Drying with no concentration gradient in large microfluidic droplets†

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In most situations, drying is accompanied by the development of strong concentration gradients. Here, we evidence theoretically and experimentally that there exist microfluidic geometries for which confined drying becomes homogeneous, i.e., with no concentration gradient regardless of the type of solute involved in the process; ions, molecules, and colloids do concentrate in the same way providing a limited set of assumptions concerning the microfluidic geometry. It thus makes possible the establishment of phase diagrams of multi-component mixtures at the nanoliter scale.

1 Introduction

The evaporation of the solvent of a complex fluid is an unconventional yet original way to explore its phase diagram upon continuously varying the concentration of the non-volatile solutes (or of dispersed colloidal particles). During drying, the complex fluid follows an out-of-equilibrium route governed mainly by thermodynamics and transport phenomena: gradients of solvent chemical potential, kinetics of phase transitions, diffusion, hydrodynamics, etc. In principle, monitoring the drying process should yield a lot of information concerning the complex fluid under study but attempts reported to date are rather scarce owing to the difficulty in relating the dynamics of drying to simple models. Indeed, in most experimental cases (droplets, films), evaporation induces a flow at a rate $E$ (units m s$^{-1}$) that drives the accumulation of the non-volatile species toward the free, fluid/air interface. Diffusion competes with convection and a concentration gradient builds up on a typical length scale $\sim D/E$, where $D$ is the diffusivity of the solutes. Upon further accumulation, a distinct layer often referred to as a crust may form, which can in turn modify the evaporation rate or lead to mechanical instabilities (e.g. buckling). For multi-component complex fluids, the dynamics is expected to be even more intricate as $D$ varies over orders of magnitude depending on the species of interest ($D \sim 10^{-13}$ m$^2$ s$^{-1}$ for micron-sized colloids to $10^{-9}$ m$^2$ s$^{-1}$ for small ions).

Here, we demonstrate that there exist geometries which lead to homogeneous drying—that is with no gradient of concentration—almost independent of the type of solution or dispersion undergoing drying, and thus even in cases where diffusion across the drop does not relax concentration gradients. These geometries are based on droplets evaporating within a microfluidic channel across a semi-permeable membrane and we work on long (\( > 1 \) cm), quasi one-dimensional (1D) droplets, see Fig. 1. The same result also holds for disk-like (2D) drops which are often encountered in microfluidics. The limited set of assumptions required to check this regime of homogeneous drying makes it very general and offers an unprecedented degree of control, which, for instance, allows us here to explore quantitatively the phase diagrams of multi-component aqueous solutions, on the nanoliter scale, without the need of any model, even though the process is out-of-equilibrium (evaporation of the solvent).

We first give below theoretical arguments to demonstrate the range of validities of this regime (section Theory). We then discuss in depth how to build experiments that verify the assumptions derived in the theoretical part (section Experimental). We finally illustrate experimentally in the Results section the robustness of our method for extracting equilibrium (phase diagram and solvent chemical activity) and out-of-equilibrium (colloidal stability) features of solutions/ dispersions.

![Fig. 1](image-url)
2 Theory

2.1 Dynamics of concentration

Let us consider a droplet confined within a long linear microfluidic channel (Fig. 1, length $L \gg h \sim w$ with $h$ and $w$ being the height and the width, respectively). The channel is embedded in a semi-permeable membrane and sealed with a non-permeable matrix. We assume that solvent permeates across the membrane at a volumetric rate $q_e$ per unit length (units m$^2$ s$^{-1}$) limited only by diffusion across the dense membrane, not by transport in ambient air. We also neglect in the following all buoyancy and thermal Marangoni effects. Note that the limited area of the fluid/fluid interface in the present experimental situation (of the order of $h \times w$) combined with the confinement imposed by the microfluidic channel probably helps to limit thermal Marangoni effects as compared to the case of films or sessile drops involving large fluid/air interfaces. Moreover, as demonstrated below, our geometry makes it possible to suppress concentration gradients during the shrinkage of the drop. This feature again prevents the buildup of buoyancy-driven flows (observed recently in similar geometries\textsuperscript{10}), as well as solutal Marangoni instabilities.

