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How do interactions control droplet size during nanoprecipitation?

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ABSTRACT

Nanoprecipitation provides colloidal dispersions through successive recombination events between nanometric objects. In the present article, we explain why the nanoprecipitation pathways induced through solvent-shifting – the Ouzo effect –, are fascinating study-cases. Indeed, they allow to address the question of how the interactions between the colloidal particles control the dynamics of the process, thus the particle size distribution. Experimental monitoring of the precipitation dynamics demonstrates that the colloidal dispersion polydispersity decreases over time as the droplets coalesce. Monte Carlo simulations within the Smoluchowski framework agree quantitatively with these observations, and show how the interactions between the particles naturally force the system to become nearly monodisperse. The mechanistic understanding gained from the solvent-shifting experiments is also relevant to other nanoprecipitation processes.

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1. Introduction

Segregation often prevails amongst molecules, which makes phase separation a general behavior for multi-component mixtures. However, certain non-equilibrium pathways may trap the system at an intermediate length-scale between molecular mixing and macroscopic phase separation: the colloidal domain.

Top–down pathways lead to the formation of colloids through successive divisions of macroscopic domains into smaller ones. The associated free energy cost dramatically increases with the amount of interfaces. Colloids with sub-micronic dimensions (1–100 nm) are thus difficult to obtain. On the contrary, bottom–up pathways start from homogeneous solutions, in which molecules are mixed at the molecular scale, and rely on a parameter change to trigger phase separation. Generally, the bottom–up pathway only ensures appearance of growing microstructures, while the formation of colloids requires a specific control of the growing process (*i.e.* a stopping mechanism). Otherwise, the microscopic objects will continue to combine until equilibrium macroscopic phase separation. A typical hindering mechanism operates through the build-up of repulsive barriers between colloids of a given length-scale, thus keeping the colloidal system in a metastable state [1].

Behind this well-documented mechanism lies an important issue: how to control colloidal system uniformity. Indeed, “monodisperse” dispersions, consisting of identical colloidal objects, are often desired as their physical properties are generally easier to control than those of “polydisperse” dispersions. Therefore, we want to understand how the interactions between colloids, and thus the barriers that oppose their recombinations, relate to the colloidal dispersion size distribution.

2. The Ouzo effect: nanoprecipitation through solvent-shifting

The addition of a bad solvent to a solute/good solvent mixture is an interesting study case of bottom–up pathways. Indeed, this solvent-shifting results in the spontaneous precipitation of the solute into a mixture of the two solvents, as observed routinely when preparing an anise-based beverage such as Ouzo. Furthermore, this process does not involve any chemical reactions, contrarily to most nanoprecipitation methods.

However, a complication arises from the mixing kinetics of the two solvents. Consider the system in its initial state: a solute is dissolved in one of its good solvents. Addition of a bad solvent that mixes with the good solvent decreases the overall solvent quality. The solute

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remains dissolved into a mixture of these two solvents, forming a single phase, up to a given amount of bad solvent, which corresponds, on a phase diagram, to reaching the solubilization boundary or binodal line. Upon crossing this phase boundary, the system starts to separate into two phases of distinct compositions given by the tie lines. However, the system has not reached its final composition yet and its representative point continues to move towards its final location, given by the global composition. A competition thus occurs between the splitting of the representative point into two sub-points along the tie line and the movement of the representative point towards its final location. This sums up as the following question: is mixing faster or slower than phase separation? Two cases can be considered, as illustrated on Fig. 1:

- if full mixing is achieved prior to phase separation, phase separation proceeds homogeneously in the sample. Interactions between the forming colloidal particles determine the final size distributions.
- if phase separation proceeds simultaneously with mixing, the system becomes heterogeneous. On a phase diagram, each mixing domain is associated with a different representative point and the effective trajectories may be complicated. Both the extent of this heterogeneity and its effect on the interactions between colloidal particles determine the final size distributions.

The latter is the most common situation in literature and has resulted in a number of observations, leading authors to distinguish between successful and unsuccessful solvent-shifting, separated by an “Ouzo-boundary”. However, one should be careful since heterogeneities are hard to control and make conclusions unreliable. In particular, all the relevant parameters (concentration, solvent ratio, ionic strength) are changing in space and time while phase separation takes place. Most of the literature on nanoprecipitation through solvent-shifting belongs to this category [2•].

