

## LIA RECYCLING 2014\_2018

### A-OBJECTIVES OF LIA “RECYCLING” CNRS/INC et MPIKG/MPG

#### Abstract in English:

This project between CNRS/INC and MPG/MPIKG has an original goal linking spectrometry and chemical reactivity in complex fluids induced by ultra-sound, and its application to control movement of ions in colloidal solutions and wet nanomaterials.

Special attention is given to fluids containing metals as ions, nano- or microparticles, with the general aim of applications related to separation and recycling and material life-time extension.

As a consequence, the central scientific objectives of the LEA “RECYCLING” for the three years period 2014-2016 will be focused on the following topics:

**1. Droplet coalescence under reactive conditions:** we aim to develop quantitative characterization and predictive modeling based on first principles during the contact of two sessile droplets containing surface active and reactive species, coupling of Marangoni effects, bulk flow reactivity producing mechanical turbulence.

**2. Metallic corrosion development during drying-wetting cycles** by aerosols containing sodium chloride: nanoscience approach to the thermodynamics and hydrodynamics on the three phase contact line between soluble ionic solid, undersaturated solution and partially oxidized metal.

**3. Develop atomic force microscopy** at an active oil-solvent interface, i.e. with respect to hydrometallurgy, i.e. when cations are selectively exchanged between an aqueous and organic solvent containing oil-soluble ion specific species.

**4. Make use of the ion specific ultra-sound adsorption** to excite oil/water interfaces and trigger transfer of ionic or colloidal species. The experiment will involve non linear optical characterisation of reflection at liquid-liquid interface and ellipsometry. The theory will involve evaluation of the potential wave associated to the macroscopic interface, as well for ions as for nanoparticles crossing the interface. This shall serve an optimized molecular, supra-molecular or colloidal exchange across the water-oil interface.

More generally, our aim is to **make use of the ion specific ultra-sound adsorption** to excite oil/water interfaces and trigger transfer of species.. This shall serve an enhanced molecular, supra-molecular or colloidal exchange across the water-oil interface. We have shown in the previous cooperation that ultrasound can be used to enhance the phase transfer between oil and water phase and thus also to dissolve ions<sup>1</sup>. This work shall be extended in cooperation between the LEA and Univ. Montpellier. There we will make use of the ion specific absorption of ultrasound that leads to streaming. In first experiments we use an already

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<sup>1</sup> Key initial reference originating from first LEA « SONO3 2008-2010 : G. Toquer, T. Zemb, D.G. Shchukin, H. Möhwald: “Ionic Physisorption of Bubbles induced by pulsed Ultrasound” PCCP 12 ( 2010) 14553 )

existing set-up to study the smearing of interfaces by ultrasound by ellipsometry. Later we intend also to study the interfaces by X-Ray reflectivity and second harmonic generation. The key issues here will be to study how much phase transfer can be enhanced. In a microfluidic system ultrasonic absorption may also lead to a deflection of a liquid beam which may be used for separation after a threshold concentration has been exceeded.

**5. Study the specific ion effects on interaction between cellulose-based fibers and hydrosoluble polymers mediated by surrounding ions.** This includes direct measurement of osmotic pressure due to concentration gradients of metal ion with respect to the surrounding liquid. This study covers in a unified approach free energy of chemical, colloidal and mechanical energy, with a wide domain of application as knowledge-based treatments of wood against (or in favor) of swelling/deswelling under osmotic stress.

The so-called “wood material” is a complex, highly anisotropic and hierarchically organized nanocomposite. It is characterized by hydrated stiff crystalline cellulose nanofibres parallel to each others (embedded in a matrix of a much softer, less anisotropic, gel of hemicelluloses, lignin and water. This matrix is hygroscopic and swells with increasing relative humidity providing a source of internal stress while the cellulose fibrils, winding with a spiral angle, i.e. the microfibril angle, MFA) around the central lumen, passively reorient following the stress applied to them. Depending on the MFA, wood fibres exhibit a wide range behaviour and mechanical properties, being able to act as stiff material to bear load, or shrink or expand in the longitudinal direction upon swelling, generating in this way either large tensile or compressive stresses or large strains.<sup>1</sup>

We are currently establishing a first equation of state (i.e, parameter-free prediction of water uptake versus relative humidity) of the un-treated wood composite. At the molecular level, the hydration force of the crystalline cellulose separated by the gel and the hydration force of the hemicelluloses are combined with van der Waals and structural long range forces. The results of the model, compared with experimental sorption data and with small angle X-rays scattering data, seem to capture the main features of the wood swelling by water.<sup>2</sup>

*The proposed Laboratoire européen associé – LEA, “RECYCLING” proposed contains five actions related to high technology for efficient usage of resources, i.e. recycling, a priority in French-German cooperation via Horizon-2020. The action proposed prolongates and amplifies a six year project that has been implemented as a six years project at the Max Planck Institute of Colloids and Interfaces and a four-plus-two-years project founded by INC/CNRS in France, based on research performed in Potsdam and Marcoule. The present proposal refers to the period 01 January 2014 to 31 December 2016.*

#### *Résumé en allemand*

Das originäre Ziel dieses Kooperationsprojektes zwischen CNRS/INC und MPG/ MPIKG ist die Verknüpfung von Spektroskopie und chemischer Reaktivität in durch Ultraschall angeregten komplexen Flüssigkeiten und die Anwendung um den Transport von Ionen in kolloidalen Lösungen und flüssigen Nanomaterialien zu kontrollieren.

Besondere Betonung soll dabei gelegt werden auf Flüssigkeiten, die Metalle als Ionen, Nano- und Mikropartikel enthalten mit dem generellen Ziel von Anwendungen in Bezug auf Trennung, Wiedergewinnung und Verlängerung der Materiallebensdauer.

Als Konsequenz werden sich die zentralen Ziele des LEA "RECYCLING" für die 3-Jahresperiode 2014-2016 konzentrieren auf die folgenden Themen:

1.) Tropfenkoaleszenz unter reaktiven Bedingungen: Wir verfolgen die quantitative Charakterisierung und die prediktive Modellierung basierend auf „first principles“ der Prozesse beim Kontakt zweier mischbarer Flüssigkeiten. Sie enthalten oberflächenaktive und reaktive Spezies, werden durch Marangoni-Flüsse gekoppelt und der resultierende Volumenfluß erzeugt auch mechanische Turbulenz.

2.) Entwicklung von Metallkorrosion während Trocknungs- und Benetzungszyklen durch NaCl enthaltende Aerosole: Eine nanowissenschaftliche Annäherung an die Thermodynamik und die Hydrodynamik der Drei-Phasenkontaktklinie von löslichem ionischem Festkörper, ungesättigter Lösung und teilweise oxidiertem Metall.

3.) Entwicklung der Rasterkraftmikroskopie an der Grenzfläche Wasser/ aktivem Öl. Dies ist relevant für Hydrometallurgie, wenn Kationen selektiv ausgetauscht werden zwischen wässriger Lösung und organischer Lösung, die eine spezifisch bindende Spezies enthält.

4.) Nutzung der ionenspezifischen Ultraschallabsorption, um die Wasser/Öl-Grenzfläche anzuregen und den Phasentransfer zu initiieren. Dieses soll einem beschleunigten molekularen, supramolekularen und kolloidalen Austausch über die Wasser/ Öl-Grenzfläche dienen.

