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Interfacial hydrodynamic instabilities driven by cross-diffusion in reverse microemulsions

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When two microemulsions are put in contact in the gravity field along a horizontal contact line, cross-diffusion can trigger the transport of one species in presence of a gradient in concentration of another species. We show here theoretically that such cross-diffusion effects can induce buoyancy-driven convective instabilities at the interface between two solutions of different compositions even when initially the less dense solution lies on top of the denser one. Two different sources of convective modes are identified depending whether positive or negative cross-diffusion is involved. We evidence the two predicted cross-diffusion driven instabilities experimentally using a two-layer stratification of Aerosol-OT (AOT) water-in-oil microemulsions solutions with different water or AOT composition.

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Keywords: Water-in-oil reverse microemulsions, Buoyancy driven instabilities, Diffusion-Convection Systems, Cross-diffusion, Multi-components systems

Aerosol-OT (AOT) microemulsions have been well studied in the context of reaction-diffusion patterns in particular when the reactants of the oscillatory Belousov-Zhabotinsky reaction are dissolved in it. Recently, such microemulsions have also proved to be good model systems to study, in absence of any reaction, convective instabilities driven in the gravity field by cross-diffusion effects when gradients in a salt concentration triggers co-flow of water and AOT. Here we show that even in a simpler three components water-AOT-octane system, cross-diffusion can trigger buoyancy-driven motions when a gradient of either water or AOT is imposed to an initially statically stable stratification of two different microemulsions. This paves the way to future understanding of cross-diffusion driven hydrodynamic instabilities and to studies of more complex reaction-diffusion-convection patterns where convective effects could be induced by gradients in concentration inherent to reaction-diffusion patterns.

I. INTRODUCTION

New dynamical properties arising from the interplay of dissipative physico-chemical systems with dispersed media and soft matter are being studied since many years. The dynamics of the well known Belousov-Zhabotinsky (BZ)^{1,2} chemical oscillator, in particular, has been studied with many self-assembled matrices³ and structured media⁴ including gels and hydrogels⁵⁻⁸, micelles⁹⁻¹⁴, polymers¹⁵⁻¹⁸ and lipid vesicles and aggregates¹⁹⁻²⁴. Particularly important from the pattern formation viewpoint, the AOT water-in-oil reverse microemulsions (ME), are probably the most thoroughly studied system in combination with the BZ reaction. Microemulsions can be defined as optically clear, thermodynamically stable and isotropic liquid mixtures of an organic component (more commonly termed *oil*), water and surfactant (see the sketch in Figure 1a for the structure). In particular, in a reverse ME the hydrophilic BZ reagents can be solubilized in water AOT-coated nano-droplets to create a great amount of coupled nano-oscillators. Early works dealt with the temporal behavior of the BZ reaction when dissolved in the ME^{25,26}. When the Brandeis group evidenced for the first time Turing structures and other exotic patterns in ME loaded with reactants of the BZ system in a spatially extended reactor²⁷⁻³⁰, the system attracted much more interest. The Brandeis group found that transport phenomena played a key role in the generation of the large amount of patterns observed in ME. Specifically, microemulsions induce two different diffusion modes for the BZ intermediates: slow diffusion for the hydrophilic activator, which can only move together with the droplets, and fast diffusion of the hydrophobic

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inhibitor, free to move alone into the oil phase with a diffusion coefficient two orders of magnitude larger than that of the activator. In order to generalize the modelling of the related pattern formation, cross-diffusion terms, *i.e.* the phenomenon by which a flux of a given species entrains the diffusive transport of another species, were introduced in reaction-diffusion equations. In their seminal paper³², Vanag and Epstein introduce cross-diffusion phenomena in reaction-diffusion models, an aspect generally neglected in chemo-physical systems. In this context, the Brandeis group developed a new method to exploit the Taylor dispersion technique (TDT, see section IB), in order to measure the diffusion matrix up to a 5-component microemulsion systems ($\text{H}_2\text{O} + \text{AOT} + 2 \text{ BZ}$ reagents in octane as the oil phase)^{33–35} and study the effect of cross-diffusion on the onset of Turing instabilities³⁵.

Besides these breakthroughs in reaction-diffusion (RD) systems, I.R. Epstein has also pioneered the studies of reaction-diffusion-convection (RDC) patterns in autocatalytic systems when convection develops around traveling fronts in solutions because of density gradients due to the exothermicity of the reaction and/or volume changes between reactants and products.^{36–39}

With the idea that RD patterns and convective effects should be able to interact in microemulsions to give rise to a wealth of possible new RDC patterns and instabilities, we recently⁴⁰ started investigating hydrodynamic convective patterns triggered by cross-diffusion in microemulsions in the absence of any reaction. The objective is twofold: first, the ME system is a perfect model system to explore new convective modes related to the introduction of cross-diffusion effects in the analysis of hydrodynamic instabilities of miscible two-layer systems.

Even though some early works have started addressing this problem in polymers^{41,42}, cross-diffusion driven convective instabilities in absence of any reaction are still poorly understood. The second objective is to understand which convective modes can be observed in microemulsions before starting to add the complexity of RD patterning to construct new RDC patterns. In this context, we first studied⁴⁰ fingered convective motions developing at the interface between two identical AOT-ME in a gravitational field, when the lower denser solution contains a simple water-soluble molecule (NaBrO_3) free to diffuse towards the upper less dense layer and generate by cross diffusion a positive co-flux of both water and AOT. In detail, when NaBrO_3 diffused from the bottom to the upper layer, it dragged along both H_2O and AOT molecules thus generating a non-monotonic density distribution around the contact line, destabilizing convectively an initially stable system. By means of a diffusion model, we explained the dependence of the hydrodynamic patterns upon $[\text{NaBrO}_3]$ cross-diffusion and we opened a new path to study the coupling between pattern formation due to RD and RDC interactions in microemulsions systems.