Solvent permeation actually translates into a velocity field within the drop given by mass conservation

$$\frac{\partial \bar{v}_x}{\partial x} = -\frac{q_e}{hw} = -\frac{1}{\tau_e} \frac{\partial \bar{v}_x}{\partial t}$$

(1)

where $\bar{v}_x$ is the height and width-averaged velocity along $x$ while $\tau_e$ defines a timescale for evaporation. $\partial \bar{v}_x / \partial t$ is related to the local shrinkage rate of volumes $dV$ within the drop according to

$$dV = \frac{\partial \bar{v}_x}{\partial x} dV = -\frac{\partial \bar{v}_x}{\partial t} \tau_e.$$ (2)

As a consequence of solvent extraction, any solute (non-soluble in the membrane) at volume fraction $\phi$ gets concentrated during the shrinkage of the droplet (Fig. 1, right). When diffusion ensures that the concentration of solute is homogeneous across the channel cross-section only, i.e., $\partial \phi / \partial y \sim \partial \phi / \partial z \approx 0$, and for an initially homogeneous drop, the local concentration rate of solute within the drop is related to the shrinkage of the volume through $dV/\tau_e = -d\phi/\phi$, which leads to

$$\frac{\partial \phi}{\partial t} = \frac{\phi}{\tau_e}.$$ (3)

A uniform permeation rate $q_e$ along the drop imposes that the contraction of volume is uniform, and thus no spatial gradient of concentration develops during the shrinkage of the droplet. It is however clear that $\phi$ increases with time as $L$ shrinks, and solute conservation implies that

$$\phi(t)L(t) = \phi_0L_0,$$ (4)

where $\phi_0$ is the initial solute concentration and $L_0$ is the initial drop length.

2.2 Regime of validity

Importantly, this regime holds for a uniform permeation rate $q_e$ over the drop, when diffusion of solutes homogenizes concentration across the height and the width of the channel during drying. Note that we do not impose in our analysis that diffusion homogenizes concentration across the length of the droplet during its shrinkage, which corresponds obviously to a trivial regime of homogeneous drying.

The last condition is valid when convection within the drop (typical velocity $V = L/\epsilon$) transports solutes during the diffusion time $\epsilon^2/D$ on a length scale smaller than $h$, i.e., $V\epsilon^2/D \leq h$. This last condition also reads $h^2/(D\epsilon) \sim \epsilon(h/L) < 1$ and can be derived rigorously in the framework of the lubrication approximation, as explained below.

Pervaporation through the permeable matrix at a rate $q_e$ induces a velocity profile $v_x$ within the drop, which is given by the resolution of the Stokes equation using the lubrication approximation ($v_z = 0$ on the walls). The components $(v_x,v_y)$ can be then estimated using the continuity equation.\textsuperscript{11} Note that this profile does not hold to the close vicinity of the receding meniscus of the droplet, as recirculating flows are expected on a scale $h$ owing to the displacement of the meniscus.

Conservation of the solute within the drop then follows the classical diffusion-equation\textsuperscript{12}

$$\frac{\partial \phi}{\partial t} + \nabla \cdot j = 0 \text{ with } j = \phi v - D \nabla \phi,$$ (5)

where $\phi$ is the volume fraction of the solute and $D$ is the collective diffusion coefficient. In this confined geometry, we introduce the normalized variables $\tilde{x} = Lx$, $\tilde{z} = hz$, $\tilde{y} = hy$, and $V = L/\tau_e$ the scale of $v_x$, i.e., $v_x = V\tilde{v}_x$. The continuity equation imposes the scale of $v_x$ (and of $v_y$) to be $\epsilon V \sim h/\tau_e$ with $\epsilon = h/L$.

These unitless variables lead to

$$\frac{h^2}{L} \frac{\partial \tilde{\phi}}{\partial t} + V h^2 \nabla \tilde{\phi} = \left( \tilde{v}_x \frac{\partial^2}{\partial \tilde{x}^2} + \frac{\partial^2}{\partial \tilde{z}^2} \right) \tilde{\phi},$$ (6)

(we consider $D$ as a constant for simplicity, without the loss of generality). If we assume $V \tilde{h}^2(D\epsilon) = \tilde{c}(\epsilon)$ (and thus $h^2/(D\epsilon) \sim \tilde{c}(h/L)$) and consider time scales $t \gg h^2/D$, the last equation imposes that $\phi$ is homogeneous over $z$ and $y$ at first order in $\epsilon$.