5.) Studium ionenspezifischer Effekte der Wechselwirkung zwischen zellulosebasierten Fibrillen und wasserlöslichen Polymeren, vermittelt durch die Ionenumgebung. Dies schließt die direkte Messung des osmotischen Drucks infolge von Konzentrationsgradienten des Metallions in Bezug auf die umgebende Flüssigkeit ein. Die Studie schließt in einer allgemeinen Annäherung die Beiträge chemischer, Kolloidaler und mechanischer Energie zur freien Energie ein. Sie schließt viele Anwendungen ein wie die zielgerichtete Behandlung von Holz entgegen( oder mit Hilfe) der Quellung / Schrumpfung unter osmotischem Druck.

Das vorgeschlagene LEA „RECYCLING“ enthält 5 Themen in Bezug auf Hochtechnologie zur effizienten Nutzung von Ressourcen, i.e. Wiedergewinnung, eine Priorität in der deutsch-französischen Kooperation Horizonte Forschung -2020. Diese Aktion basiert auf und nutzt ein früheres 6-jahres-Projekt zwischen dem Max-Planck-Institut für Kolloid- und Grenzflächenforschung und CNRS/INC mit Forschung in Marcoule und Potsdam.

Der gegenwärtige Vorschlag bezieht sich auf den Zeitraum 1.1.2014.31.12.2016.

## OBJECTIFS SCIENTIFIQUES DU LIA « RECYCLING » proposé pour 2014-2018

Ce projet trisannuel 2014-2017 de laboratoire européen associé entre CNRS/INC et MPG/MPIKG se propose de mettre en œuvre des synergies sur des études originales d'analyse comprenant la pression osmotique et la réactivité chimique dans des fluides complexes, en étudiant les transformations physiques et chimiques induites par les ultra-sons, avec son application au contrôle des mouvements et du transfert d'espèces ioniques ou colloïdales dans des nanomatériaux contenant de fortes proportions d'eau. Les cinq thématiques proposées sont liées aux objectifs de développement franco-allemand (Horizon 2020) en technologies avancées pour le recyclage et la préservation des ressources.

Une attention particulière portera sur les fluides contenant des métaux sous forme d'ions, d'agrégats chargés, de nanoparticules ou de microparticules.

En conséquence, les cinq objectifs centraux proposés pour le LEA « RECYCLE » pour la période 2013-2016 sont :

**1. Etude de la coalescence de gouttes sessiles en conditions réactives** le but initial est de développer des méthodes quantitatives de caractérisation en même temps que la modélisation prédictive du comportement attendu lorsque deux gouttes sessiles contenant des espèces à la fois chimiquement réactives et physiquement actives de surface. Il s'agit ici de coupler les effets de type Marangoni, la réactivité dans les flux induits et les flux induits par l'hydrodynamique, notamment la turbulence. L'objectif est de développer des méthodes de synthèse de matériaux dans le recyclage après les étapes de dissolution et séparation de métaux.

**2. Etudier de la corrosion de métaux induite par des cycles de séchage-remouillage** par des aérosols contenant des sels corrosifs comme le chlorure de sodium. On utilisera une approche de type « nanoscience » liant thermodynamique à l'hydrodynamique et l'électrochimie sur la ligne de contact tri-phasique : eau saturée en sel-métal partiellement corrodé – air qui constitue une demi-pile de corrosion avec des gradients de concentration et des distributions de tensions de surface associée aux points de corrosion en formation.

**3. Développer la microscopie à force atomique près d'une interface liquide-liquide active.** On entend par interface active une interface liquide-liquide traversée par un flux constant d'espèces chargées sous l'action d'un fort gradient de potentiel chimique dans l'interface, comme dans l'application industrielle de l'extraction liquide-liquide. La compréhension des fluctuations associées au transfert est cruciale pour le développement de l'hydrométallurgie, actuellement la méthode la plus employée industriellement dans le recyclage des métaux. On met en œuvre pour cela des formulations entraînant la sélectivité de l'échange entre phase aqueuse et phase solvant, lorsque des cations sont échangés sélectivement entre phases : ces flux d'ions facilités par des « extractants » induisent des flux de fluides qui eux-mêmes induisent des fluctuations d'interface

**4. Utiliser l'adsorption aux fréquences ultrasonores** pour exciter l'interface solvant-eau afin de faciliter les transferts d'espèces colloïdales ou de sels entre phases. La partie

expérimentale consistera à suivre la forme de gouttes de solvant dans l'eau (ou l'inverse) en temps réel en présence et en absence d'excitations ultrasonores. On vise à évaluer expérimentalement l'augmentation des flux d'ions, d'agrégats supramoléculaires ou de nanoparticules à travers l'interface eau-solvant, qui est structurée à l'échelle nanométrique.

**5. Etudier les effets spécifiques d'ions sur l'interaction entre fibres à base de cellulose ou des ses dérivés :** la microstructure du bois comprend un arrangement de cristaux de cellulose, réticulés par un fluide ternaire comprenant hydroxyéthylcellulose, lignine et eau en équilibre mécanique à l'échelle colloïdale. L'effet des ions multivalents sur la dissolution du bois ainsi que les effets spécifiques d'ions entraînant l'hydrophobie du bois et donc sa résistance à la dégradation via des attaques enzymatiques seront suivis par établissement de l'équation d'état reliant le gonflement au potentiel chimique de l'eau adsorbée. On mesurera expérimentalement le gonflement ou dégonflement consécutifs à la présence de gradients de potentiel chimique du à la présence de sels en conditions ordinaires ou dans l'eau sous-critique associée aux traitements industriels hydrothermaux du bois.

Cette étude comprend une approche globale de l'énergie libre du système bi-phasique bois-solution, en incluant les termes mécaniques, chimiques et colloïdaux, qui sont à l'échelle de la mécanique, de la liaison chimique et mais aussi à l'échelle mésoscopique. Les retombées espérées sont dans le large domaine d'application qui comprend les traitements du bois pour favoriser ou empêcher sa dissolution et dégradation, et sont donc liés au recyclage du bois et à l'utilisation/recyclage des tiges de végétaux.

Le bois est un matériau nanocomposite complexe, fortement anisotrope et hiérarchiquement organisé. La microstructure à l'échelle nanométrique est caractérisée par des nanofibres rigides de cellulose cristalline parallèles les unes aux autres et noyées dans une matrice d'une beaucoup plus molle, moins anisotrope. Cette matrice est un gel d'hémicelluloses et lignine, avec une absorption contrôlée par l'entropie et les liaisons hydrogène entre cellulose, lignine et surface de micro-cristaux de cellulose.

Cette matrice est hygroscopique et se gonfle avec les changements de l'humidité relative, fournissant une source de stress interne, tandis que les fibrilles de cellulose s'enroulent en spirale autour de la lumière centrale à un angle précis (l'angle des micro-fibrilles, AMF). Ces micro-fibrilles se réorganisent passivement selon la contrainte osmotique appliquée. Selon l'AMF, les fibres de bois montrent se positionnent en éventail/ les propriétés mécaniques varient. Ceci entraîne une grande variation des propriétés mécaniques le matériau rigide se rétrécit ou s'allonge dans le sens de la longueur lors du gonflement, en générant de cette façon une grande déformation anisotrope.

L'équation d'état comprenant entropie et termes chimiques, termes colloïdaux comme la force d'hydratation ainsi que les termes mécanique macroscopiques a été établie pour la première fois en couplant expérience et modélisation à l'échelle colloïdale par une collaboration Max Planck de Postdam et ICSM. Cela permet de prédire sans paramètre l'absorption d'eau en fonction de l'humidité relative du composite de bois non traité .

