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A B S T R A C T

This study focuses on the mechanisms governing the ability for fractionated lignins to stabilize emulsion depending on the pH. It is hypothesized that adsorption mechanisms of lignins at the oil/water interface sharply impact their ability to stabilize emulsions. Stabilization mechanisms may vary because lignins could exist either in the form of particles and/or in the form of surfactants depending on pH treatment. The interfacial layer formed by lignins was examined by both interfacial tension and interfacial viscoelasticity as a function of pH history. Emulsifying capacity of corresponding lignins dispersions was investigated and correlated with both the lignins adsorption performance at the oil/water interface and the interfacial rheological properties. The coexistence of two distinct mechanisms responsible for O/W stabilization as a function of pH was identified. First, for lignins in the form of surfactants, emulsion is formed but a marked coalescence occurs rapidly. Secondly, when lignin mainly exists in the form of particles, rapid phase separation occurs due to poor interfacial properties. Finally, when both lignin particles and lignin surfactants coexist, a synergy between Pickering and micellization mechanisms leads to stable emulsion. This study proves a synergistic effect between lignin particles and lignin surfactants resulting in optimal interfacial stabilization.

1. Introduction

Lignins are aromatic polymers and the second most abundant natural macromolecules after cellulose [1]; they are widely available from different industrial processes aimed at biomass deconstruction. Their valorization as versatile and multifunctional ingredients due to their advantageous properties such as antioxidant [2–4], anti-UV [5–8], antibacterial [9–10] and emulsifying properties [11–13] meets the current high demand to valorize such by-products for personal care, cosmetic, food, agricultural and pharmaceutical industries. They can be considered as promising alternatives to synthetic surfactants due to their ability to increase liquid surface activity as a result of their high amphiphilic properties thus making them good candidates to stabilize oil/water emulsions [14]. Their emulsifying capacities have been demonstrated in previous works showing lignins potential to stabilize interfaces [13,15–17] in both Pickering and non-Pickering oil-in-water emulsions. Emulsion stabilization of lignins could be performed either by their adsorption at the oil/water interface as surfactants, either as

Pickering particles; in both cases stabilization results from various intermolecular interactions including Van der Waals interactions, repulsive electrostatic interactions, and hydrogen bonds [13,18]. Therefore, interfacial activity of lignins can be controlled whether in the form of surfactants or in the form of solid particles. On one hand, when stabilization occurs via macromolecular colloids, the charge and functional groups of lignins as well as their solubility highly impacts their adsorption at the oil/water interface. On the other hand, when stabilization occurs via particles, the surface charge as well as the size and wettability of lignin particles are key properties for their adsorption via Pickering stabilization [13–14]. Pickering emulsions show the advantage that they are more resistant against coalescence by forming a rigid layer around the oil droplets thus the emulsion stability increases [16]. The presence of lignin particles causes the repulsion among droplets, which prevents the coalescence of oil droplets. It also increases the viscosity of the emulsions because adjacent oil droplets share lignin particles adsorbed at the interface thus forming a tridimensional network of interconnected droplets. Enhanced emulsifying capacities

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are gathered with Pickering emulsions because of a larger surface area occupied by particles [19]. Thus, examples of lignin particles have been produced recently for encapsulation of active ingredients [20] within emulsions, which were well stabilized by lignin particles, due to their emulsifying properties as well as protective behavior thanks to their abundant UV chromophoric groups. Lignin particles used for food Pickering emulsions have also been developed [21–22].

Different parameters govern the mechanism of adsorption of lignins at the oil/water interface thereby affecting their emulsifying performance [23]. Controlling the pH of the continuous aqueous phase of lignins emulsions could highly influence the solubility properties of lignins and their charge, then impacting their behavior/conformation at the interfaces. According to literature, lignins obtained using soda process are more soluble in alkalized aqueous phase [24–25]. Thus, the influence of the pH on lignins emulsions' stability must be evaluated. It has been shown that emulsions prepared with neutral and acidic solutions of straw lignins expressed low stability in contrast with alkaline solutions [26]. In alkaline medium, the presence of ionic groups such as carboxylates and phenolates brings a negative global charge to lignins; therefore, the stability of the corresponding emulsions is due to the repulsion interactions between negatively charged emulsion droplets formed by lignin surfactants when using lignins alkaline solution. In acidic and neutral medium, electrostatic repulsions play a second role in the emulsion stability and lignins can form a rigid film at the interface by a more complex stabilization mechanism [26]. Other authors established that irreversible adsorption of lignin particles at the oil interface at pH 3 could be achieved by giving a stable emulsion [27]. On the contrary, lignin surfactants could only partially adsorb at a pH 7 giving a less stable emulsion and with a complete demulsification at pH 11 for non-Pickering emulsions [27]. Silmore et al. [28] have demonstrated the ability of modified lignins particles to form stable emulsions at neutral pH.

