{water/air}$ (m^3/m^3)	$K_{hematite/air}$ (m^3/m^2)	p_L^*
1,2 dichlorbenzene	2.5	10	8.08×10^{-5}	180
1,3 dichlorbenzene	1.7	5.3	n.a.	252
1,4 dichlorbenzene	0	5.5	7.38×10^{-5}	235

4) All arguments in this chapter were based on the free energy of interactions. This is plausible because the free energy is directly linked to the partition coefficient. However, a free energy always has an enthalpy and an entropy contribution. Why was this not discussed here?

Answer: The short answer is: because it was not necessary. In many cases of partitioning the three thermodynamic entities are directly proportional to each other. This is quite plausible because it means that stronger interactions in terms of enthalpy result in a stronger reduction in entropy, or in other words: the stronger a molecule is sorbed, the more freedom it will loose. And when ΔH and ΔS are correlated, then ΔG must also be correlated to both entities because of $\Delta G = \Delta H - T \Delta S$. In this case it is not necessary to bother with ΔH and ΔS unless one is explicitly interested in the temperature dependence of the partition equilibrium which is described by ΔH. In fact, the frequently observed correlation between ΔH, ΔS and ΔG can be used for simple empirical tools to estimate ΔH for various partition processes as is shown in Chapter VII in the textbook. In the literature the correlation between ΔH, ΔS and ΔG is termed enthalpy – entropy compensation. Interestingly, in the partitioning to water one does not find a correlation between ΔH and ΔS when going from very small to larger non-polar molecules. When water molecules have to accommodate (cavity formation) a small molecule they try to keep all the H-bonds with their neighbours. To this end they have to bend themselves a lot. This results in a high loss of entropy but little loss of enthalpy. For larger molecules this is not possible any more so that the entropy contribution to the cavity formation becomes relatively smaller while the enthalpy loss (due to released H-bonds) becomes relatively higher. In this case, ΔH and ΔS do not show a steady trend when plotted versus the size of the solutes. Interestingly, however, there is still a compensation such that the resulting ΔG does show a steady trend with the size of the molecules. In this case the rules outlined here hold for ΔG and thus for log K but they do not apply to ΔH and ΔS.