Le but de la thèse 2013\_2016 en co-tutelle entre UM2 et Université de Postdam est d'étendre cette équation d'état au bois traité par absorption d'électrolytes en conditions hydrothermales. La partie expérimentale sera effectuée sur les montages spécialisés et de la micro-diffraction tomographique. La partie théorique sera effectuée dans le cadre de l'équation intégrée fondamentale liant chimie, colloïdes et mécanique. Les résultats du modèle, seront comparés avec les données expérimentales de sorption d'électrolytes formulés en fonction de la balance chaotrope/cosmotrope de l'échelle de Hofmeister.

Le LEA proposé franco-allemand CNRS/MPI proposé ici contient ainsi cinq thématiques scientifiques dans le domaine des hautes technologies pour l'utilisation optimale des ressources, via le recyclage par des procédés avancés, une priorité dans les actions européennes dans le cadre d'Horizon 2020. Cette action suit dans le temps et s'appuie sur des études commencées et des chercheurs contractuels en place grâce au LEA «SONO» 2008-2013 impliquant des échanges de chercheurs, des recherches coordonnées et de l'appareillage partagé entre Marcoule (INC/CNRS) et Potsdam (MPG/MPIKG). Le projet actuel est présenté pour la période du 01/01/2014 au 31/12/2016.

Fait le 09 décembre 2013 à Potsdam

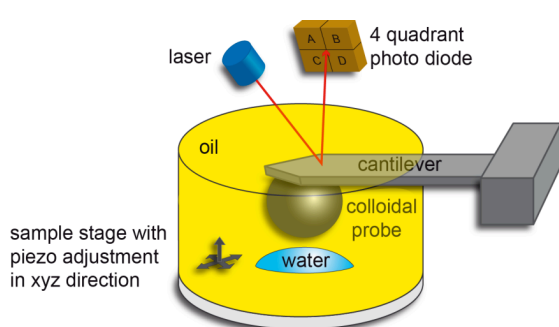
Pr Dr *Helmuth Möhwald* et Pr Dr *Thomas Zemb*



## B- 2014 DETAILED ACTIVITY REPORT

### I- Atomic Force Microscopy at the Oil-Water Interface (Exploratory work Anne Heilig)

In liquid-liquid extraction, metal ions are transported from an aqueous phase into an oil phase by assistance of surfactant and extractant molecules. This process is currently applied on large scale in industrial application such as the treatment of waste from consumed nuclear fuel, PUREX process. Although the process is thus widely used, the knowledge on the fundamentals of the transfer of metal ion from aqueous to organic phase is limited. Currently, there are efforts to promote understanding of these processes by investigating the colloidal properties of the system and identify individual interaction or contribution of molecules within this process.

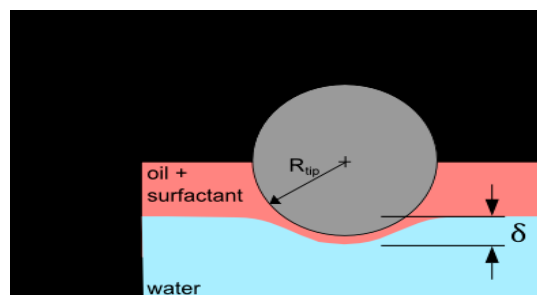


**Figure 1:** A schematic representation of the AFM setup for the investigation of the liquid-liquid interface is given. Atomic force microscopy (AFM) with a colloidal probe is used to probe the interface and thus the interfacial tension and the osmotic pressure in vicinity to the interface.

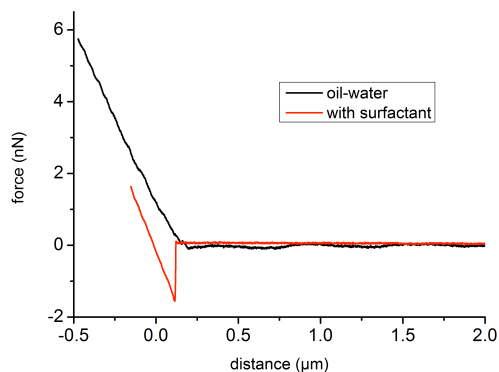
Our initial studies were mainly concerned in establishing an appropriate combination of equipment and materials that are suitable to fulfill the requirements implied by an investigation of the liquid-liquid interface. To investigate kinetic phenomena as

well as the surface tension by AFM, it is necessary to utilize an AFM with a closed loop scanner allowing for a reduced scanner creep of less than 1 nm per minute. Due to small forces under investigation, it is also necessary to exclude electrostatic effects originating from a charge build up in the liquid cell, which is commonly made of an inert polymer such as Teflon<sup>®</sup>. The next step was the establishment of the suitable colloidal bead to measure forces. It finally was possible to obtain the right functionalization and size.

**Figure 2:** Schematics of the arrangement used to measure forces between a bead and water through a liquid film of varying thickness.



With this experience, we are now in a position to measure surface tension of the oil-water interface. A characteristic measurement is presented in figure 3. One realizes that upon approach of bead and water there is only weak attractive interaction, before repulsion sets in, the presence of surfactant causes a strong attraction.



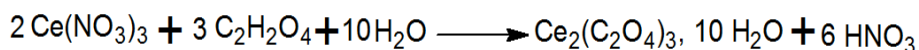
These measurements still have to be optimized, also the distances need to be calibrated, but the feasibilities have been demonstrated. In the near future, the influence of surfactants, extractants and their mixture should be studied. The data will be used to establish the required post data treatment finally used to begin with the study of metal-ion extraction kinetics by mimicking the PUREX process in the liquid cell of AFM.

**Figure 3:** A typical force distance curve as obtained on an oil-water interface without and with extractant contained in the oil phase.

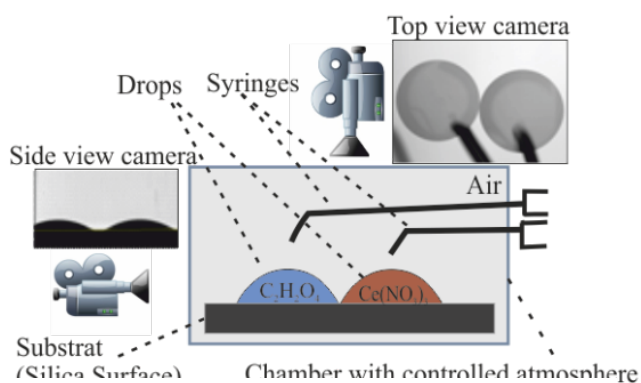
## II Coalescence of droplets in reactive conditions ( PhD Marie Jehannin):

Surprisingly, two droplets of completely miscible liquids can remain separated for some seconds up to minutes after their contact. This non-coalescence behavior can be explained by a surface tension gradient between the liquids of the two drops. The gradient creates a Marangoni flow which competes with the capillary forces and may delay the coalescence of the droplets. Yet, coalescence and non-coalescence of inert sessile droplets is well understood. However, when reactants are dissolved in both droplets, the system gets more complicated. Indeed, the reaction modifies locally the chemical concentrations, thus influencing the surface tension gradient and the Marangoni flow. This research study on coalescence of reacting droplets is led in a coupled way, both at CEA Marcoule (DEN/DTCD), for which this topic is a key issue for a recently patented process, and at MPIKG (Max Planck Institute of Colloids and Interfaces), which studied coalescence of sessile inert drops. The interplay between a precipitation reaction and the immediate coalescence of sessile drops is investigated. We have found that the combination of a Marangoni flow with a fast reactive process could lead to a periodic pattern of alternating black and colorless stripes. The study was therefore focused on the characterization of these stripes: what are they made of? When do they appear? What are the responsible phenomena?