The integration of eqn (5) over the width and the height of the channel, combined with eqn (1) and no-flux boundary conditions for the solute on the walls, leads to

$$\frac{\partial \phi}{\partial t} = \frac{\phi}{\tau_e} = v_x \frac{\partial \phi}{\partial x} + D \frac{\partial^2 \phi}{\partial x^2}.$$ (7)

since we assume that $\phi$ is homogeneous (at first order in $\epsilon$) over the transverse dimensions of the droplet. For an initially uniform drop, the right-hand side term of eqn (7) vanishes, and the concentration of solute increases homogeneously during the droplet shrinkage, following eqn (3).

3 Experimental

Note that the above theoretical results also hold for circular geometries, as in Shim’s work\textsuperscript{13} where droplets were squeezed
under a poly(dimethylsiloxane) (PDMS) membrane across which water permeates (diameter ≈ 300 μm, height 40 μm, and membrane thickness 15 μm). Yet, for these small drops, diffusion smoothen concentration gradients over the diameter of the droplet. We now reduce the need of small drops and argue that in the membrane-based geometry, concentration fields are actually homogeneous whatever the diameter of the droplet.

Back to the linear geometry, the homogeneous drying criterion holds under two assumptions only: (i) the permeation rate must be identical over the whole length of the drop—but may vary with time—and (ii) \( h^2/D \tau_e \ll 1 \). The first assumption is made possible, thanks to the versatility of microfluidics and we give below the corresponding design rules. The second one is related to the diffusivity \( D \) of a species with a precise geometry and we found that the scaling analysis is actually more restrictive than what we observe experimentally.

### 3.1 Microfluidic chip

The successful design of an experiment with homogeneous drying relies on rapid mass transfer through the membrane and a homogeneous permeation rate over the drop. These rules lead us to the geometry sketched in Fig. 2: two symmetrical dead-end channels facing each other, with a serpentine shape of length 15 mm, and embedded in a thin PDMS membrane. These two channels are connected to feeding channels themselves connected to one inlet and one outlet.

In a typical experiment, we confine two identical droplets (without the need of syringe pumps) by closing first outlet 2 and filling the network with an aqueous solution from inlet 1 thanks to the permeability of PDMS to gas. Then, we gently flow an inert oil (Fluorinert, FC40) from inlet 1 to outlet 2. This oil flow combined with the geometric constrictions at the entrance of the two dead-end channels (width ≈ 20 μm and length ≈ 30 μm) segments the aqueous solution and leads to two identical drops confined in the serpentine region only. The whole network is captured under the field of view of our microscope (2.7 × 3.2 mm²). Upon an accurate measurement of the meniscus position (±5 μm), such a long serpentine allows us to determine with a high precision the concentration inside the drop from the drop’s length using eqn (4).

### 3.2 Mass transfer

Evaporation is due to the permeability of PDMS to water and the latter diffuses across the elastomer following a near-Fickian process (diffusion coefficient \( D_w \approx 8.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \) and solubility \( c_0 \approx 40 \text{ mol m}^{-3} \)). For our membrane \( (\varepsilon \approx 30 \mu \text{m}, \text{Fig. 2}) \), the typical permeation rate leads to \( \tau_e = (hw)q_e = 1500 \text{ s} \) originating from a permeation flux \( \sim q_e/h \approx 30 \text{ nm s}^{-1} \) (for pure water, the external humidity \( h_e \approx 0.4 \), see next section). Mass transfer of water within the membrane takes place on the time scale \( \sim \varepsilon^2/D_w \approx 1 \text{ s} \) smaller than the shrinkage kinetics \( \tau_w \). We can thus neglect transient effects and assume that the permeation rate adapts instantaneously to the concentration within the drop, which is itself related directly to its length. Note that all these arguments are strictly valid because the main resistance to mass transfer comes from the PDMS membrane \( (\varepsilon/[D_w c_0]) \) while the resistance of water transport in air is negligible \( (l/(D_w c^*)) \), with \( D_w \approx 2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} \) being the diffusivity of water in air, \( c^* \approx 1.2 \text{ mM} \) being the concentration of water at saturation and \( l < 1 \text{ mm} \) being the typical scale of the diffusion–convection boundary layer.

### 3.3 Cross-talking effects

To obtain accurate measurements of the dynamics of concentration over a wide range of solute concentrations \( \phi \), it is necessary to perform experiments with rather long drops, see eqn (4). According to the size of the field of view of our microscope (2.7 × 3.2 mm²), we chose the serpentine shape displayed in Fig. 2 with \( L_0 = 15 \text{ mm} \). This specific length arises from the possible ‘cross-talking’ which can take place between neighbouring channels.\(^{15}\) Indeed, to ensure an homogeneous pervaporation rate during the shrinkage of the drop, it is crucial that the permeation of water from one channel through the membrane is not altered by the presence (or the absence) of water in another, nearby channel. This effect ceases to be detrimental when channels are far apart from each other, in our design for \( \delta \approx 10h \).