In this paper, we show that cross-diffusion drives con-

vective instabilities in an initial statically stable stratification between two microemulsions (without any added salt) in a Hele-Shaw cell by just imposing a gradient in water or AOT concentration. By using the TDT we characterise the diffusion matrix of the Water/AOT mixture and show how ME represent a convenient model to study cross-diffusion-driven convection. On the basis of Fick's equations including cross-diffusion coefficients, we predict two different possible convective instability scenarios based on the sign of the cross-diffusion terms. We use these results to devise experiments where the species free to diffuse from one layer to the other present either positive or negative cross-diffusion coefficients. We demonstrate experimentally the difference in convective patterns for the two predicted instability scenarios and compare the properties of the obtained convective patterns.

The paper is structured as follows, in section IA we briefly sketch transport properties of a microemulsion system. In section IB the main features of the Taylor dispersion method are described. The experimental methods and setup are presented in section II while results are discussed in section III. In particular, in section III A the diffusion matrices of the Water/AOT systems investigated are characterised. In sections III B 1 and III B 2 we introduce a theoretical approach to cross-diffusion-driven convection and, by analyzing the shape of the density profiles, we characterize two classes of instability scenarios that are next demonstrated experimentally in section III C. Finally, conclusions are drawn in section IV.

A. Transport processes in microemulsions

Sodium bis(2-ethylhexyl) sulfosuccinate, usually referred to as Aerosol-OT, or simply AOT, is able to feature stable reverse microemulsions in a simple three-component system for a broad range of compositions. The geometry of the dispersed domains may range from spherical or elongated droplets to lamellar phases, through interconnected channels of various length and local topology. The exact shape of the water and oil pseudophases depends upon a number of factors, such as chemical nature and concentration of the microemulsion components, temperature and pressure. However, at fixed temperature and pressure, the structural properties of AOT reverse microemulsions can be basically described by two parameters²⁷:

- the water to AOT molar concentration ratio $\omega = [\text{H}_2\text{O}]/[\text{AOT}]$ which, in the case of droplets, gives an estimation of the water core radius, expressed in nanometers, according to the relation³⁰ $R_w \simeq 0.17\omega$.
- the volume fraction of the dispersed phase $\phi_d = \phi_{\text{H}_2\text{O}} + \phi_{\text{AOT}}$ which can be used as an indicator of the interactions among water domains. In fact, higher values of ϕ_d result in clusters formation and

eventually in the onset of a continuous aqueous²³⁹
phase (percolation threshold^{30,43} $\phi_d \sim 0.5 - 0.6$).²⁴⁰

In a ternary system like ME (H₂O (Species 1) / AOT²⁴¹
(Species 2) + Octane as the solvent), the diffusion ma-
trix consists of 4 elements: 2 diagonal main diffusion²⁴²
coefficients (D_{11} and D_{22}), which account for the mo-
tion of water and AOT in octane respectively, according²⁴³
to their own concentration gradient and 2 off diagonal²⁴⁴
cross-diffusion coefficients (D_{12} and D_{21}), related to the²⁴⁵
motion of water generated by a gradient of AOT and²⁴⁶
vice versa. Diffusion is therefore described by a set of²⁴⁷
two equations and four diffusion coefficients as

$$J_1 = -D_{11}\nabla C_1 - D_{12}\nabla C_2 \quad (1)^{245}$$

$$J_2 = -D_{21}\nabla C_1 - D_{22}\nabla C_2 \quad (2)^{246}$$

where J_i is the flux of the i species and C_1 and C_2 are²⁴⁸
the concentrations of H₂O and AOT, respectively.²⁴⁹

The cross-diffusion coefficients were found to be neces-²⁵⁰
sary to describe in details ME systems, in particular a
flux of AOT generates a large co-flux of water (D_{12} posi-²⁵¹
tive), while the flux of H₂O generates a counter-flux of
AOT (D_{21} negative)⁴⁴⁻⁴⁶. The presence of solutes in ME
also generates large cross-diffusion effects, which where
measured up to a 5 components system³³⁻³⁵. **Excluded**
volume effects, are the most important mechanisms in
generating cross diffusion in ME, because the motion of
AOT or H₂O changes the size of the droplets' water core
influencing the actual concentration of the two species.
Further mechanisms related with the size of the water
droplets are, however, at play^{34,45}.

B. The Taylor dispersion technique

The Taylor dispersion technique (TDT)⁴⁷⁻⁵⁰ is a²⁵²
fast and reliable method for measuring the diffu-
sion coefficients of solutes in one- or multi-component
solutions^{33-35,45,51,52}. The TDT is based on the diffusive
spreading of a drop of solution injected into a laminarly
flowing stream of the same mixture but with slightly dif-
ferent concentrations. A small volume of the perturbing²⁵⁴
solution is injected into the flowing eluent at the entrance²⁵⁵
of a long capillary tube having a radius R_0 . As it moves²⁵⁶
along the tube at a constant speed u_0 (cm/s), the injected
sample is deformed by the flow and by radial diffusion. If
the flow has a parabolic velocity profile, the drop spreads
out into a shape that can be fitted by a combination of n
Gaussian functions for an $(n + 1)$ -component system (n
solutes + 1 solvent). The eluted peak is monitored by a
suitable detector, chosen according to the composition of²⁵⁸
the analyzed samples. The diffusion coefficients are cal-
culated from the parameters of the Gaussian functions²⁵⁹
that fit the eluted peak.²⁶⁰

Taylor demonstrated that if the elution process is slow²⁷⁰
enough, the radial variation of the sample concentration²⁷¹
is small relative to the axial variation and the concen-²⁷²
tration profile of the i -th species (c_i) in a n -component²⁷³

system can be described with a one-dimensional equation
(c_i is averaged over the cross section of the tube) taking
the form^{33,47}

$$\frac{\partial c_i}{\partial t} = \sum_{j=1}^n F_{ij} \frac{\partial^2 c_j}{\partial z^2} \quad (3)$$

where F_{ij} are called dispersion coefficients. They have
the same units as the molecular diffusion coefficients D_{ij}
(cm² s⁻¹) and are related to them through the relation

$$F_{ij} = \frac{R_0^2 u_0^2}{48 \det(\mathbf{D})} \det(\mathbf{M}_{Dji}) (-1)^{(i+j)} \quad (4)$$

$\det(\mathbf{D})$ is the determinant of the $n \times n$ diffusion matrix
 \mathbf{D} and $\det(\mathbf{M}_{Dji})$ is the determinant of the minor asso-
ciated with element D_{ji} of \mathbf{D} .

