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**Producing 10-100 nm emulsions with a physico-chemical trigger**

Emulsions are colloidal systems consisting of a dispersion of liquid droplets into another liquid. As the two liquids are not miscible, the mixing is not achieved on the molecular scale, contrarily to a solution which is therefore transparent (such as wines), and this results in the scattering of the incident light. If the droplets’s diameters are big (above 150 nm) the emulsion will be milky (milk is an emulsion), it is the same scattering that occurs in... clouds. If the droplets’s diameters are smaller (10-100 nm) the emulsion will be blue when looked perpendicular to the sun light and red when looked parallel to the sun light, it is the same scattering that explains why the sky is blue but red at the sun set. It is very easy to make an emulsion of the first type, simply shaking water and oil result in the dispersion for example of oil into water. However this cost energy to make, as we create some surfaces, which means emulsions are not stable systems but rather unstable. Several solutions exist to address that problem, the most popular is certainly to use surfactants. Surfactants are everywhere in everyday’s life : detergents, soap, cosmetics, food, cells etc... Those species are so called amphiphilic molecules : one part likes the water (hydrophilic from the greek “hydro” : water and “philic” : like) and the other one dislikes water (hydrophobic from the greek “hydro” and “phobic” : dislike). Then it is easy to understand that those molecules could be seen at a two ends sticks, one end will want to be in the water the other in the oil. This is called the adsorption of the surfactant molecule at the interface water/oil. This allows to reduce the energy cost associated with the creation of the droplets. The surfactant layer also acts as a shield that protects the droplets from merging with each other. Then emulsions are not really unstable though they are not stable systems, they are called metastable (from the greek "meta" : in between) systems.

It is however extremely difficult to create the second type of emulsions which are called nanoemulsions considering their typical size. Extremely high energies are indeed required. Another possibility is to design a system with a physico-chemical trigger. This trigger can be the composition of the sample (adding a component to the system) or the temperature for example. One of the very first method was the PIT method (phase inversion temperature) which relies on a very peculiar behavior of a certain surfactant molecule which dislikes more and more the water when the temperature increases. This induces several transformations on the molecular scale which in turn produces changes on our scale. Fast cooling of the samples, temperatures quenches, after heating allow us to produce nanoemulsions. This method has been used widely in the industry for years now. However it required a lot of surfactant, diameters range was quite narrow and the mechanism did not account for all the observations.

In this work I extended to lower concentrations of surfactant the process and showed that the believed mechanism was not coherent with some experiments, so that another explanation is advanced and open doors to connected seminal problems in the emulsion field : a new state was found at temperatures below PIT where the emulsion is obtained through a simple stirring and can be kept in a metastable state by cooling quickly. This also gives rise to new applications as both the system and the
mechanisms are much better understood. Typically it is possible to design nearly monodisperse (all the droplets have the same diameter) emulsions with diameters in the range 10-100 nm by tuning a single composition parameter: the amount of oil over the amount of surfactant.

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**Formation of 10-100nm size-controlled emulsions through a sub-PIT cycle**

We have reexamined the Phase Inversion Temperature (PIT) emulsification process. This is a low-energy method that uses a physico-chemical drive to produce very fine oil/water in absence of high shear flows. We used the polyoxyethylene 8 cetyl ether $C_{16}E_8$/hexadecane/water system, which has a PIT of 76.2°C. We find that successful emulsification depends on two conditions. First the mixture must be stirred at low speed throughout the whole process, this makes it possible to produce emulsions at surfactant concentrations that are too low to form an equilibrium microemulsion. Second the stirred mixtures must be heated above a threshold called the clearing boundary (CB) and quenched to lower temperatures. The clearing boundary is determined experimentally by a minimum in the turbidity of the stirred mixture, it results from solubilization of all the oil into swollen micelles. This matches the emulsification failure boundary defined by Safran and it is expressed mathematically by the condition $R^* C_0 = 1$, where $R^*$ is the radius that matches the oil/surfactant composition for monodisperse spheres and $C_0$ is the spontaneous spherical curvature of the surfactant. Thus we show that such cycles do not need to cross the PIT. In fact sub-PIT cycles and cross-PIT cycles give exactly the same result. With these conditions emulsions with very low dispersity and a mean diameter controlled by the oil/surfactant ratio are produced. The typical range of those diameters is 20-100 nm. These emulsions have moreover an excellent metastability in contrast with emulsions made with shorter oil and surfactant molecules.

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