

Chapter 29 The HSP of gel formation

We are all familiar with adding polymers to low viscosity solutions in order to create a gel. Poly(ethyleneoxide) added to water does just this. HSP considerations can tell you which polymers would be most suitable, and entanglement theory tells you that you have a trade-off between adding large amounts of low MWt polymer or small amounts of high MWt polymer.

In the Handbook (pp271-273) a different type of polymer gelator concept is described. An alkyd paint polymer is nicely soluble in mineral spirits (white spirit) and, because it is not yet cross-linked the viscosity is low – and this can lead to dripping and spattering on application. The same alkyd (a vegetable oil modified polyester) but with a grafted Versamid block forms a gel. The gel is easily disrupted by stirring, brushing, or spraying – the paint is a thixotrope. The gelation does not come from conventional polymer entanglement. Instead, the Versamid block is insoluble in mineral spirits so it self-associates to form a loose network, strong enough to gel but easily disrupted by mild shear forces.

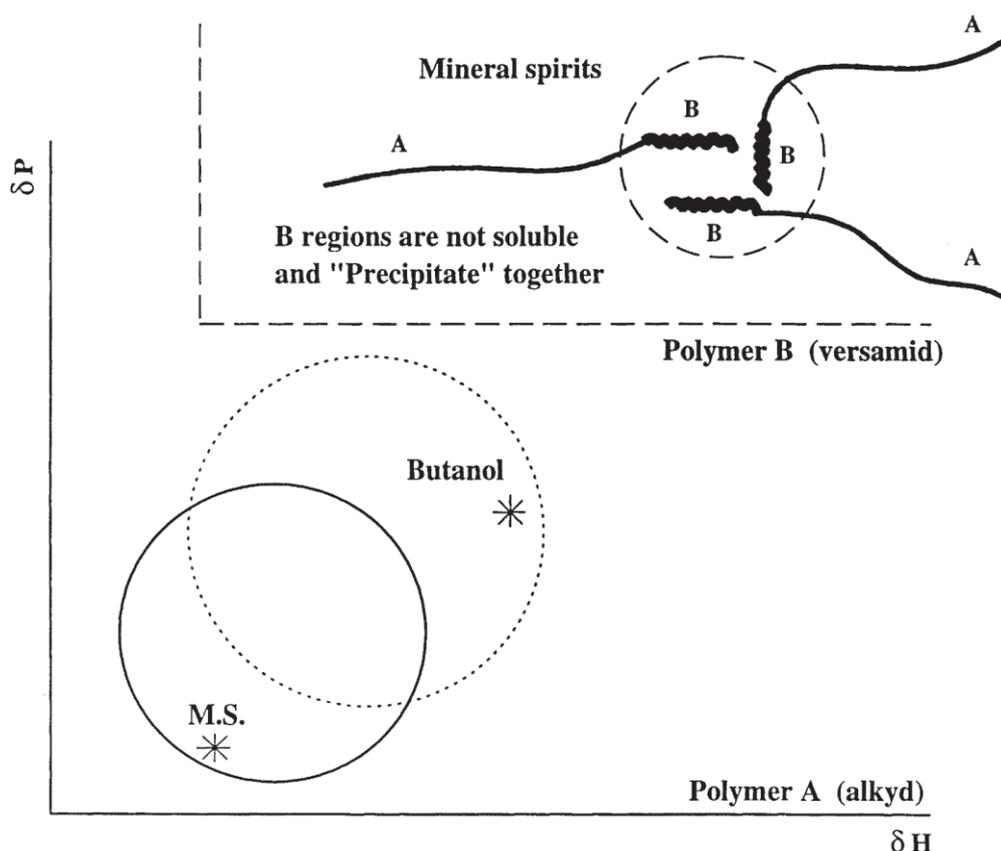


Figure 0-1 HSP relations for establishing thixotropy in an alkyd-type paint. The solid circle represents the solubility of the alkyd (A) and the dotted circle that of the Versamid (B). The Versamid segments associate because they are not soluble in the mineral spirits. Addition of n-butanol destroys the thixotropic effect, since the solvent then becomes too good for the associating Versamid segments and they no longer associate, being truly soluble.

