# On precipitation during the coalescence of reactive droplets

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The coalescence of sessile drops of completely miscible liquids can be affected by a Marangoni flow, resulting from the surface tension difference of the two liquids [1,2]. Although the surface tension is strongly related to solute's concentration, and particularly hydrotropes [3], the coalescence of drops containing reactive liquids was not investigated so far. However, the coalescence behavior of reactive droplets is encountered in a wide range of applications such as liquid−liquid extraction, ink jet printing, nanoparticles synthesis, etc. Moreover, controlling the reagents mixing and transport phenomena during the droplets coalescence is of major importance in the new precipitation in emulsion process we are currently developing [4,5].

We consider the coalescence behavior of sessile drops containing aqueous solutions of cerium nitrate and oxalic acid. Upon contact, these compounds form insoluble, color-less cerium oxalate.

$$\mathbf{Ce(NO_3)_3 + 3C_2H_2O_4 + 10H_2O \rightarrow Ce_2(C_2O_4)_3.10H_2O + 6HNO_3}$$

We observed that in a given and limited range of component concentrations and surface tension differences between both liquids (the latter can be controlled using diols/water structured binary solvents), the precipitating cerium oxalate surprisingly forms periodic patterns of fringes with different light-scattering properties that allow easy detection by strongly contrasted images (Figure 1).

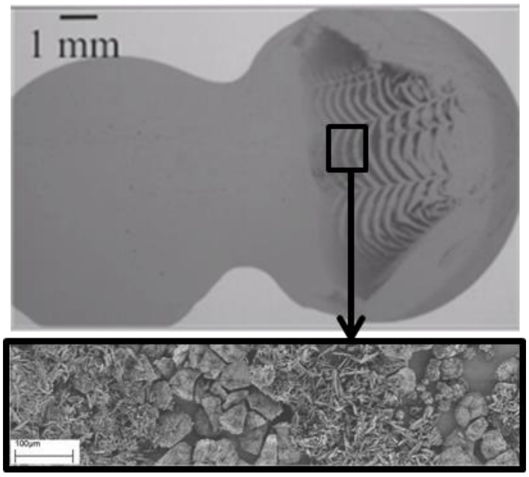


**Figure 1: Periodic patterns appearing during drop coalescence (optical imaging via top view camera) and (after drying) by scanning electron microscopy. Black domains in the top picture correspond to needlelike crystals, while microflowers of micron-size aggregated needles are observed in the light domains. The fringes formation is observed regardless of the Marangoni flow direction.**

SEM observation, performed after complete drying of the sample, reveals individual needle-like particles of typical length 25µm in the dark, strongly light-scattering zone; whereas the latter appear aggregated in large "microflowers" (*i.e.* 65 µm) in the light areas. Additional experiments using confocal microscopy indicate that the two types of particle result from different precipitation mechanisms. However, XRD shows that particles exhibit a monoclinic structure typical of cerium oxalate decahydrate, regardless of their shape.

The relation between the various control parameters (initial contact angles, reactant concentrations, viscosity, surface tension difference), the stripe property (spacing of the fringes), and the Marangoni flow was further analyzed by optical microscopy and image processing. The results highlight a strong coupling between the transport processes and the fast chemical reaction [6]. On the other hand, for given "hydrodynamic" parameters (*e.g.* initial contact angle and surface tension difference), the occurrence of the reaction appeared to modify the coalescence behavior, compared to the non-reactive cases investigated by Karpitschka and Riegler [1,2]. Coalescence of reacting droplets has therefore proved to be a valuable tool to further study crystal nucleation and growth mechanisms.

In this aim, the solvent influence on the precipitates is currently examined. Water, binary water/diols and ternary water/oil/hydrotrope mixtures are considered as solvent [7]. Still triggering the reaction by the coalescence of sessile droplets, first results have highlighted that mesoscale solubilization in structured solvents changes the particle morphology to a more compact mesocrystal shape described by [8].


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