Two drops, one containing cerium nitrate and the second one containing oxalic acid, are deposited on a silica surface at some distance from each other. Cerium nitrate and oxalic acid react together according to the following equation:



Mixtures of 50% water, x% 1,2-propanediol, (50-x)% 1,3-propanediol are used as solvent in order to tune the surface tension difference between the liquids of the two droplets, without modifying the reactants concentrations, the viscosity and the density. Both liquids wet the surface; the droplets spread, get into contact and coalesce. The whole process is recorded simultaneously from the top and from the side (Figure 1). The humidity in the chamber is adjusted to avoid both evaporation and condensation.

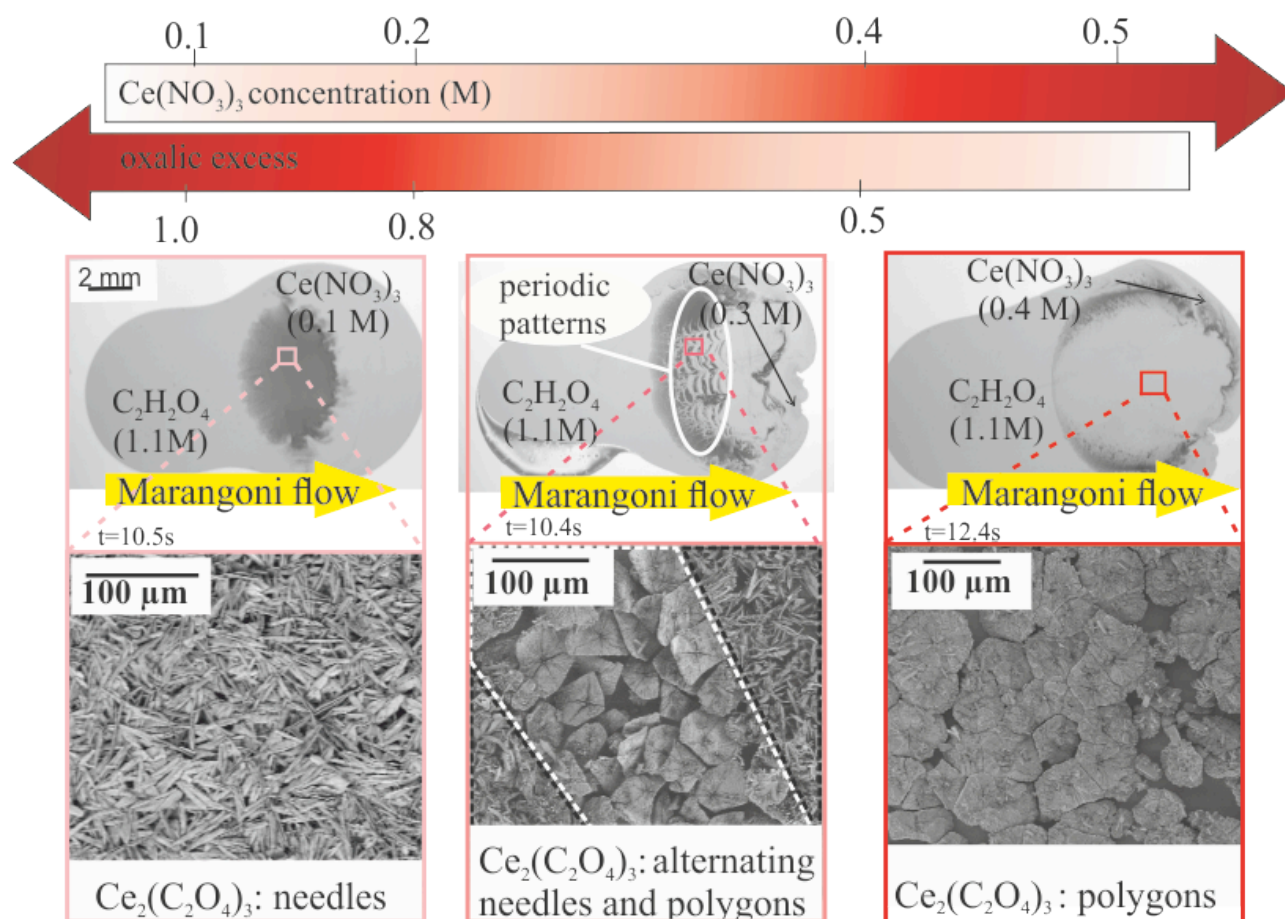


**Figure 1 : Set-up used for the study of droplet coalescence. The two drops are deposited on a silica surface using syringes. The side and the top views are recorded simultaneously.**

In the range of concentrations used, cerium nitrate and oxalic acid are soluble in the solvent, whereas the reaction product, namely cerium oxalate, is insoluble in aqueous solution. For constant surface tension gradient and oxalic acid concentration, we investigated the effects of the oxalic excess by modifying the cerium nitrate concentration. Three behaviors were observed (Figure 2). At low oxalic excess, diffracting light precipitates are obtained above the high surface tension drop. At high oxalic excess, a transparent domain of precipitates is observed above the high surface tension drop. At intermediate cerium nitrate concentration, fringes are created. These fringes are alternating of transparent and diffracting light domains.

In order to characterize the precipitates obtained, the samples were dried, at atmospheric humidity and temperature, immediately after droplet coalescence. Then, they were investigated using scanning electron microscopy (SEM) and X-Ray diffraction (XRD). As indicated by microscopy analyses, the transparent domains correspond to polygons like precipitates whereas diffracting light domains are made of needles precipitates. Fringes result from a well-defined block alternation of both morphologies.

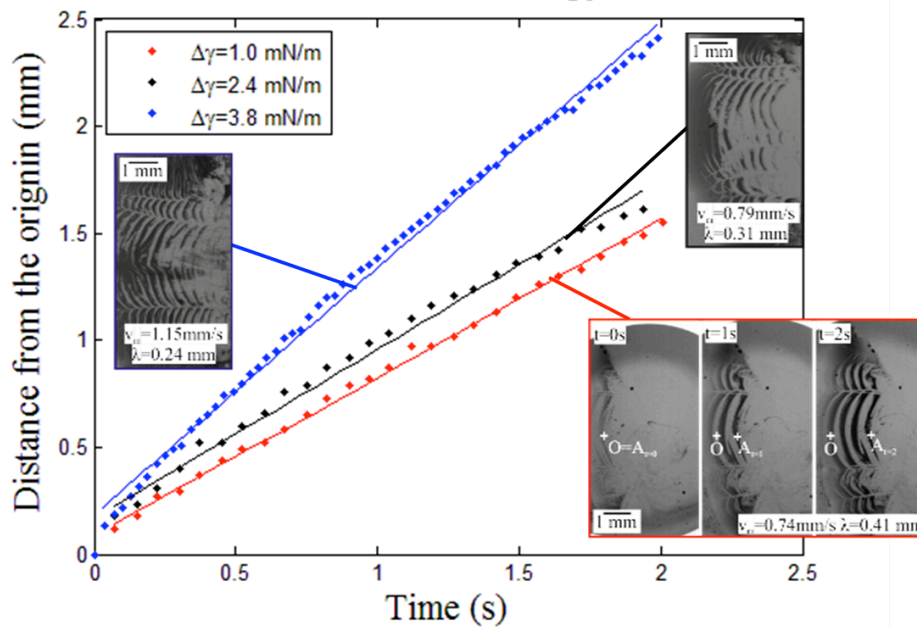




**Figure 2 :** Top: Coalescence of sessile drops for different initial concentration of cerium nitrate at a constant surface tension difference ( $\Delta\gamma=3\text{mN/m}$ ). The Marangoni flow is directed from the oxalic acid drop over the cerium nitrate one. Three behaviors are observed. Bottom: SEM images of the corresponding resulting cerium oxalate morphologies, namely: needles (left), polygons (right) and, for intermediate oxalic excess, alternation of both morphologies (middle).