To show that the thickening is not due to classic polymer effects, if some n-butanol is added, bringing the Versamid block into true solution, the viscosity greatly reduces and the gel effect is lost.

As another example, similar HSP concepts have been used to carefully balance the formulation of wet-on-wet flexographic printing inks to allow gel formation between the applying the successive colours. This development is still in its early stages, but promises to transform the flexographic printing industry into a greener one.

There is a third way to make gels which uses low MWt additives. These are called LMWGs (Low Molecular Weight Gelators) or LMOGs (Low Molecular-Mass Organic Gelators). Just 1% of an organic gelator or 0.1% of an organic supergelator can create an impressively strong gel. A delightful paper A. Vidyasagar, K. Handore, and K. M. Sureshan, *Soft Optical Devices from Self-Healing Gels Formed by Oil and Sugar-Based Organogelators*, *Angewandte Chemie*, July 2011, gives you a good idea of the effect:

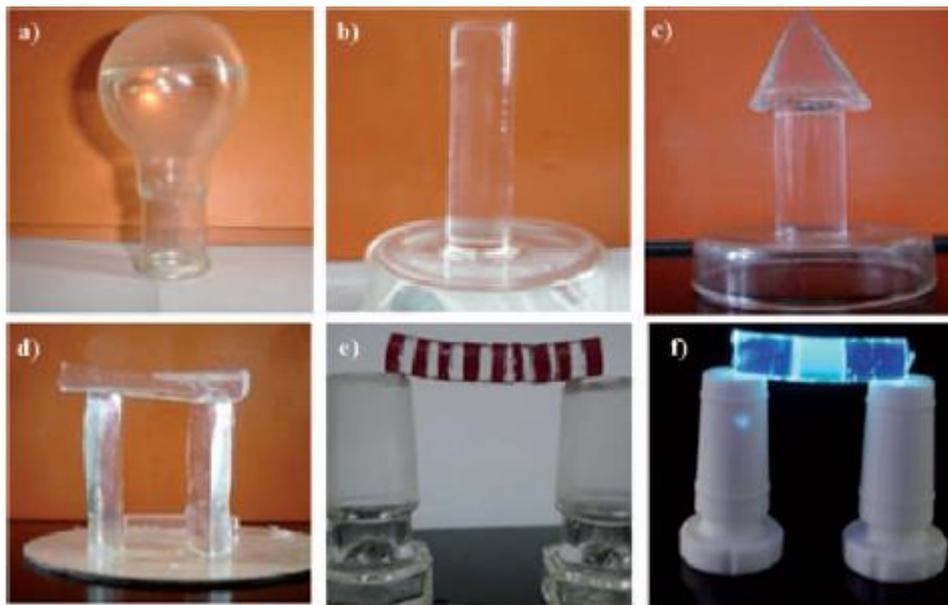


Figure 0-2 Gels formed in pump oil or silicone oil with ~0.3% of organic gelators. Typical dimensions in the images are 2-5cm. For explanations of shapes and colours, please read the original paper.

They are prepared by heating the gelator in the solvent then cooling to the gel phase. Such gels can be used in many applications such as optics, printing, cosmetics, coating etc.

The way they work is that the gelators have a tendency to self-aggregate into long chains and networks – forming a virtual polymer.

So how does one choose the right gelator for their particular system? It seems beyond the state of the art to be able to predict *ab initio* that molecule A will gelate system B. Instead one has to look in the literature for molecules that happen to gelate systems based on B. If you are lucky you will find a molecule that is cheap, safe, effective and perfect for B. But suppose, for example, that you want to gelate a cosmetic formulation based on isopropyl myristate (IPM) and you can't find any literature references to gelators for IPM. How do you then choose a gelator? You look for solvents that have been successfully gelled by a given gelator and that are also "close" IPM, but how "close" does it have to be?

The key problem is obvious. By definition the gelators like to self-associate. So a poor solvent for the gelator will not break up the self-association and the gelator will be simply insoluble. At the other extreme, really good solvents will be so good that the gelator doesn't self-associate so you simply have a solution.