To get this quantitative criterion, we performed numerical calculations in our precise geometries. We consider the geometry depicted in Fig. 3 corresponding to an infinite array of linear and parallel channels embedded in a permeable membrane.

Each channel is filled with water which permeates in air through the matrix. The permeation rate \( q_w \) of each channel can be estimated from the numerical resolution of the steady diffusion-limited transfer of water within this 2D matrix. We thus solve numerically \( \Delta c = 0 \) in this specific geometry (\( c \) being the water concentration within the membrane) using Matlab (toolbox Partial Differential Equation). We fully exploit the symmetry of the problem and the linearity of the diffusion equation to solve only the box shown in Fig. 3 using the unitless dimensions \( h = 1, w = 2h, e = h, and \xi = h/5, \) and for various \( \delta \) values. These values correspond to the typical dimensions of our experiments \( (h = 25–35 \mu \text{m}, w = 50 \mu \text{m}, \xi = 5–6 \mu \text{m}, \) and \( e = 30–35 \mu \text{m}) \). Boundary conditions corresponding to the permeation of water through the membrane into dry air are shown in Fig. 3 and follow the symmetry of the problem.

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**Fig. 2** Perspective view of the microfluidic chip. Two identical droplets (≈ 1.5 cm) are facing each other and separated by \( \varepsilon \approx 40 \mu \text{m} \). The side view shows the transverse dimensions of the channels embedded in a PDMS membrane and sealed by a glass slide covered by a thin PDMS layer. Typical dimensions: \( h \approx 25–35 \mu \text{m}, w = 50 \mu \text{m}, e \approx 30–35 \mu \text{m}, \delta = 350 \mu \text{m}, \) and \( \xi \approx 5–6 \mu \text{m} \).
The homogeneous drying assumption also requires $h^2/(D\tau_e) \sim c(h/L) \ll 1$. In our specific geometry ($h \sim 30\,\mu m$, $\tau_e \approx 1500$ s) and this assumption restricts the range of diffusivities to $D > 10^{-10}\,m^2\,s^{-1}$ for length $L_0 = 1.5\,cm$. In practice, the scaling analysis is too restrictive and we observe experimentally, see below, homogeneous concentration fields during the drop’s shrinkage for species with diffusivities up to $D \approx 10^{-11}\,m^2\,s^{-1}$.

To obtain homogeneous pervaporation rates over the droplet, it is also crucial to minimize tip effects, i.e., geometrically enhanced pervaporation from the dead-end of the channel and from the receding meniscus as compared to the body of the linear channel. Such effects are however expected to be small and of the order of $q_e/h$. To further minimize such effects, we chose the specific design shown in Fig. 2, i.e., two drops facing each other and we minimized the distance $e$ between the two channels to reduce permeation from their tips.

4 Results

4.1 Pure water drops

In the case of water, the permeation rate remains constant over the course of the shrinkage kinetics and its dynamics is especially simple given by the simple integration of eqn (2), leading to $L(t) = L_0 \exp(-t/\tau_e)$. Fig. 5 shows the shrinkage dynamics of a water droplet in this geometry. $L(t)$ decays exponentially, in agreement with the assumption of homogeneous (and constant) $q_e$ without any tip effects, leading to $\tau_e \approx 1500$ s. Moreover, the meniscus velocity $V$ (estimated using numerical derivatives of $L(t)$) indicates that $V(t) \rightarrow 20-30\,nm\,s^{-1}$ for $L(t) \rightarrow 0$, and thus negligible tip effects of the order of $q_e/h$ are expected. Deviations from the exponential decay are thus only observed for small length, typically $L < 4w$, when the assumption of a long linear drop does not hold anymore and where 3D mass transfer should be taken into account.

Fig. 3 (a) Cross-section of an infinite array of channels embedded in a permeable membrane sealed on a glass slide. (b) Zoom on the box shown above. No flux boundary conditions are applied on the dotted lines, $c = 1$ on the thick lines and $c = 0$ on the thin line.