The F_{ij} can be obtained from the experimentally found
parameters characterizing the Gaussian fit to eluted
peaks: $P_{i,exp}$, K_i , and σ_i through the following equation

$$l_0^{-1} \sum_{i=1}^n \sigma_i P_{i,exp} = \sum_{j=1}^n c_{j0} \sum_{i=1}^n K_i F_{ij} \quad (5)$$

where l_0 (cm) is the length of the capillary occupied by
the sample injected at the initial time ($l_0^{-1} = \pi R_0^2 / V_0$,
 V_0 is the injected volume), $P_{i,exp}$ are the pre-exponential
parts of the Gaussian, σ_i are the dispersions of the Gaus-
sian functions which are equal to the eigenvalues of the
dispersion matrix \mathbf{F} , c_{i0} is the difference between the con-
centration of component i in the injected sample and in
the carrier stream, K_i is the instrumental sensitivity with
respect to that component (typically linear in the con-
centration). The experimentally measurable quantities
 $P_{i,exp}$, K_i , and σ_i can be found by fitting all the exper-
imental peak curves $v(t)$ (generated with injections of
different compositions) according to

$$v(t) = \sum_{i=1}^n \frac{P_{i,exp}}{\sqrt{4\pi\sigma_i t}} \exp \left[-\frac{u_0^2(t-t_0)^2}{4\sigma_i t} \right] \quad (6)$$

where u_0 is the mean velocity of the carrier stream and t_0
is the retention time. The coefficients K_i can be found by
analyzing different experiments involving injections with
only one $c_{i0} \neq 0$ as

$$K_i = l_0^{-1} \left(\sum_{j=1}^n P_{j,exp,i} \right) / c_{i0} \quad i = 1 \dots n \quad (7)$$

II. EXPERIMENTAL SETUPS

A. Taylor Dispersion setup

In all experiments a 15 m silica glass dispersion capil-
lary (inner radius $R_0 = (0.016 \pm 0.002)$ cm) was placed
between the injector and the cell of the differential flow-
through thermostated refractive index detector, RID

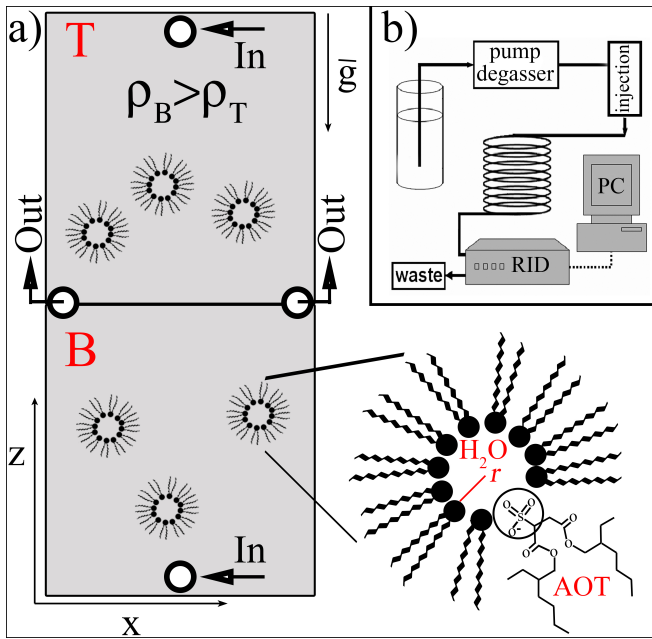


Figure 1. (a) Sketch of the experimental configuration used for the Hele-Shaw experiments. (b) Scheme of the HPLC apparatus adapted for the Taylor dispersion measurements.

(Agilent G1362A). The RID measures the difference between the refractive index of the eluent which is present in a reference cell and the refractive index of the flowing solution containing the sample, which passes through a measuring cell. The refractive index is, in fact, dependent on the composition of the system and, for dilute solutions, it is a linear combination of the refractive index of each component weighted by its concentration. In order to eliminate small bubbles from the solutions, an inline ion exchange resin based de-gasser (Agilent G1322A) was placed between the eluent reservoir and the pump.

The tubing was coiled in a 30 cm diameter helix and immersed in a thermostated water-bath (Julabo ME-16G), kept at 25 °C. The eluent flow was kept steady and constant at 0.015 mL/min by using an isocratic pump (Agilent G1310B). A 2 μ L sample loop was used for samples injection. The detector was connected to a personal computer for data acquisition.

Solutions were prepared by using bidistilled water, AOT (Aldrich) was of analytical grade and used as received. Octane (Sigma) was further purified by mixing with concentrated sulfuric acid for seven days.

Samples were injected every 60 min to avoid the overlapping of the peaks. Experimental peaks generated with different injections were simultaneously fitted, by using the Levenberg-Marquardt algorithm⁵³, to equation (6). In order to correct the instrumental drift, a baseline of the form $(a + bt)$ was previously subtracted from the recorded signals with the help of a suitable software.

B. Hele-Shaw cell

The experimental reactor used to study convective dynamics at the interface between two MEs of different compositions consists of a vertically oriented Hele-Shaw cell, composed of two borosilicate glasses separated by a spacer of 0.10 mm (Figure 1(a))⁵⁴. Two different water-in-oil (W/O) reverse microemulsions were filled in the reactor through the inlet ports positioned at the top and the bottom of the cell (“In” arrows in Fig. 1(a)). The excess of the solutions is pumped out through the cell’s outlets (“Out” arrows in Fig. 1(a)) until a flat interface between the two liquids is obtained. Each of the two microemulsions having different composition initially occupies half of the reactor height. The top and bottom solutions are prepared at room temperature ($\sim 21^\circ\text{C}$) by means of distilled water and of a 1.5 M AOT in octane stock solution, conveniently diluted until the desired ϕ_d (0.16 – 0.20) is reached. The top and bottom microemulsions are prepared at slightly different droplet size ($\omega = 8 - 14$), with the bottom solution always denser than the top one. Different ω ratios are obtained by varying the amount of H₂O (AOT) while keeping the amount of AOT (H₂O) constant.