Nevertheless, further understanding of the partitioning and adsorption kinetics of lignins at the oil/water interface remains challenging. In addition, only poor research has been made with the aim to better understand the impact of pH on lignins migration and on lignins structure at the oil/water interface. Therefore, there is a high need to explain how lignins adsorb and stabilize the interface, as well as how they change interface's physical properties, depending on the pH and thus on their solubility state. This could be achieved by various interfacial properties investigations. Interfacial tension measurement is known to provide useful information on the attachment/displacement of the particles at the oil/water interface as well as on the adsorption of surfactants at this same interface [29]. This may give crucial information on their ability to prevent droplet coalescence through different mechanisms which could be the occurrence of electrostatic repulsion or mechanical barrier by the formation of a viscoelastic film around the droplets of the dispersed phase [30]. Another powerful technique to characterize the viscoelastic film formed by the emulsifiers at the interface and to evaluate the physical stability of the emulsion is interfacial rheology. Interfacial rheology describes the functional relationship between the deformation of an interface, the stresses exerted in and on it, and the resulting flows in the adjacent fluid phases [31]. Interfacial rheology has gained a lot of interest these recent years for the characterization of complex interfaces such as oil/water interfaces composed of particles or surfactants; nevertheless, it remains relatively undeveloped [32–34] probably due to technical constraints. Interfacial modulus could differ whether the interface is stabilized by particles or by surfactants [31,35]. G′ and G″ modulus values give information on the stability and dynamics of the interface and on the behavior of the interfacial film [34,36]. Dilatational viscoelastic properties bring information on the capability of polymers to resist displacement [34]. In all cases, the interfacial viscoelasticity is influenced by the diffusion, adsorption, and intermolecular interaction of the molecular chains. Therefore, the kinetics of the adsorbed layer formed can be studied by determining the changes in interfacial moduli [37].

The aim of this work was to further understand the adsorption behavior and interfacial properties of fractionated alkali lignins at the oil/water interface depending on pH adjustments ranging from 3 up to 11 prior to final reacidification to pH = 6 to allow envisaging cosmetic-type formulation. Lignins solubility being limited because of their structural features, a fractionation process was performed using MEK as extraction solvent, according to our previous work [38] to recover fractionated lignins (FL). Such step allows to remove MEK insoluble lignins which are the higher molar mass chains of TL and represent 39% wt. Several pH adjustments have been assessed to obtain different states of lignin solubility, and therefore different emulsifying performances of lignins.

This original work investigated for the very first time to our knowledge the physico-chemical relationship between the microstructure of the interfacial film formed by lignins and their emulsifying properties. To this end, firstly the fraction (%w/w) of insoluble lignins within each dispersion was determined. Secondly, the rigidity of the interfacial film layer formed by lignins was characterized by interfacial tension and interfacial shear rheology; then O/W emulsions stabilized with lignins were prepared and, finally, their emulsifying properties were investigated by characterizing their microstructure, droplet size, and organoleptic stability.

2. Materials & methods

2.1. Chemicals

Methyl ethyl ketone (MEK), hexane, and tetrahydrofuran (THF) stabilised with butylhydroxytoluene (BHT) were purchased from Carlo Erba reagents (Val de Reuil, France) and used as received. Grass soda technical lignins Protobind1000 (mixture of wheat straw and sarkanda) were purchased from Green Value (Orbe, Switzerland). Propanediol (Zemea) was purchased from DuPont (Delaware, USA) and sweat almond oil from Jan Dekker (Saint Germain en Laye, France).

