Self-segregation of polymer and salt along hydration gradients in evaporating aqueous solutions

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Drying multicomponent solutions is a ubiquitous situation in both industrial processes, for instance coatings, and environmental ones, such as saliva aerosols [1] . However, as water is removed by evaporation, the remaining non-volatile species may self-segregate along the resulting hydration gradient, strongly impacting both drying kinetics and the final morphology and properties of the material [2,3] .

To quantify this, we use a model system composed of water, potassium nitrate (KNO_3), and a non-ionic hydrophilic polymer (PNIPAM). Using a one-dimensional microfluidic drying geometry combined with in situ Raman confocal microscopy, we measure spatial composition profiles during evaporation and reconstruct drying trajectories in the ternary phase diagram.

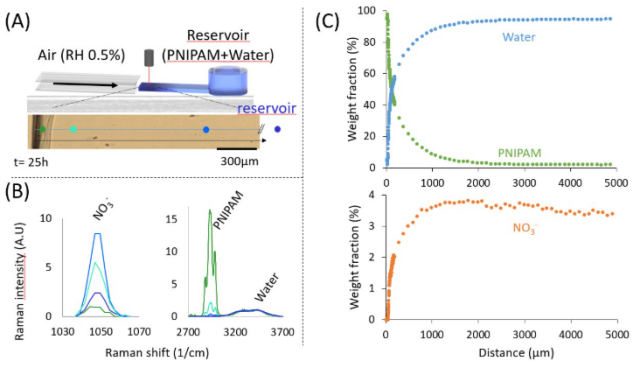
We show that drying does not follow a simple dilution path but instead gives rise to non-trivial composition trajectories. In particular, we observe a robust non-monotonic, S-shaped (serpentine) pathway, reflecting successive regimes of salt enrichment and depletion along the drying direction. This behavior arises from the coupling between evaporation-induced concentration gradients, multicomponent diffusion, and preferential interactions within the mixture.

Depending on the initial composition, two additional regimes emerge. At intermediate salt content, the trajectory crosses the binodal, leading to liquid–liquid phase separation and subsequent evolution within the two-phase region. At higher salt concentrations, rapid crystallization at the air–liquid interface dominates, trapping the system out of equilibrium.

Remarkably, for a given initial condition, the drying trajectories collapse onto a single path in the phase diagram, showing that the composition pathway can be rationalized from the interplay between mixture thermodynamics and multicomponent transport coefficients, rather than by time.

Overall, this work establishes a direct link between hydration gradients, self-segregation, and phase behavior, and provides a framework to rationalize non-equilibrium drying pathways in complex fluids.

Keywords:
evaporation, self-segregation, hydration gradient, Raman spectroscopy



(A) Microfluidic drying setup, the chip contains a solution of PNIPAM 2.5% KNO3 1.5%. The imaging is performed after 25 h of drying. (B) Raman spectrum of different points in the microfluidic cell. (C) Weight fraction of the water, PNIPAM and NO3-, from the air/liquid interface toward the bulk

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