The dynamics of the interface is tracked by using the Schlieren technique^{40,55}, which allows to observe the gradients in the refractive index between both microemulsions, due to their density differences and, therefore, monitor the convective motions in solutions without the presence of dyes.

The solutal expansion coefficient of each i -component ($i = \text{H}_2\text{O}, \text{AOT}$) was determined according to $\alpha_i = \frac{1}{\rho_0} \frac{\partial \rho}{\partial C_i}$ where ρ_0 is the density of the solvent (octane) and C_i the molar concentration of the i -th species. In order to measure these coefficients the volume of both the solvent and of one of the components was fixed, while the concentration of the other was gradually increased. The densities were measured by using an Anton Paar densimeter and it was found that the solutal expansion coefficients were 0.0051 M⁻¹ for H₂O and 0.154 M⁻¹ for AOT.

III. RESULTS

A. Diffusion matrices

In order to characterize the diffusion matrix of the microemulsions used for the Hele-Shaw experiments, three systems below the percolation limit were investigated; namely, microemulsions with the smallest and the largest value for the concentration ratio, ω , and the volume fraction, ϕ_d , (8.15 ; 0.165) and (14 ; 0.2), respectively and one composition in the middle of the interval, (11.84 ; 0.18). Several experiments were performed by injecting samples with an excess of one (H₂O or AOT) or two

356 components. All Taylor dispersion peaks obtained were
 357 then simultaneously fitted using eq. (6) with $i = 1, 2$ to
 358 extract the experimental parameters ($P_{i,exp}$, σ_i). As an
 359 example, figure 2 shows the peaks obtained by injecting
 360 samples with an excess of only AOT (\blacktriangle) or only H₂O
 361 (\blacksquare) into a carrier stream of microemulsion with $\omega = 14$
 362 and $\phi_d = 0.2$. The sensitivity coefficients K_i were found
 363 by introducing the fitted parameters in eq. (7). By using
 364 eq. (5), we find the dispersion coefficients F_{ij} and finally,
 365 by using eq. (4) we transform F_{ij} to diffusion coefficients
 366 D_{ij} . The complete procedure to fine-tune the diffusion
 367 matrix values is reported elsewhere³³.

Table I. Ternary Diffusion Coefficients (in 10^{-6} cm²/s) for the H₂O (i=1)/AOT (i=2)/Octane systems at different ω and ϕ_d .

ω	ϕ_d	D_{11}	D_{12}	D_{21}	D_{22}
8.15	0.165	0.8 ± 0.1	3.6 ± 1.0	-0.0015 ± 0.0020	1.10 ± 0.01
11.84	0.18	0.60 ± 0.04	7.8 ± 2.0	-0.010 ± 0.002	1.30 ± 0.04
14	0.2	0.3 ± 0.1	1.1 ± 0.2	-0.005 ± 0.004	0.96 ± 0.01

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Table I reports the diffusion matrices of the investigated systems, which span the whole range of the microemulsions composition used for the Hele-Shaw cell experiments. Since both ω and ϕ_d have been varied simultaneously, it is difficult to find a clear trend for the dependence of D_{ij} upon the system composition. However, for the purpose of this work, we were more interested⁴⁰² in finding the nature and the order of magnitude of the⁴⁰³ cross-diffusion coefficients to be used in simulations (see⁴⁰⁴ section III B). The results reported in Table I fit well with⁴⁰⁵ literature data determined for other compositions of the⁴⁰⁶ microemulsions^{33-35,44,45}, in particular we find that the⁴⁰⁷ motion of AOT generates large co-fluxes of water (D_{12} ⁴⁰⁸ large and positive) and the motion of water generates⁴⁰⁹ small counter-fluxes of AOT (D_{21} small and negative)⁴¹⁰ for all the parameters range explored in the Hele-Shaw⁴¹¹ experiments.⁴¹²

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B. Theoretical approach

1. Cross-Diffusion Model

The possible convective instabilities which take place at the horizontal interface between two microemulsions⁴¹⁷ in a vertical Hele-Shaw cell (see Figure 1a)), can be in⁴¹⁸ terpreted by studying the corresponding temporal evolu⁴¹⁹ tion of one-dimensional density profiles along the vertical⁴²⁰ axis Z , where the gravitational acceleration \bar{g} is oriented⁴²¹ downwards. The density profiles give qualitative infor⁴²² mation about the instabilities to be expected, as their⁴²³ morphology shows whether and where local regions of⁴²⁴ denser fluid overlying less dense zones may develop along⁴²⁵ the gravitational axis.⁴²⁶ Consider a spatial domain of length L_Z where a solu⁴²⁷