The problem is solved, therefore, by finding areas of marginal solubility – not too little and not too much. And how would you find this? HSP seem to be the natural way to approach the problem.

We are most grateful to Matthieu Raynal and Laurent Bouteiller for giving us permission to use their wonderful paper *Organogel formation rationalized by Hansen solubility parameters*, Chem. Commun., 2011, 47, 8271–8273 to show you how it's done. The datasets are taken, with their kind permission, from the Supplementary Data to their paper.

They did a simple HSP scoring of 0 and 1 for insoluble/soluble and, separately, for no-gel/gel. You therefore get two HSP values, one is the classic “solubility” and the other is the “gelator” value.

Knowing these values for the range of 8 gelators that span a wide range of structures it then becomes possible to find which one has a gelator sphere suited, for, say, IPM.

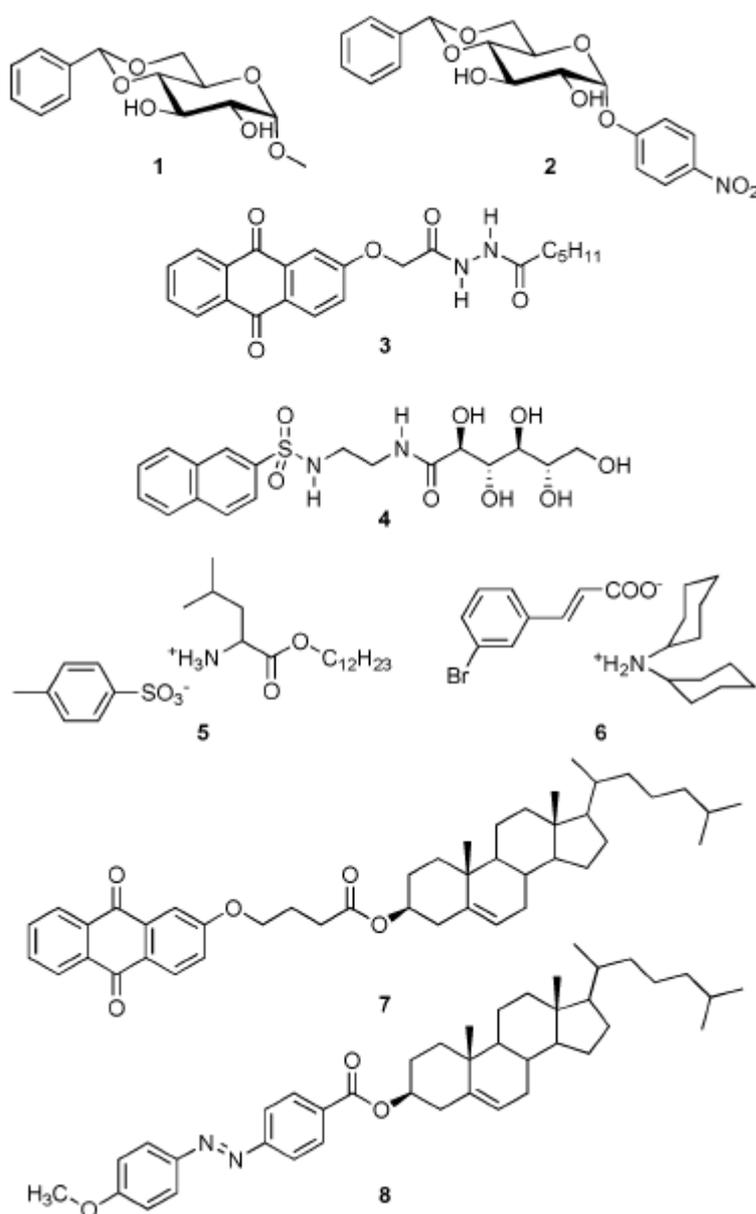


Figure 0-3 The 8 gelators used in the study. We will focus on 1 & 2 and 7 as they represent opposite ends of the gelator spectrum - (1) involves H-bonding, (7) involves π -stacking.