Fig. 4 (a) Water concentration field $c$ within the membrane for the case $\delta = 6h$. Arrows indicate the flux field $-\nabla c$. (b) Pervaporation rate $q_e$ from a single channel vs. $\delta$. The continuous line ($q_e = w + \delta$) corresponding to the highly screened regime fits correctly the results for low $\delta$.

Fig. 5 (a) Shrinkage of a water droplet (channel width $w = 50\,\mu m$). Inset: zoom on the receding meniscus. (b) Temporal evolution of $V$ vs. $L$. Slight deviation from the exponential decay is observed below $L \approx 4w$. Inset: meniscus velocity $V$ vs. $L(t)$, zoom on $L \rightarrow 0$. 

Note that for very small $\delta$, $q_e \approx w + \delta$, as this highly screened regime turns to be a simple 1D problem (negligible diffusive flux along $y$).\textsuperscript{15} At larger $\delta$, $q_e$ reaches a plateau value corresponding to the case of an isolated channel. In our experimental configuration, we choose $\delta = 10h$ in order to fully neglect any cross-talking effects between the neighbouring channels. This criterion is coherent with analytical approximations given in ref. 15, which investigates a similar problem (in a slightly different geometry) to unveil the mechanisms of pervaporation in leaves.

Typical results are shown in Fig. 4a which displays both the concentration field $c$ and the associated flux $-\nabla c$ for the case $\delta = 6$. The unitless permeation rate $q_e$ is estimated from the numerical integration of the flux field around the channel. Fig. 4b shows $q_e$ for various $\delta$ values in the 0.5–10 range. For small distances between channels ($\delta < 5$), $q_e$ increases significantly with $\delta$ evidencing the screening induced by the presence of the neighbouring channels. This criterion is coherent with analytical approximations given in ref. 15, which investigates a similar problem (in a slightly different geometry) to unveil the mechanisms of pervaporation in leaves.
4.2 Application 1: colloidal stability

Homogeneous drying is first validated experimentally on a dilute dispersion of nanoparticles, namely citrate-stabilized gold nanospheres (15 nm in diameter, initial volume fraction $\phi_0 = 2 \times 10^{-5}$). The dispersion is concentrated enough to be colored yet dilute enough to have no impact on the chemical activity of water during drying ($q_e$ constant).

Fig. 6 displays three snapshots zooming on the end of the dead-end serpentine, the movie being available in the ESI.† We extract the position of the meniscus $L(t)$ and observe that it follows an exponential dynamics (not shown). Meanwhile, the color gets more and more pronounced, with no sign of concentration gradient. At $t \approx 2040$ s, the color turns almost instantly ($\pm 50$ s) and homogeneously to gray, which is a sign of the destabilization of the dispersion.

These results show that the concentration of particles or ions is homogeneous within the drop, as expected from the criterion $h^2/(D\zeta) \sim 0.02$ (with $D \approx 3 \times 10^{-11}$ m$^2$s$^{-1}$ for the particles). Interestingly, the destabilization of the dispersion does not affect the shrinkage dynamics, probably owing to the very small amount of nanoparticles involved. The exponential decrease of $L(t)$ supports the assumption of the homogeneous and constant pervaporation rate $q_e$. Therefore, $\phi_0 L_0/L(t)$ provides a fair estimate of the concentration, regardless of the species, ions or nanoparticles.

Equally interesting, we compare these results with the situation of the ‘open-tube’ geometry—let us say a 3 cm round capillary, half-filled, open at the top through which vapor may escape—in which we would set a similar meniscus velocity $V \approx 5$ µm s$^{-1}$. In such a virtual case, gradients would develop on a length scale $\xi \sim \sqrt{\nabla V}$, that is of the order of 1 to 100 µm for particles to ions. Here, if $\xi < L(t)$, while the particles are immobile on average in the frame of the capillary, the moving meniscus gathers particles and ions and concentration gradients form near the meniscus in a zone of extent $\xi$, which is then permanently fed with time by a flux of matter $\phi_0 V$. The only possible way to suppress gradient would be to slow down $V$ or to diminish the size of the capillary so as to reach $\xi \sim L$, in sheer contrast to the membrane-based geometry for which we can suppress gradients.

4.3 Application 2: ternary phase diagram

We can now establish an appropriate phase diagram for a non-ideal, non-dilute solution. We focus on a ternary mixture made of polymer and salt in water (3.35 kDa polyethylene glycol and ammonium sulfate (NH$_4$)$_2$SO$_4$) and we proceed as above. Two droplets of the dilute and homogeneous solution are formed and let to evaporate. At a well-defined time that depends on the initial concentrations, a liquid–liquid demixion occurs homogeneously within the drop, Fig. 7a and b (the complete movie is available in the ESI†).