Whatever the shape of the particles, the X-Ray diffraction results correspond to a crystalline solid. No significant difference is observed in the diffractograms of precipitates resulting from the three precipitation behaviors, which indicates that there is no huge difference in their crystallographic structures. In all cases, the structure corresponding to the one resolved in 1956 by Ollendorf for the cerium oxalate ten times hydrated is observed.

Marangoni flow is known to occur in the surface layer of the high surface tension drop. The exact thickness of this layer is not known yet. We attempted to address this point by studying the location of the precipitation process. Assuming the reaction height represents the width of the Marangoni layer, we probe, using confocal microscopy, on in-situ coalesced droplets (without drying), the height (i.e. vertical position) of the first detected crystal. Unfortunately, in most cases, this height was dependent on the horizontal position, thus preventing us from accurately measuring the Marangoni layer's width. However, confocal microscopy was helpful to characterize the growth kinetic of the different precipitates. Growth rates (typically minutes) are slow as compared to the coalescence and nucleation processes (typically seconds). The first images recorded on the confocal set-up exhibit mostly nanoparticles and show evidence of neither polygons nor needles (as in SEM observations shown on Figure 1, bottom). Therefore it is likely that during the first seconds of coalescence, the transparent and diffracting light areas recorded by the top view camera (illustrated by Figure 1, top), are due to nanoparticles having different light diffraction properties and not to grown crystals. However, after coalescence is achieved, these nanoparticles will grow and/or aggregate in the quiescent daughter droplet, and during the drying process, to give preferably either polygons or needles. Further study of the nucleation of these nanoparticles, and their relation with the specific environment achieved during the coalescence of reactive droplets, although very interesting, is out of the scope of this thesis.



**Figure 3** : Distance from the origin evolution in time during fringes formation at different surface tension gradient  $\Delta\gamma$ . The oxalic excess (0,6M) and the average contact angle ( $\theta_a=9+0.5^\circ$ ) are identical for all experiments. The Marangoni flow speed,  $v_M$ , increases with the surface tension gradient whereas the wavelength of the periodic pattern,  $\lambda$ , decreases.

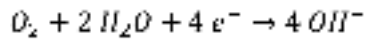
Now that we elucidated the nature of the fringes, we aim to identify the phenomena responsible for their formation. It is likely that this oscillatory behavior is due to a competition or a feedback between at least two mechanisms, which could be the convection and/or the diffusion (i.e. transport mechanisms) and/or the chemical reaction. In order to address this issue, the first step is to identify the potential control parameters among the average contact angle of the droplet  $\theta_a$ , the surface tension difference of the liquids  $\Delta\gamma$ , the initial concentration of cerium nitrate and oxalic acid, the proportion of 1,2-propanediol and 1,3-propanediols. The dependence of the Marangoni flow velocity and of the average wavelength of the periodic unit with respect to these potential control parameters is currently investigated thanks to image processing analysis. Preliminary results indicate that, for a given contact angle, the higher the surface tension difference, the higher the Marangoni flow speed, and the lower the wavelength (Figure 3). Moreover, the periodic patterns can be observed in both flow directions that is to say when the oxalic acid drop goes over the cerium nitrate or when the cerium nitrate drop goes over the oxalic acid one. The knowledge of the parameters mainly influencing the fringes characteristics is the first step of the development of a numerical model, which would enable sensitivity analysis.

To conclude, the coalescence of droplets is investigated in reacting conditions. In our case study, sessile drops containing cerium nitrate and oxalic acid, the coalescence can lead to three precipitation behaviors depending on the initial oxalic excess. Surprisingly, at intermediate oxalic excess periodic patterns are created. Whatever the behavior, the produced solid particles (after drying) are observed to have identical crystallographic structures but different morphologies, namely polygons or needles morphologies. The periodic patterns correspond to alternating polygons and needles morphologies. Currently, we aim to understand the periodic patterns formation by identifying the parameters controlling the fringes properties. This will enable the development a theoretical model for the coalescence of reactive droplets.

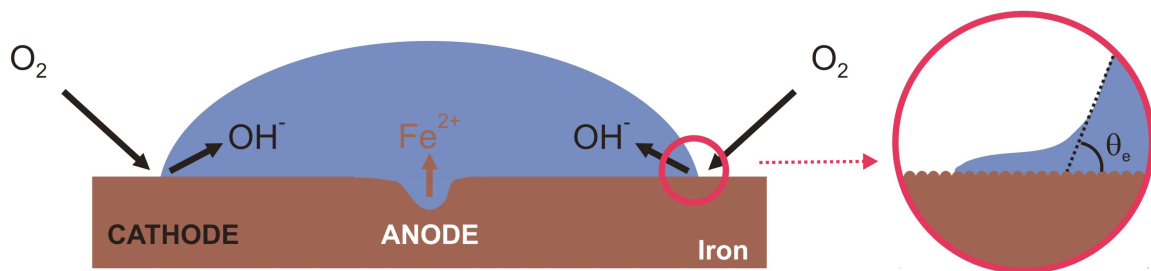
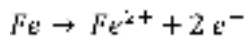
### **III- Pitting Corrosion of Iron under a Sessile Droplet from Aqueous Saline Solutions**

A sessile droplet from an aqueous saline solution is deposited on a planar iron surface. It is in (dynamic) equilibrium with its environment i.e., there is any evaporation/condensation from the solution droplet and the iron surface in contact with the vapour phase of a given (fixed humidity). The contact of a macroscopic and stationary aqueous electrolyte droplet with a metal surface creates a

localized electrochemical cell known as “Evans droplet”. In the classic Evans droplet model the oxygen reduction ( $O_2$ ), which results in the production of hydroxyl ions ( $OH^-$ ) occurs mainly at the droplet edge at the substrate/solution interface because the diffusion path length of oxygen from the environmental vapour phase to the substrate/solution interface is shortest at the contact line region. Thus a cathode is formed at the periphery (perimeter) of the droplet as depicted in Figure 1.



The corresponding anode is established at the substrate/solution interface where oxygen is deficient (i.e., away from the contact line). There  $Fe^{2+}$  ions generated from the metal are released into the droplet solution. This reaction forms pits in the iron surface somewhere close(r) to the droplet center (Figure 1) via:



**Figure 4:** The classic Evans droplet model under an electrolyte droplet: the oxygen is reduced at the droplet edge, acting as the cathode whereas the iron dissolution occurs in the droplet center acting as the anode. The inset shows the existence of a microscopically thin film ahead the macroscopic contact line.

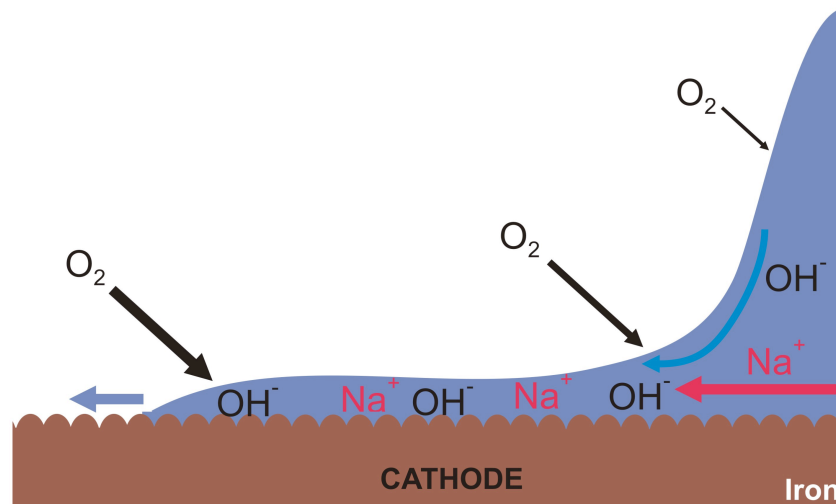
We found that the cathodic site is established along a microscopically thin film ahead of the macroscopic contact line as shown in the inset of the Figure 1. This peripheral thin film of liquid is the result of the local cathodic oxygen reduction in the course of the corrosion process. Most likely it is emanating from the three-phase contact line region. But it is rather thick (it can be seen by eye) for a “classical” molecularly thin precursor film and it is not simply the result of adsorption of water layers on the metal surface.