To overcome this difficulty, Prud’homme’s group pioneered the use of efficient mixing cells to perform solvent-shifting in homogeneous conditions. The initial design used two confined impinging jets, adapted from Hartridge&Roughton mixers. Mixing times below a few milliseconds were achieved due to highly turbulent flows [3•]. However, this setup requires streams of equal momentum and thus realizes only a 1-1 mixing ratio. They therefore developed a multi-inlet vortex mixer with tangential streams that allows the mixing of streams of equal or non-equal momentum [4]. A large range of mixing ratios can then be used, which allows to explore the whole phase diagram.

Rapid mixing tools have also been used for decades in commercial instruments such as stopped-flow devices. However, since the mixing chambers have been designed mainly for aqueous solutions mixing, their applicability or solvent-shifting is problematic. Nevertheless, Roger et al. [5••] used a commercial stopped-flow from BioLogic company coupled to the intense X-ray beam of the ESRF synchrotron facility (instrument ID02). The first measurement was performed 10 ms after mixing and regular monitoring showed that colloidal dispersion reaches its metastable size distribution in about a second. This demonstrates that practical uncoupling of mixing (a few milliseconds) and phase separation (one second) is possible using adequate mixers.

3. The repulsive barriers

In the case where all components are liquid, the bottom–up solvent-shifting process occurs through a sequence of droplet coalescence. Droplet surfaces are generally electrically charged [6, 7], and the interaction between two droplets is the sum of a long-range attractive potential (Van der Waals attraction) and a small-range repulsive potential (double-layer electrostatic repulsion). This is the basis of the DLVO theory [1, 8, 9].

For two charged spheres of radius R_i and R_j respectively, with h being the distance between their two surfaces, the total interaction energy writes:

$$U_{i,j} = \frac{R_iR_j}{R_i+R_j}\left(-\frac{A_H}{6}\frac{1}{h} + \Gamma e^{-\kappa h}\right) \tag{1}$$

A_H is the Hamaker constant for the liquid forming the droplets (A_H is a few k_BT) and quantifies the Van der Waals attraction. Γ quantifies the repulsion between two ionic double-layers and can be expressed either using effective surface charge densities [10] or effective electric potentials [11]. It is independent of the values of the radii at

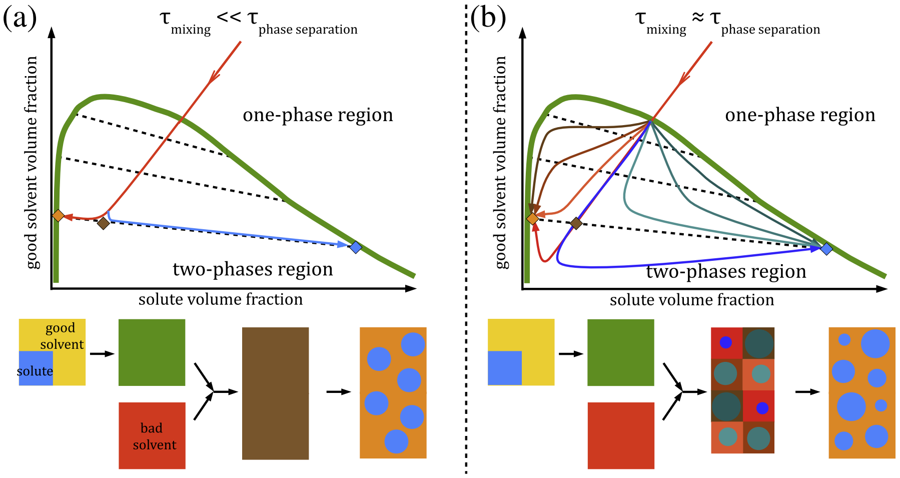
(a)
$\tau_{\text{mixing}} << \tau_{\text{phase separation}}$
good solvent volume fraction
one-phase region
two-phases region
solute volume fraction
good solvent
solute
bad solvent
(b)
$\tau_{\text{mixing}} \approx \tau_{\text{phase separation}}$
good solvent volume fraction
one-phase region
two-phases region
solute volume fraction

Fig. 1. Typical phase diagram for a solute (blue)/good solvent (yellow)/bad solvent (red) ternary system. The addition of a bad solvent leads to a phase separation upon crossing the solubilization boundary (green line). The compositions of each separating phase are given by the tie lines (dotted lines). (a) Corresponds to uncoupled mixing and phase separation. Rapid mixing brings the system to a homogeneous supersaturated solution at the final composition, which then phase separates. (b) Corresponds to simultaneous mixing and phase separation. Phase separation occurs at different and varying compositions. These heterogeneous conditions usually lead to less uniform dispersions.

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