For these gelators, the best fits were obtained with GA Classic mode. Here are the results:

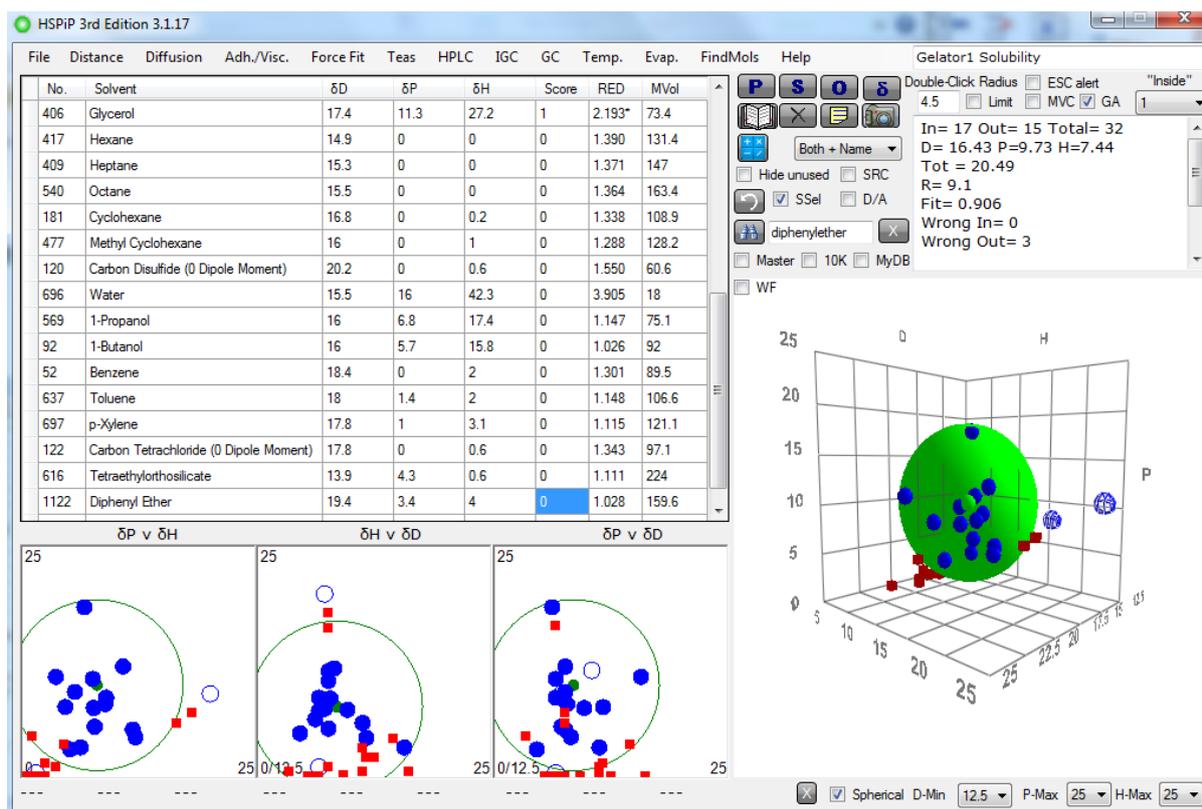


Figure 0-4 The solubility sphere for Gelator 1

The gel sphere, not surprisingly, is much smaller and in a very different region:

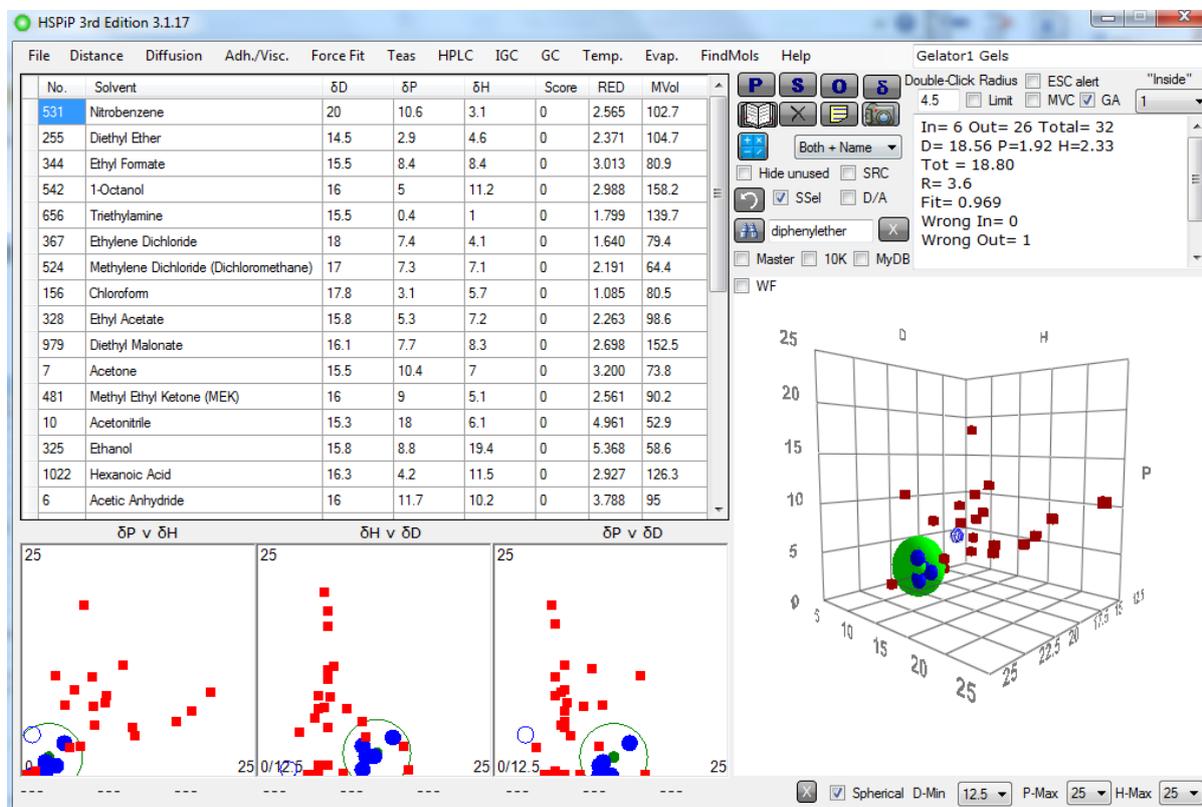


Figure 0-5 The gel sphere for Gelator 1

The HSP distance from this gelator sphere to IPM $\sim[16, 4, 4]$ is greater than the radius of 3.6 so this gelator will probably not be useful.

For Gelator 7, which relies on aromatic pairing for gelation rather than $-OH$ bonds, the spheres are very different.