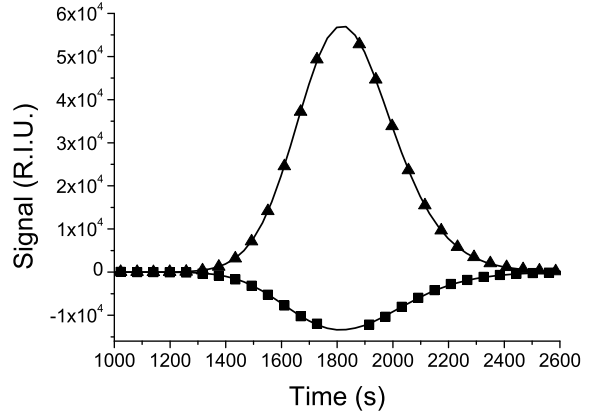


Figure 2. Taylor dispersion peaks for the system H₂O/AOT/octane. (\blacktriangle) Experimental peak for a sample containing an excess of AOT, $\Delta[\text{AOT}] = 0.1$ M, $\Delta[\text{H}_2\text{O}] = 0$ M. (\blacksquare) Experimental peak for a sample containing an excess of H₂O, $\Delta[\text{AOT}] = 0$ M, $\Delta[\text{H}_2\text{O}] = 2$ M. The composition of the eluent is $[\text{H}_2\text{O}] = 4.38$ M, $[\text{AOT}] = 0.31$ M and $[\text{octane}] = 5.14$ M ($\omega = 14$ and $\phi_d = 0.2$), $T = 25$ °C. Solid lines are the best fit obtained with sum of two Gaussian curves with $P_{1,exp} = 1.4 \times 10^7$ R.I.U. \times cm, $P_{2,exp} = 1.7 \times 10^7$ R.I.U. \times cm (\blacktriangle) and $P_{1,exp} = -2 \times 10^5$ R.I.U. \times cm, $P_{2,exp} = -7 \times 10^6$ R.I.U. \times cm (\blacksquare). For both peaks, $\sigma_1 = 6$ cm²/s, $\sigma_2 = 12$ cm²/s, $K_1 = -2.85 \times 10^6$ R.I.U./M and $K_2 = 1.07 \times 10^8$ R.I.U./M.

tion T of density ρ^T , containing the solute 1 (H₂O) with the initial concentration $C_{1,0}^T$ and the solute 2 (AOT) with concentration $C_{2,0}^T$ is placed on top of the solution B , with concentration $C_{1,0}^B = C_{1,0}^T$, $C_{2,0}^B > C_{2,0}^T$ (or *vice versa*, depending on the type of cross-diffusion we are interested in). The density ρ^B is always larger than ρ^T in order to start from a stable configuration with regard to a Rayleigh-Taylor instability⁵⁶. Upon contact, the two miscible solutions, initially separated along the horizontal interface $z = L_Z/2$, start mixing by diffusion. The diffusion of each species is affected by concentration gradients in the other one and hence the spatio-temporal dynamics of the system obeys a set of fickian equations including the cross-diffusive terms of the diffusion matrix \mathbf{D} :

$$\partial_t C_1 = D_{11} \nabla^2 C_1 + D_{12} \nabla^2 C_2 \quad (8)$$

$$\partial_t C_2 = D_{21} \nabla^2 C_1 + D_{22} \nabla^2 C_2 \quad (9)$$

Although main (D_{ii}) and cross-diffusion coefficients (D_{ij} , $i \neq j$) depend on the chemical composition of the system (see Table I), as a first approximation, we consider them here as constant^{35,40}.

We solve eqs (8)-(9) with a constant concentration of either water or AOT and a jump in the concentration of the other specie centered around $z = L_Z/2$. No-flux boundary conditions are imposed at the borders of the spatial domain. We obtain numerically the concentration profiles $C_1(x, t)$ and $C_2(x, t)$ which are next used to reconstruct the related density profiles according to the

state equation:

$$\rho(C_1, C_2) = \rho^T (1 + \alpha_1(C_1 - C_{1,0}^T) + \alpha_2(C_2 - C_{2,0}^T)) \quad (10)$$

This expansion relies on the assumption that concentrations slightly change with respect to the initial composition of the reference top solution with density ρ^T and we can then admit a linear dependence of the global density ρ upon the solute concentration. In eq. (10), $\alpha_i = \frac{1}{\rho^T} \frac{\partial \rho}{\partial C_i}$ is the solutal expansion coefficient of the i -th species.

2. Density profiles analysis

The double-layer initial condition represents a key specificity of the cross-diffusion problem under study. Depending upon the starting concentration profile of the two species, we can “select” a specific cross-diffusion path and, in turn, the related convective dynamics. For instance, when a concentration jump is initially imposed to AOT at constant water content, this induces a diffusive motion in the initially homogeneous distribution of H_2O *via* the cross-diffusion term D_{12} , while the other cross-diffusion term (D_{21}) plays a negligible influence. In particular, species 2 (AOT) generates a co-flux of the species 1 (water) since D_{12} is positive. *Vice versa*, when the initial concentration jump is imposed on water at constant AOT, cross-diffusion effects, triggered by the propagation of water towards the upper layer, influence the evolution of AOT as controlled by D_{21} . In this case the diffusion of H_2O generates a counter-flux of AOT.

These mechanisms are shown in Fig.3. Both panels (a) and (b) describe in the first two graphs the spatio-temporal evolution of the species concentration starting from one of the two initial configurations under analysis; the third graph displays the resulting density profiles. The concentration profiles are obtained by solving in one spatial dimension (Z) the diffusion equations with the characteristic diffusion matrix of the ME (see sec. III A):

$$\mathbf{D} = \begin{pmatrix} 0.6 & 7.8 \\ -0.01 & 1.3 \end{pmatrix} \times 10^{-6} \text{cm}^2 \text{s}^{-1}, \quad (11)$$

while the density distribution is found according to eq. (10), using the solutal expansion coefficients measured experimentally (see sec. II): $\alpha_{H_2O} = 0.0051 \text{M}^{-1}$ and $\alpha_{AOT} = 0.154 \text{M}^{-1}$. Fig.3.a illustrates how the diffusion of species 1, featuring an initial concentration jump, generates a counter-flux of species 2 ruled by the negative cross-diffusivity $D_{21} = -0.01 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$. In the concentration profile $C_2(Z, t)$ this induces a local depletion area in the upper layer and a symmetric accumulation of species 2 just below the initial interface $L_Z/2$. By contrast, when the initial concentration jump is imposed