The ring of peripheral thin film is expanding with time. Its width increases “diffusively”, i.e. in proportion to the square root of time. On the other hand at a given time its width is inversely proportional to the surface tension of the aqueous saline solution.

A SEM analysis of the dried system showed that most of chlorides are found in the footprint area of the main droplet without the peripheral film, which also contained the iron oxide. The cations (sodium or magnesium, lithium and potassium) on the other hand are concentrated around the droplet, at the peripheral film (cathode) area. Most likely this selective ion distribution is the result of the cathodic reaction preferentially at the peripheral part (film) of the droplet and the anodic reaction preferentially at the interface of the main drop body with the iron substrate.

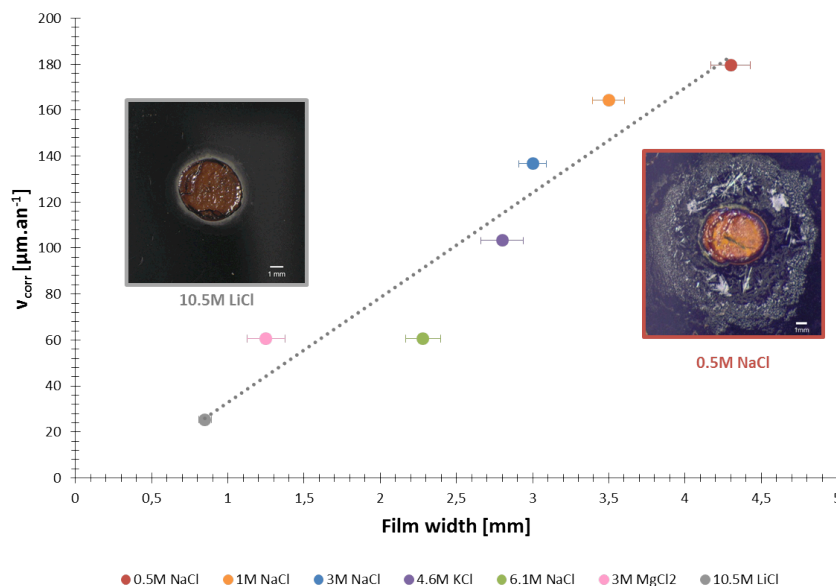
At the peripheral part of the droplet (either the droplet edge or/and the peripheral film), hydroxide ions are generated by oxygen reduction. This creates a highly localized alkaline environment in this region. As a consequence the cations migrate towards the droplet edge/thin film to maintain electroneutrality. The formation of a concentrated cation-hydroxyl solution in this area may induce a water movement (maybe Marangoni flow?) from the droplet bulk (surface) towards its edge. Since oxygen reduction

preferentially occurs at the peripheral part of the droplet, the expansion of the thin film is controlled by the cations displacement and water movement through it as illustrated in Figure 2.



**Figure 5:** Expansion of the alkaline thin film by sodium ions displacement compensating the electroneutrality heterogeneity within the droplet and by water movement induced by concentration gradient for a sessile droplet of aqueous NaCl solution deposited on an iron surface.

In the course of the formation of a peripheral film it is found that the corrosion rate (i.e., weight loss of the iron substrate per unit droplet area per unit time) is proportional to the film width (Figure 3). It is also inversely proportional to the surface tension of the aqueous electrolyte solution (Figure 4). The latter very much suggests some peripheral/radial flow/transport which is influenced by (peripheral) surface tension gradients.



**Figure 3:** The corrosion rate induced by a sessile droplet from aqueous electrolyte solution deposited on an iron substrate depends to the width of the peripheral film. The measured film width is obtained after 1 day of experiment. Microscopy images of the dried system after 1day experiment from aqueous sessile droplet of 10.5M LiCl and 0.5M NaCl.

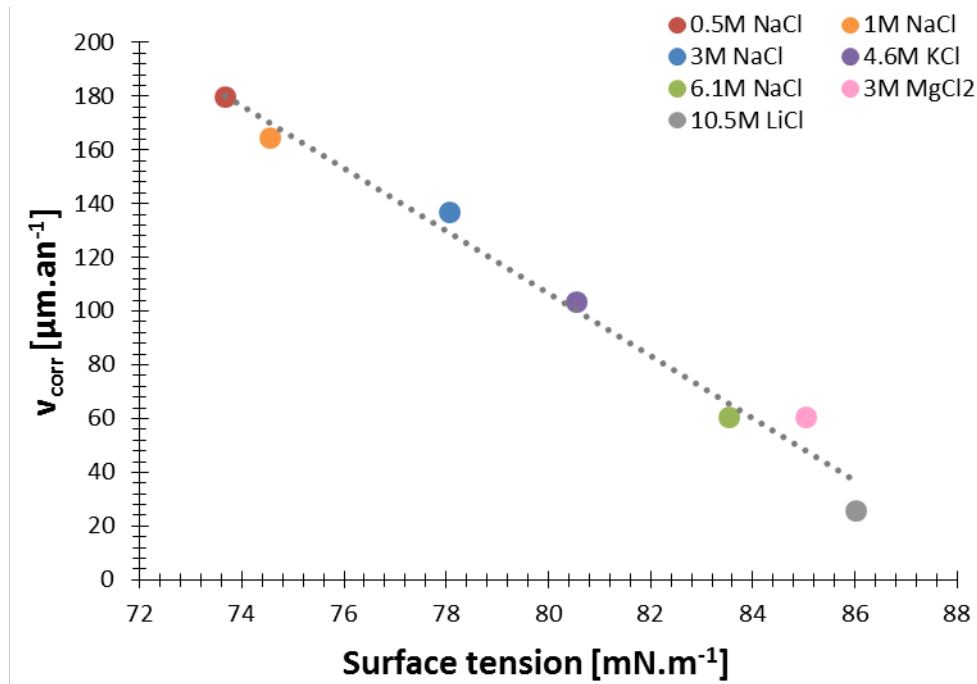


Figure 4: Corrosion rate versus surface tension of the aqueous electrolyte solution contained in the sessile droplet deposited on an iron substrate.

Without the peripheral film, for a given NaCl concentration, the corrosion rate is independent of the droplet radius. It is also independent of the chloride concentration within the aqueous saline solution.

This study provides phenomenological results on corrosion reaction of metals under a sessile droplet from aqueous saline solution. Our experiments reveal an extension of the classic Evans droplet scenario: the cathodic site is established along a peripheral film whose its width mainly induced by peripheral surface tension gradients controls the corrosion process.