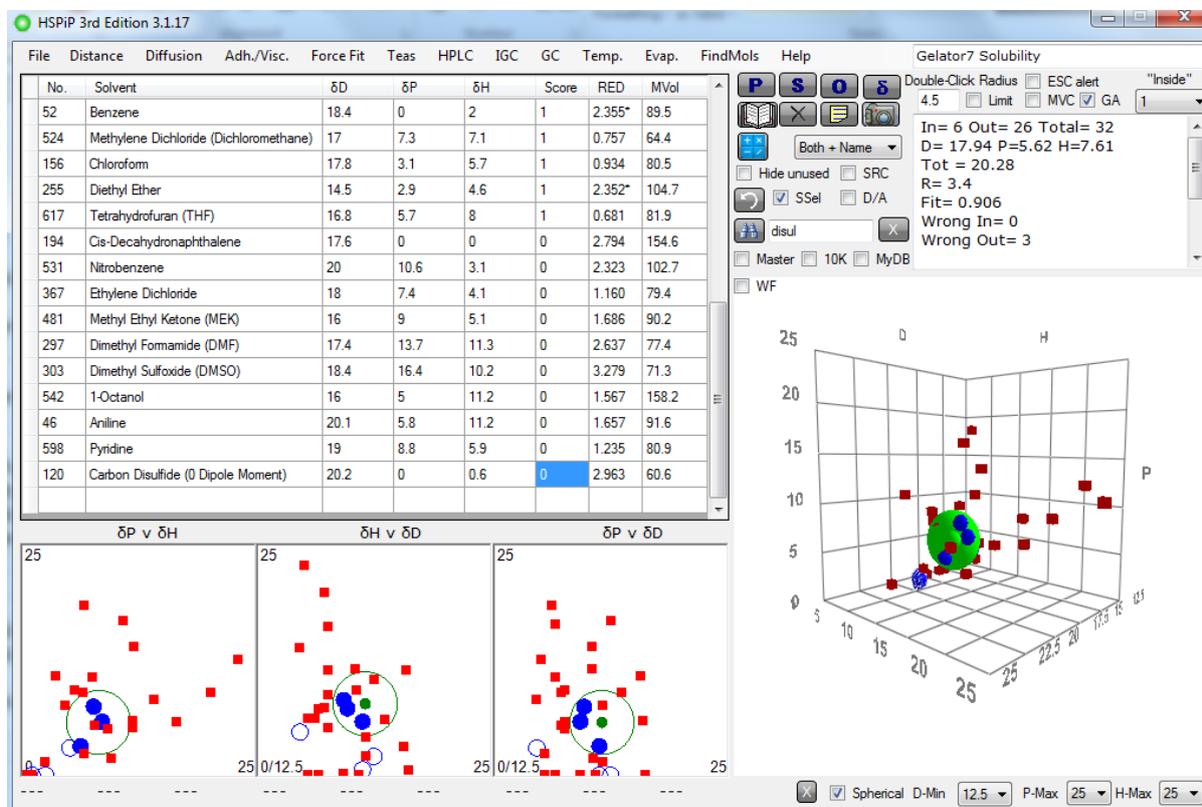


Figure 0-6 The solubility sphere for Gelator 7

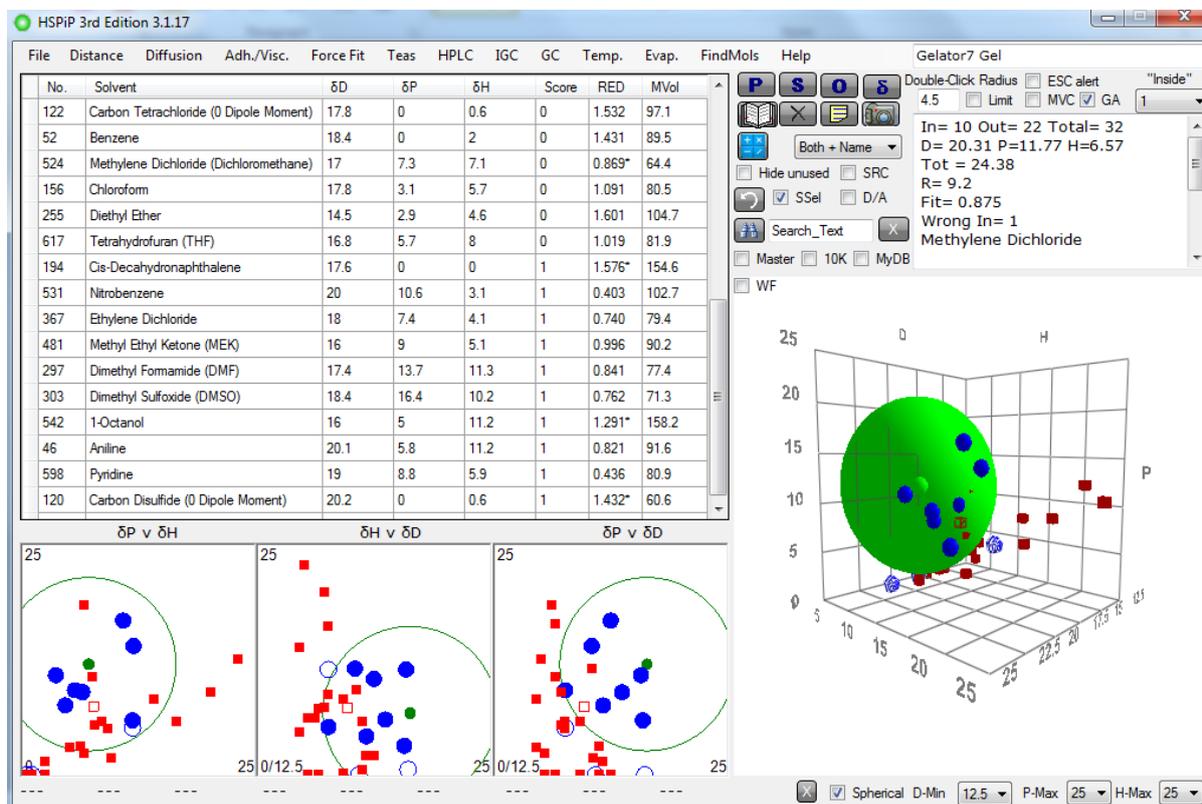


Figure 0-7 The gel sphere for Gelator 7

Again, this is unlikely to be a gelator for IPM

Finally, when we try Gelator 2 we get a solubility sphere (not shown) at [18.3, 13.8, 10.1] and a gel sphere which is close enough to IPM that it might well be a reasonable gelator for it:

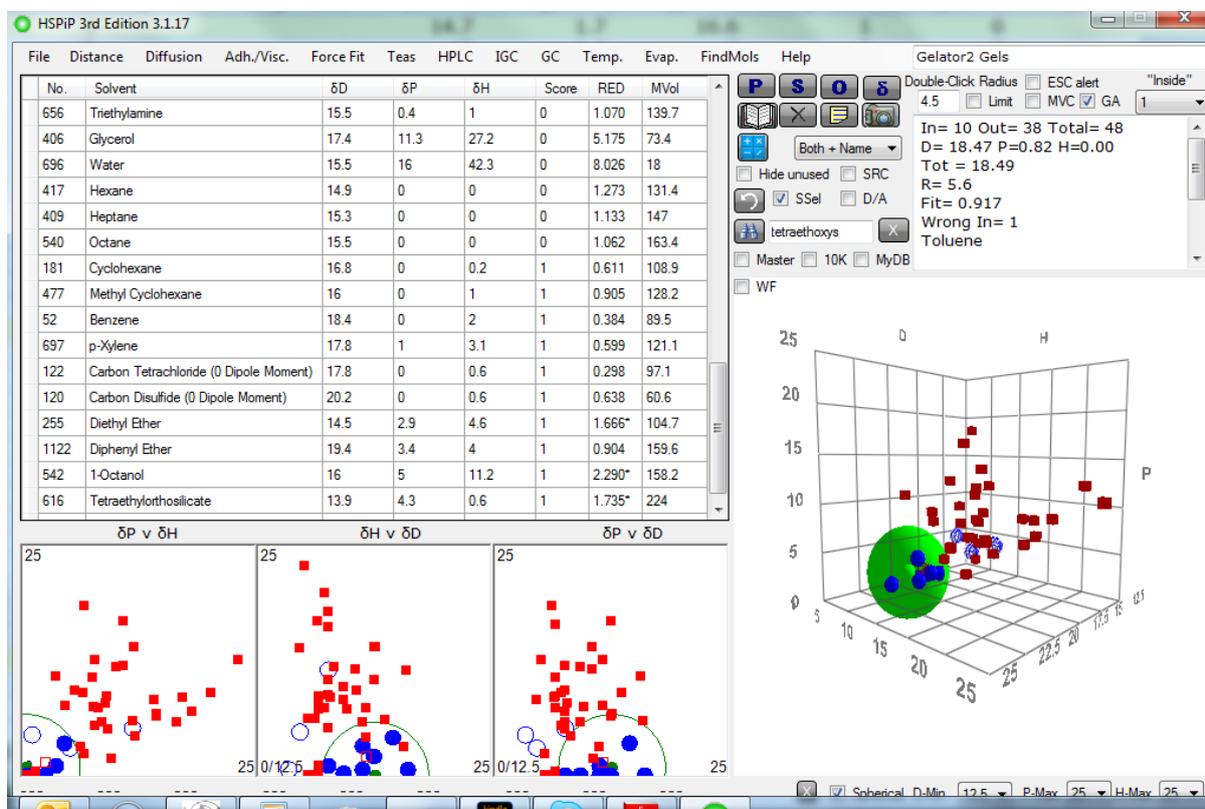


Figure 0-8 The gel sphere for Gelator 2

As the authors point out in their paper, not all the fits are perfect, and some of the datasets need careful interpretation as gelation behaviour is complex with time-dependent effects that can make what looks like a gel become a precipitate after a time.