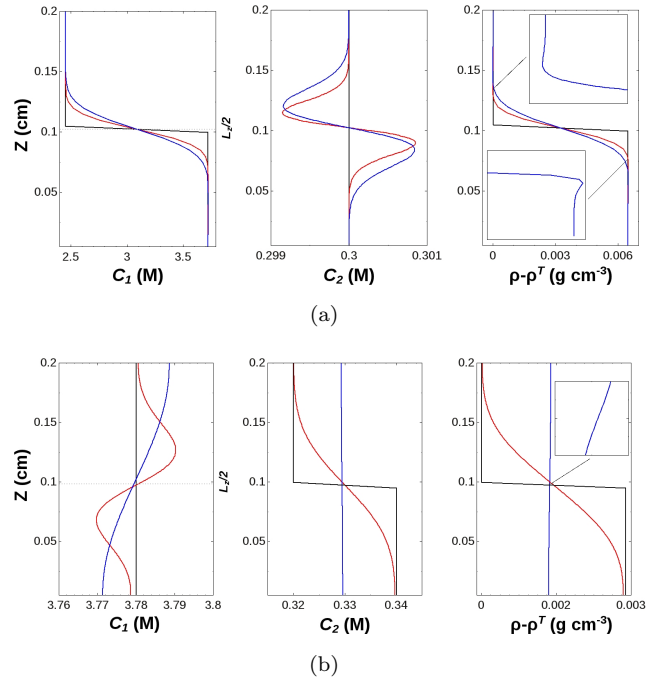


Figure 3. Spatio-temporal evolution of the concentration profiles $C_1(Z, t)$, $C_2(Z, t)$ and of the density excess $(\rho - \rho^T(z))$. In each graph we show with black lines the initial distribution of the variables, while red and blue profiles depict the spatial concentration and density at intermediate and long times, respectively. a) NCC mechanism due to the negative cross-diffusion term (D_{21}) and induced by means of a concentration jump in the species 1 (water). b) PCC scenario with positive cross-diffusion (D_{12}) triggered by the upwards diffusion of the species 2 (AOT).

to the AOT (species 2) (Fig.3.b), its diffusion from the bottom to the upper layer promotes a co-flux of the water (species 1), quantified by the positive cross-diffusivity $D_{12} = 7.8 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$. As a result, the concentration profile $C_1(Z, t)$ develops a non-monotonic shape with a local maximum and a minimum symmetrically located above and below the initial interface, respectively. We clearly observe an inversion in the morphology of the non-monotonic density profiles depending whether the initial jump is imposed on species 1 (water) or species 2 (AOT), as this activates different cross-diffusion terms with opposite sign.

Non-monotonic density profiles will develop because of cross-diffusion effects provided a sufficient influence of the non-monotonic concentration to the global density. In the first case (Fig.3.a), though the small negative cross-diffusion D_{21} drives the formation of concentration extrema of small amplitude in $C_2(Z, t)$, the AOT has a large weight (α_{AOT}) to the density and we can identify a minimum and a maximum above and below the interface, respectively. This profile is reminiscent of typical density profiles characterizing Diffusive Layer Convection (DLC) scenarios^{56,57} and we can expect that, starting from an

500 initial constant AOT concentration and a jump in H_2O ,⁵⁵⁵
 501 convective modes will grow in the upper and the lower
 502 layer, without deforming the initial contact line between
 503 the two stratified solutions. We will refer to this scenario
 504 as Negative Cross-diffusion-driven Convection (NCC).
 505 Analogous considerations can be drawn for the opposite
 506 initial configuration shown in Fig.3.b. Here the cross-
 507 diffusion term responsible for the non-monotonic evolu-
 508 tion of $C_1(Z, t)$, D_{12} , is positive and large. This means
 509 that $C_1(Z, t)$ can develop concentration extrema but,
 510 since H_2O presents a small relative contribution to the
 511 system density, the smoothing of the initial AOT gradi-
 512 ent must be waited to observe the influence of H_2O in the
 513 density evolution. Fig.3.b (third panel), allows to appre-
 514 ciate how, starting from an initial condition in which the
 515 density increases downwards the gravitational axis, the
 516 density profile changes in time into a monotonically de-
 517 creasing profile. In real experiments this results in a fin-
 518 gered deformation of the initial interface and hereunder
 519 we refer to this scenario as Positive Cross-diffusion-driven
 520 Convection (PCC).

521 **C. Hele-Shaw results**

522 In order to confirm the theoretical predictions, we per-⁵⁵⁶
 523 formed experiments in a Hele-Shaw cell by stratifying⁵⁵⁷
 524 two microemulsions with different initial concentrations
 525 of water and AOT. In all experiments, we start from an
 526 initial statically stable stratification, *i.e.* the microemul-
 527 sion located in the bottom is denser than the one on
 528 the top. We explore two different scenarios to analyze
 529 the negative (NCC) and positive (PCC) cross-diffusive-
 530 driven instabilities. In the negative cross-diffusive case
 531 (Fig.3.a) the AOT concentration is initially constant ev-
 532 erywhere while the microemulsion on the top has less
 533 water than that placed below, as depicted in Figure 4(a).
 534 When the difference in water concentration is relatively
 535 small ($\Delta[H_2O]_{\text{bottom-top}} < 0.75$ M) we do not observe
 536 any buoyant instability. This can be understood as a
 537 limitation of our experimental device in discerning small
 538 gradients in the refractive index. However, for larger gra-⁵⁵⁸
 539 dients ($0.75 \text{ M} < \Delta[H_2O]_{\text{bottom-top}} < 1.75$ M) the ini-⁵⁵⁹
 540 tially stable configuration becomes unstable after 5 – 6⁵⁶⁰
 541 minutes exhibiting convective vortices at symmetric dis-⁵⁶¹
 542 tances above and below the unperturbed interface (see⁵⁶²
 543 Figures 4(b) – (d), features that compare favorably with⁵⁶³
 544 the classification given in sec. IIIB for the same ini-⁵⁶⁴
 545 tial configuration (NCC scenario). We recover the typi-⁵⁶⁵
 546 cal nonlinear dynamics of DLC modes where convectives⁵⁶⁶
 547 vortices develop at symmetric distances around an un-⁵⁶⁷
 548 perturbed interface^{56,57}. We track the evolution of the⁵⁶⁸
 549 mixing zone, defined as the distance between the most⁵⁶⁹
 550 upwards and downwards tip of the fingers. Figure 5⁵⁷⁰
 551 demonstrates that the larger the initial jump in water⁵⁷¹
 552 concentration the slower the mixing of the microemul-⁵⁷²
 553 sions. This is expected as the cross-diffusion effects have⁵⁷³
 554 then to overcome a larger stabilizing density jump to pro-⁵⁷⁴

500 mote convection.