#### IV - Salt-Induced Marangoni Flow in Evaporating Sessile Droplets (phD Virginie Soulié (DEN/DCP and ICSM))

The evaporation behavior of a sessile drop is rather complicated because of the subtle issues arising from its description such as the non-uniform evaporative flux. The evaporation at the contact line region is enhanced, which induces a capillary flow towards the edge (leading to the "coffee-ring" effect [1]). For complex fluids the evaporation behavior becomes even more complex, because the non-uniform evaporative flux will lead to an inhomogeneous distribution of the fluid constituents within the drop. This can induce a surface tension gradient, which in turn may lead to a Marangoni flow [2] in addition to the capillary flow.

We study the evaporation of sessile drops from aqueous sodium chloride solutions on solid planar surfaces. The diverging evaporative flux locally enriches NaCl at the droplet edge (Figure 1.a). Since chaotrope salts are depleted from the air-water interface, the surface tension locally increases in the edge region. This can lead to a Marangoni flow in the same direction as the capillary flow, i.e. towards the contact line. Diffusive dilution resulting from the salt concentration gradient will reduce the evaporation-induced gradient (Figure 1.b).

We investigate how the flows within the drop and, in particular the Marangoni flow along its surface, are related and affected by: (i) the initial NaCl concentration, (ii) the contact angle, (iii) the drop size and (iv) the evaporation rate. To this end the shape and the contact angle of the drop are analyzed by simultaneous optical imaging from the top and the side [3] and the liquid flow is studied by particle tracking velocimetry (PTV) with polystyrene particles.

We find that the flow behavior is strongly affected by the initial NaCl concentration. At low initial NaCl concentrations, PTV experiments reveal only a flow towards the contact line. This may arise from the capillary flow compensating for the local evaporative losses, possibly increased by a Marangoni flow component. Thus, capillary and Marangoni flows both favor the formation of a coffee-stain deposit (Figure 1.b). However, above  $10^{-3}$ M NaCl, the surface tension gradient respectively Marangoni flow leads to a such strong flow towards the drop edge that the capillary pressure in this region increases. Therefore, the compensating capillary flow is now directed inward and we observe a convection roll near the drop edge. This circulating flow can lead to a more uniform salt deposition or a wider coffee-ring, depending on the initial NaCl concentration (Figure 1.c). Experiments reveal that the flow patterns are also affected by the ambient vapor pressure, the drop size and contact angle.

To conclude, the flow behavior of an evaporating drop of a saline solution is dominated by a solely outward flow (combination of Marangoni and capillary forces) at low salt concentrations. At high salt concentrations, the flow behavior changes drastically and is governed by compensating Marangoni and capillary flows that lead to convection rolls

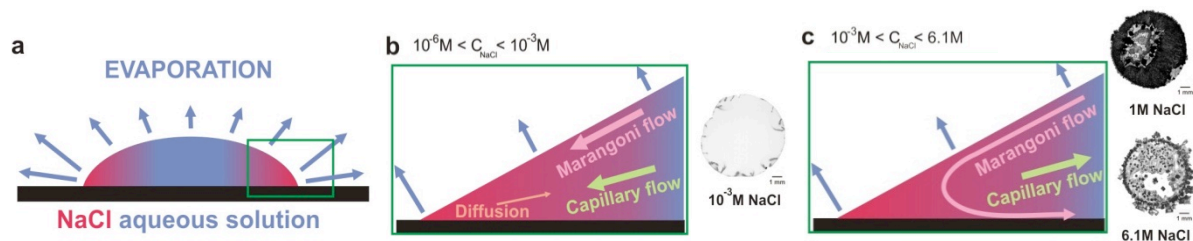


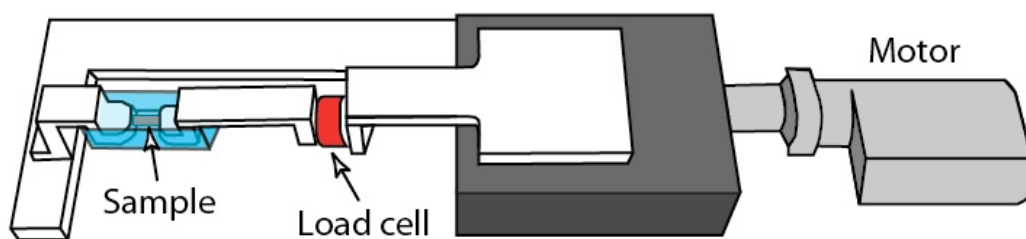
Figure 6: (a) Evaporation behavior of a sessile droplet from aqueous sodium chloride solutions. Locally varying evaporation rate and resulting concentration gradient: below (b) or above (c)  $10^{-3}$ M NaCl. Typical microscopy images of the final deposit patterns from droplets of  $10^{-3}$ , 1 and 6.1M NaCl on silica wafers at  $T = 25^{\circ}\text{C}$  and  $\text{RH} = 0\%$ .

**V-Thermodynamics of water adsorption in model structured molecular systems including analogues of hemicellulose, crystalline cellulose and lignin (pH of Aurelio Barbeta , MPIKG/Biomaterials and ICSM)**

"Wood material" is a complex, highly anisotropic and hierarchically organized nanocomposite. At the nanometric scale, it is characterised by stiff crystalline cellulose nanofibres, parallel to each other, and embedded in a matrix of a much softer, less anisotropic gel of hemicellulose, lignin and water. When samples are immersed in solution, the solvent uptake is controlled by molecular forces like entropy, Hydrogen-bonding of polysaccharides to cellulose nanocrystals, and hydration force. The matrix is hygroscopic, and swells with increasing relative humidity providing a source of internal stress, while the cellulose fibrils, winding with a spiral angle around the central lumen (so called "microfibrillar angle", MFA), passively reorient following the stress applied to them. Depending on the MFA, wood fibres can exhibit a wide range of behaviours and mechanical properties.

The study of water absorption of untreated softwoods as a function of relative humidity changes led to the elaboration of a first equation of state including terms of different nature (entropic, chemical, colloidal, mechanical), that can be further integrated with electrostatic terms derived from the presence of electrolytes in water. This is one of the goals of this project, which combines the expertise of the Max Planck Institute of Potsdam in wood mechanisms with the experience in colloidal systems of the Institut de Chimie Séparative de Marcoule.

First part of this work has been focused on producing experimental data to test the effects of solutes introduced by equilibration with a solution used as osmotic reservoir. In order to measure the swelling induced by different salt solutions on spruce compression wood foils, a particular tensile stage has been set up and used for iso-stress experiments (*Fig.1*). In this stage the sample is clamped between two holders, with the possibility to fit all these parts of the stage in a plexiglass cuvette with a volume of 10 cm<sup>3</sup>. One of the holders is fixed to a load cell to control and measure the axial tensile force, and a linear motor stage controls the strain.



*Fig.1:* tensile stage for isostress measurements of samples immersed in solution

At the beginning, I developed this stage using collagen samples, extracted from rat tail tendons and turkey leg tendons, which are well defined and characterized tissues. For these experiments, the osmotic pressure surrounding the samples was controlled by changing the relative humidity or by means of concentrated PEG solutions. These results are part of a submitted paper (*Osmotically driven tensile stress in collagen-based mineralized tissues*, Bertinetti†, Masic†, Schuetz, Barbeta, Seidt, Wagermaier, Fratzl).

The setup allows to measure the volume changes the sample undergoes through the axial strain of the tissue. To study how the electrostatic interactions modify the water uptake of wood tissues, highly concentrated salted solutions were prepared. As the water uptake is heavily influenced by osmotic pressure (OP) of the surrounding environment and because solutions exert a significant OP depending on the nature of the ions, their stoichiometry, their total concentration. It has been important to work with solutions producing the same osmotic pressure, even with different concentrations, in order to be able to compare results for different salts. This has been possible by choosing the osmotic pressure generated by a saturated NaCl solution as reference, and then fitting the different values of the osmotic coefficient at different concentrations for each salt to calculate the concentrations in which solutions of different salts produce the same osmotic pressure.