Another suggestion from the authors is to create double-sphere fits. The reason is that although two different solvents can both be gelators, the type of gel (the network fibre structure) can be different.

The double-sphere option in the GA mode is ideal for this. As you can see in the above fit for Gelator 2, some of the gel solvents are outside the fitted sphere. Here are the same data fitted with the double-sphere option.

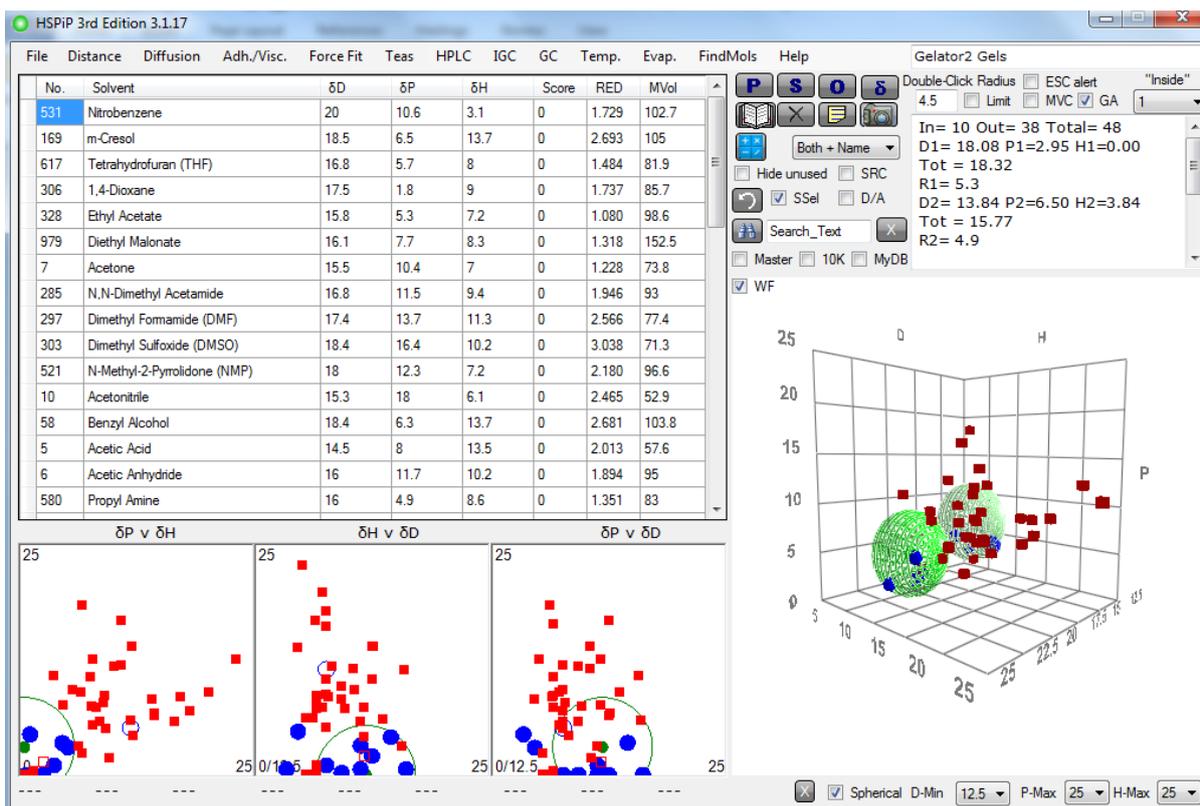


Figure 0-9 A double-sphere “fit” to Gelator 2. The value for the second sphere is unconvincing.

In this example it is clear that the fitted values are rather unconvincing – a δD of 13.8 is unlikely. Perhaps it would be better to do a sub-analysis of the different types of gel (if they exist for this particular molecule) and fit them separately.

The point of this brief chapter is not to draw definitive conclusions about using HSPiP with gelator data but to show that this sort of analysis may well be highly fruitful for further exploration.