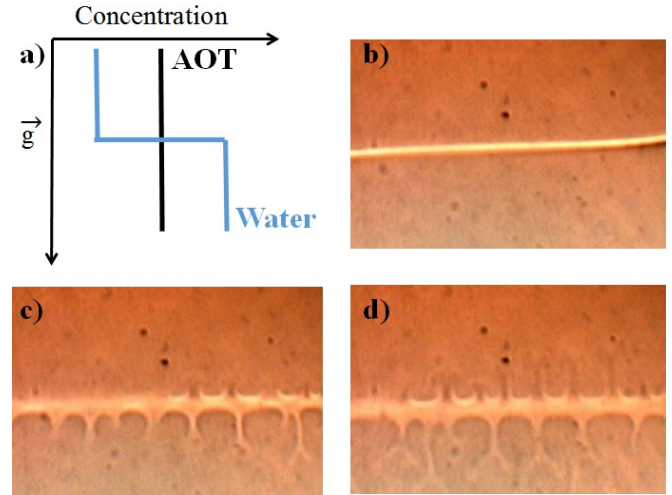


Figure 4. Experimental negative cross-diffusive instability. a) Sketch of the experimental initial conditions required to achieve negative cross-diffusion. b)-d) Three snapshots showing the evolution of the DLC mode obtained with $\Delta H_2O_{\text{bottom-top}} = 1.15$ M taken at $t = 0, 700$ and 1200 s. $ME_T \omega = 8.15, \phi_d = 0.16$; $ME_B \omega = 12.2, \phi_d = 0.185$. Frame sizes (b) – (d) = $11.45 \text{ mm} \times 8.9 \text{ mm}$

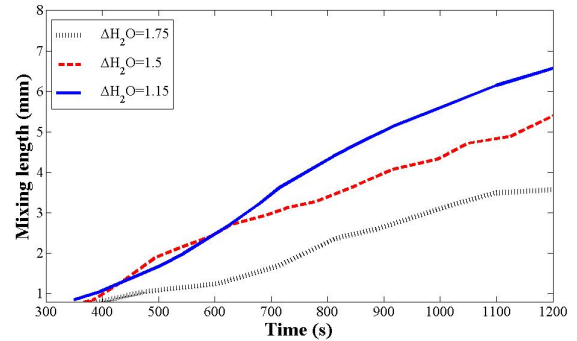


Figure 5. Temporal evolution of mixing length for different values of the initial water concentration jump.

In order to analyze the positive cross-diffusive (PCC) driven convective instability, we start with a jump on the AOT surfactant concentration between both microemulsions at a homogeneous amount of water, as sketched in Figure 6(a). By imposing a surfactant jump in the range $0.02\text{M} < AOT_{\text{bottom-top}} < 0.06$ M, the initial contact line deforms into equally separated fingers that grow vertically with time at the interface (Figures 6(b) – (d)). These structures are successfully predicted by the analysis of the density profile obtained from the cross-diffusion model in analogous conditions (PCC scenario) and can be better perceived by performing spatio-temporal plots along the horizontal and vertical axis (Figure 7). Horizontally, along the initial contact line between both microemulsions (dashed line in Figure 7(a)), we observe

575 how convective fingers (vertically oriented white stripes
 576 in Figure 7(c)) have a characteristic hydrodynamic wave-
 577 length. This feature, defined as the average distance
 578 between consecutive convective fingers, has been calcu-
 579 lated before being altered due to the appearance of lateral
 580 flows in the system. Analysis at different density jumps
 581 between both microemulsions show that the larger the
 582 initial jump in AOT concentration the smaller the wave-
 583 length as reported in Figure 7(d). The vertical space-
 584 time plot (Figure 7(b)) accounts for the induction pe-
 585 riod, defined as the interval of time that convective fin-
 586 gers require to develop. This characteristic time is short-
 587 ened as the initial jump in AOT concentration is reduced
 588 (Figure 7(e)). Furthermore, Figure 7(b) gives us infor-
 589 mation about the asymmetric growth rate of convective
 590 fingers ($90 \mu\text{m}/\text{min}$ for ascending fingers in contrast to
 591 $75 \mu\text{m}/\text{min}$ for the descending ones).

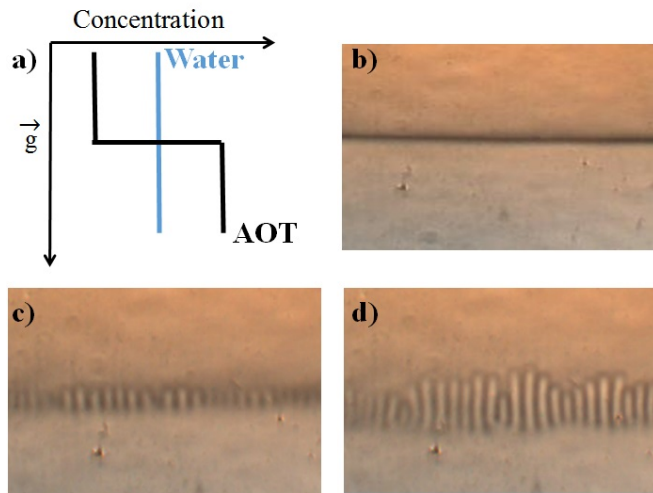


Figure 6. Experimental positive cross-diffusive instability. a) Sketch of the experimental initial concentration of a jump of AOT between both microemulsions while the water concentration is constant. (b) – (d) Three snapshots taken at $t = 0, 700$ and 1250 s displaying the evolution of double diffusive modes obtained with $\Delta\text{AOT}_{\text{bottom-top}} = 0.06$ M. ME_T $\omega = 11.95$, $\phi_d = 0.19$; ME_B $\omega = 9.8$, $\phi_d = 0.2$. Frame sizes (b) – (d) = $11.45 \text{ mm} \times 8.9 \text{ mm}$.