Samples have been immersed cyclically in water and then in salted solution, and their strain has been plotted as a function of the number cycles. Results can be interpreted both from a dynamic and a thermodynamic point of view.

In general, the kinetics of water and electrolytes diffusion depends on the charge of the ions. Passing from water to salt solutions, we observed a fast decrease in the sample length, followed by a progressive swelling (*Fig.2*). Two processes are occurring at different times: at the beginning an osmotically driven process determines the flowing out of the water from inside the tissue to the external salt reservoir, where the relative humidity is lower (relative humidity is related to osmotic pressure by a logarithmic dependence). Then, electrostatic swelling occurs, due to the absorption of ions within the tissues. The kinetics of this process is basically determined by the hydrodynamic size of the ions. This is why the two phenomena are more distinguishable for CaCl<sub>2</sub> while for NaCl the two processes exhibit very similar speeds, as it can be seen comparing Fig 2A with Fig 2B. While passing

from salted solution to water, we can exactly observe the reverse process: water flows inside the tissue, and slowly ions come out (water molecules are always moving faster).

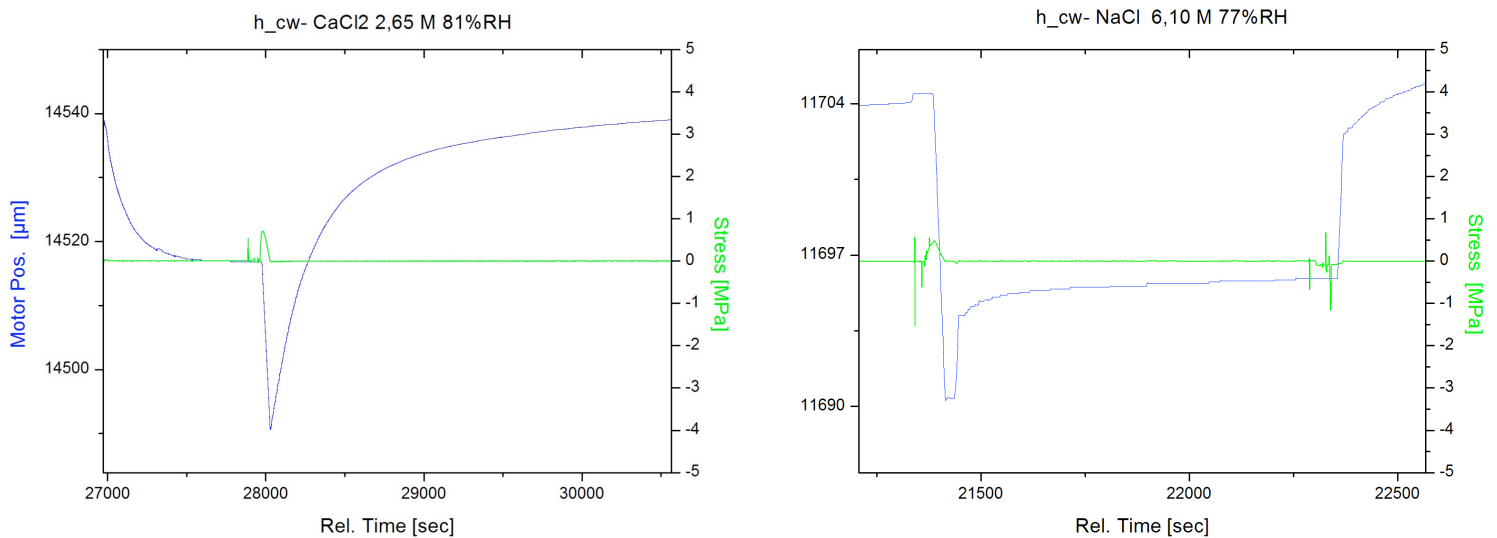


Fig.2 : (left): length versus time at constant strain when impregnating from a concentrated Calcium Chloride solution right: same experiment impregnating from a concentrated Sodium Chloride solution

As a general trend, all salts determine a positive strain of the sample, i.e. promote the water uptake by wood tissues. For a semi-quantitative analysis, it can be useful to keep in mind the Hofmeister classification (Fig.3), in which salts are defined according to their capacity to interact with water weaker than water itself (structure-breakers, or "chaotropes") or to have the opposite effect (structure-makers, or "kosmotropes").

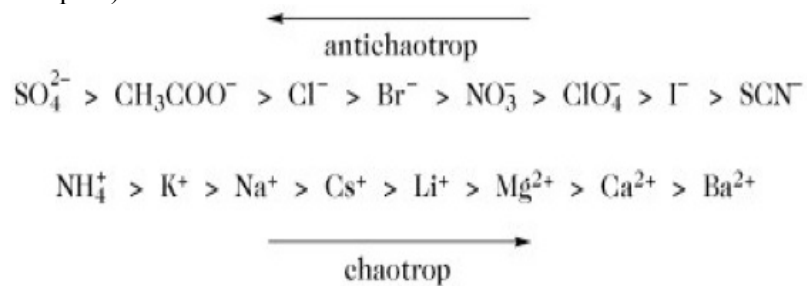


Fig 3: the Hofmeister series

Comparing strain at the equilibrium, after the same number of cycles, of samples treated with different salts, it is evident how swelling is more pronounced if the salt is made by one chaotropic and one kosmotropic ion, such as NaI or CaBr<sub>2</sub> (Fig.4). Supposedly, this happens because ions that can easily lose their hydration sphere adsorb on the cellulose structure while the one of opposite charge stays in the more hydrated space between the crystals. This way, a net electrical field acting as repulsive force between cellulose crystal is generated and the hydration of the material increases.



### **Annex : activities and origins LIA RECYCLING ACTIVE Members 2014**

Name: Thomas Zemb  
Title: Prof. Dr. (CEA/INSTN)  
Time spent on LEA activities: 15%

Name: Olivier Diat  
Title: Dr., chercheur CEA  
Time spent on LEA activities: 5%

Name: Pierre Bauduin  
Title: Dr., chercheur CEA  
Time spent on LEA activities: 5%

Name: Marie Jehannin  
Title: PhD Student (CEA)  
Time spent on LEA activities: 100% in collaboration between ICSM/LEA and CEA/DEN-Marcoule/DTEC

Name: Virginie Soulié  
Title: PhD Student (CEA)  
Time spent on LEA activities: 100 %, in collaboration between ICSM/LEA and CEA/DANS-Saclay/DPC

Name: Aurelio Barbetta  
Title: PhD Student registered at University of Montpellier 2 and at TU Berlin  
Time spent on LEA activities: 100%

Name: Sophie Charton  
Staff scientist at CEA/DEN/DTCD  
Time spent on LEA activities : 10%

### **Members of Max Planck Institut of Colloids and Interfaces, Potsdam**

Name: Pr Helmuth Möhwald  
Title: Prof.Dr. (MPIKG and University of Potsdam)  
Time spent on LEA activities: 10 %

Name: Hans Riegler  
Title: Privat-Dozent Dr.  
Time spent on LEA activities: 25% (from October 2012)

Name: Gerald Brzezinski  
Title: Professor Dr. permanent staff  
Time spent on LEA activities: 10%

Name: Dr Luca Bertinetti  
Title: Dr., Postdoctoral fellow  
Time spent on LEA activities: 25 %

Name: Anne-Liese Heilig  
Title: Engineer permanent staff: chemical engineer/technician  
Time spent on LEA activities: 20%