The analysis of $L(t)$ leads to an initial exponential decrease with a similar $\tau_e \approx 1000$ s (not shown). For PEG 3.35 kDa, we estimate $D \approx 10^{-16}$ m$^2$s$^{-1}$ and the criterion $h^2/(D\zeta) \ll 1$ is fulfilled. Therefore, we convert the size of the drop into a concentration and the (long linear) geometry makes it possible to reach a very good accuracy ([%]) for the measurement of the concentration, a significant improvement and simplification as compared to ref. 13. Upon iterating the same experiment with different polymer/salt ratios, we always observe the liquid–liquid transition at some stage and we build pointwise the phase diagram of the ternary mixture, as shown in Fig. 7c.

Importantly, we stress that only the length of the drop matters, not the actual time at which demixion occurs. Indeed, environmental humidity or chemical potential of water inside the drop may vary. It alters the shrinkage kinetics but not the actual size of the drop, making our tool a robust device for physical-chemistry.

4.4 Application 3: activity of binary mixtures

Going a step further, we now extract more equilibrium data from the out-of-equilibrium shrinkage kinetics of a binary molecular mixture. In this experiment, we measure simultaneously the shrinkage kinetics $L(t)$ of a droplet containing glycerol in water and the external humidity ($h_e(t)$), temporal fluctuations within 2%). As the chemical potential of water changes with the concentration of glycerol upon drying, we modify eqn (3) and stipulate that the driving force for evaporation follows instantaneously (thanks to the thin membrane).
both the changes of external humidity $h_e$ and the chemical activity of water $a(\phi)$:

$$\frac{\partial \phi}{\partial t} = \frac{\phi}{\tau_e} (a(\phi) - h_e), \quad (8)$$

where $\tau_e$ is the reference evaporation time defined for pure water and for a vanishing external humidity ($a = 1$ and $h_e = 0$). We can thus extract $a(\phi)$ using eqn (8) and solute conservation $\phi \partial_0 = \phi(t)L(t)$; note that these measurements require a high accuracy as temporal derivatives of $L(t)$ are involved.

For a dilute mixture of glycerol in water ($\phi_0 = 0.02$), we observe that $L(t)$ decreases exponentially during the initial stage (Fig. 8). For these low concentrations, $a(\phi_0) \approx 1$ and the dynamics of shrinkage of the droplet should indeed follow an exponential decay at early times, from which we extract $\tau_e = 890$ s. Then, a significant deviation is observed at $t > 3000$ s and shrinkage even stops at the long stage to reach here a plateau which translates into $\phi \approx 0.9$, in agreement with the measured $h_e = 0.12$ (see movie in the ESI!). From the temporal evolution of $L(t)$ and using eqn (8), we estimate the water activity $a(\phi)$ against the glycerol volume fraction, as shown in Fig. 8, in good agreement with literature values.\(^{17,18}\)

We emphasize that such a result, if not unexpected, is achievable only when the design and diffusivity criteria are fulfilled. If not, we observed strong discrepancies between the measured and reference values of $a(\phi)$. Also, long droplets are again required to cover the whole range of relevant concentrations.

### 5 Conclusions

We demonstrated theoretically and experimentally that a drop confined within a microfluidic channel and pervaporating through the matrix of the device yields homogeneous concentration fields during its shrinkage. We derived theoretically the range of validities of this striking regime which is mainly due to the pervaporation-induced velocity profile within the drop: (i) a homogeneous pervaporation rate $q_e$, and (ii) $h^2/(D \tau_e) = \mathcal{O}(h/L)$. We stress again that we do not assume that diffusion only suppresses concentration gradients, *i.e.* $L^2 \ll \mathcal{O}(\tau_e)$, leading to a very restrictive condition, $L \ll 100 \mu m$ (for $\tau_e = 1500$ s and $D = 10^{-11}$ m$^2$ s$^{-1}$), as compared to our design ($L = 15$ mm).

Eventually, the microfluidic format of such experiments, combined with the possibility to design parallel experiments, may offer great opportunities in the field of physical-chemistry. Future improvement may rely on the use of a wider range of membranes\(^{19,20}\) in order to be able to explore other solvents, or even coupling the solvent exchange with ionic exchange, thanks to the use of dialysis membranes.

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### References