IV. CONCLUDING DISCUSSION

To conclude, through a combined experimental and theoretical study, we have demonstrated that ME are a simple and ideal model system where different convective instabilities driven by 2-component cross-diffusion can be induced. Thanks to the TDT method we have first characterized the AOT- H_2O diffusion matrix of the microemulsion solutions for the concentrations used in the HS cell convective experiments. These measurements show that the diffusion matrix consists of a positive D_{12} and a negative D_{21} cross-diffusion term and that there

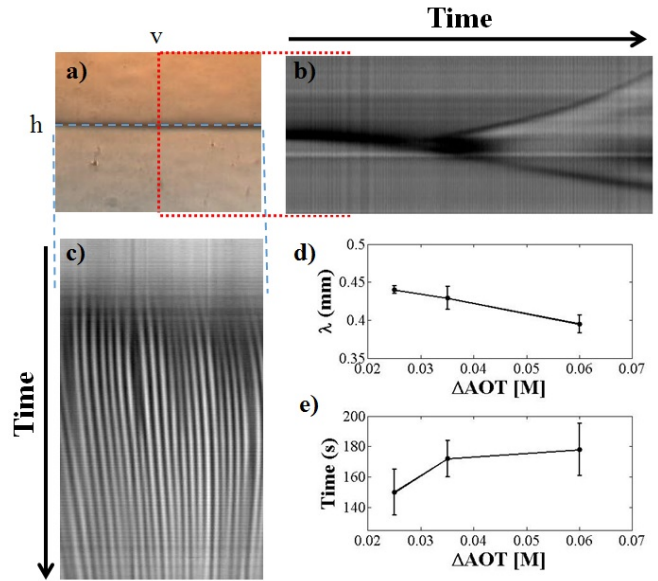


Figure 7. Analysis of positive cross-diffusive driven instability. (a) Initial frame ($1.45 \text{ mm} \times 8.9 \text{ mm}$) displaying the horizontal contact line between two microemulsions carried out at $\phi_d = 0.18$ and $\Delta\text{AOT}_{\text{bottom-top}} = 0.06$ M. (b) Spatio-temporal dynamics obtained along the vertical red dotted line v showing the deformation of the contact line along the gravitational axis. Frame size = $8.9 \text{ mm} \times 2000 \text{ s}$. (c) Spatio-temporal plot constructed along the horizontal line h demonstrating the emergence of fingers at different locations of the interface and their temporal evolution. Frame size = $11.45 \text{ mm} \times 2000 \text{ s}$. Variation of wavelength (d) and induction time (e) for different initial jumps in the AOT concentration between the bottom and top microemulsions. A solid line was drawn in (d) and (e) to help the reader following the data trend.

is a suitable concentration range where H_2O and AOT can be varied without changing dramatically the actual values of the diffusion coefficients. With this information and knowing the solutal expansion coefficients of the two species, we could theoretically predict two possible cross-diffusion driven convective scenarios, depending upon which species features the initial concentration jump in the starting statically stable stratification. When the initial concentration jump is imposed on the water concentration, DLC-type convective patterns grow driven by the negative cross-diffusivity D_{21} (NCC). On the contrary DD-type of instabilities can develop in time in presence of an initial concentration jump introduced in AOT when the cross-diffusion dynamics is controlled by the positive D_{12} (PCC). The positive and negative cross-diffusion-driven convective scenarios have been described on the basis of one-dimensional density profiles directly constructed using experimental data. By studying the spatial dependence of these density profiles we can also interpret some features obtained from the analysis of experimental data. For instance, in our simulations we find that the time needed to form the monotonically decreasing profile in

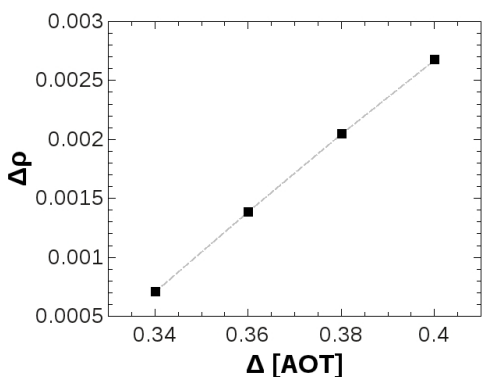


Figure 8. Dependence upon $\Delta[\text{AOT}]$ of the maximal density jump ($\Delta\rho$) between the top and the bottom layer in the monotonically decreasing profile developing in the PCC scenario.

the PCC (featuring a denser fluid over a less dense medium, like the blue profile in Fig.3.b (third panel) is independent of the initial concentration jump imposed to the AOT. By contrast, the related density jump, $\Delta\rho$, which measures the maximal density difference between the top and the bottom layer as $\max(\{\frac{\rho(L_z,t)-\rho(0,t)}{\rho(0,t)}\} \forall t)$, slightly increases with $\Delta[\text{AOT}]$ (see Fig.8). Considering the experimental error, these features are substantially recovered in the characterization of the experiments shown in Fig.7.d and Fig.7.e. Here, we cannot recognise any significant trend in the onset time of the instability (the average value is almost constant) while, the decreasing drifting of the pattern wavelength with $\Delta[\text{AOT}]$ can be ascribed to the increasing magnitude of $\Delta\rho$. The larger this initial density jump, the more intense the resulting convective dynamics and, in turn, the shorter the characteristic wavelengths to be expected. Our results can be generalised to any multi-component system showing either positive or negative cross-diffusion terms in the diffusion matrix \mathbf{D} . Similar results have been found for polymer-sugar systems⁴¹ and polymer-polyelectrolytes systems⁵⁸, both showing positive cross-diffusion terms due to an excluded volume mechanism. Microemulsions allowed us to investigate, for the first time, the effect of negative cross-diffusion on the development of hydrodynamic instabilities and we found that the sign of the cross-diffusion coefficients is important to select the type of instability. These results also show that microemulsions will be a suitable experimental model to investigate the coupling among reaction-driven and diffusion-driven hydrodynamic instabilities.

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