2.2. Fractionation

Fractionation has been performed according to our previous work [38]. Technical alkali lignins TL were magnetically stirred in MEK (25 g/L) for 2 h at room temperature. The mixture was filtered on glass filter, rinsed with MEK, and the filtrate was concentrated under reduced pressure prior precipitation into hexane under magnetic stirring. The precipitated lignins were recovered by filtration on glass filter and dried under vacuum overnight to recover fractionated lignins (FL) as a brown powder with a yield of 61%wt.

2.3. Preparation of FL dispersions and FL formulations

Different pH alkalizations were performed to obtain different states of FL solubility. However, the present work targeting skin care formulations, where human skin pH should be respected [39–40], a final pH of 6 was targeted. Therefore, when pH exceeded 6, FL dispersions were reacidified up to 6 with citric acid solution; this last compound was chosen as it is often used as a pH adjuster in skin care formulations [41], and it is also known as a chelating agent [42–43] which could impede FL's sedimentation.

For the preparation of FL dispersions, FL (0.5% w/w) were presolubilized in propanediol (10% w/w) under stirring with the Bench mixer Turbotest® (VMI, France) equipped with a deflocculator turbine (diameter mm) at 700 rpm for 5 min and then gently poured in ultrapure water (QSP) under stirring (550 rpm, 10 min).

Four dispersions were prepared according to pH treatment performed on the dispersion. A first dispersion with no pH readjustment (pH = 2.9) was prepared corresponding to the initial pH of FL dispersions (pH3-D). A second dispersion was prepared with alkalization to pH = 6.0 (pH6-D). A third dispersion was prepared using a back-acid

procedure: firstly pH was alkalized to 8.5 and then reacidified to 6.0 (pH8.5–6-D). Lastly, a fourth dispersion was prepared with a back-acid procedure with first pH alkalized to 11.0 and then reacidified to 6.0 (pH11-6-D).

Alkalization was performed using NaOH aqueous solution (30 g/L) while citric acid aqueous solution (30 g/L) was used for acidification. The volume fraction of water in the propanediol/water mixture takes into account the volumes of NaOH and citric acid solutions added.

The same procedure was used for the preparation of the FL aqueous phase of emulsions with FL at 2.5% w/w. Emulsification of the aqueous phase in the presence of sweat almond oil (10% w/w) was performed at 10 000 rpm for 10 min using a T25 digital Ultra-Turrax® (IKA, Germany) equipped with the rotor–stator turbine S25 N-25F. Accordingly, so-called pH3-E, pH6-E, pH8.5–6-E and pH11-6-E were obtained.

2.4. Characterization of FL dispersions and FL emulsions

2.4.1. Fraction of insoluble lignins

Centrifugation of each dispersion (pH3-D, pH6-D, pH8.5–6-D, and pH11-6-D) at 10 000 RCF, 20 °C, 10 min has been performed. The soluble part was removed, and the insoluble part was dried through lyophilization for 48 h. The dried lignins were weighed to calculate the fraction (% w/w) of insoluble lignins within each dispersion. Data are presented as means ± SD.

2.4.2. Static Light scattering SLS

Droplets size measurements were performed by means of a laser diffraction particle size analyzer SALD 7500 Nano (Shimadzu Co., Ltd., Japan), equipped with a violet semiconductor laser (405 nm) and a reverse Fourier optical system. The emulsions were dispersed in purified water to reach an absorption value of 0.200 ± 0.10. To ensure homogenous dispersion of emulsions, continuous stirring was applied during analysis in the batch cell (7 cm^3). All measurements were performed at ambient temperature on at least three freshly separately prepared samples. Data were collected using WingSALD II-7500 software.

2.4.3. Optical microscopy

A drop of emulsion sample was placed on a microscope glass slide covered with a coverslip, and visualized by an optical microscope Nikon (Ni-U NIKON, Japan) equipped with a digital camera DS-Fi3 (5.9 MP CMOS 2880 × 2048 at 15 images/s) at magnification of G × 400 under the bright field at ambient temperature of storage. NIS-Elements Viewer 5.21 was used to analyse the micrographs.

2.4.4. Interfacial tension

Interfacial tension was measured by the pendant drop method as a function of time. The dynamic interfacial tension of FL aqueous dispersions in sweat almond oil was measured with the goniometer (GBX, Digidrop, France). A drop of FL aqueous phase, initially contained in a syringe (Poulten & Graf, glass syringe with stop, 1 mL) equipped with a needle (internal diameter of 0.51 mm and external diameter of 0.82 mm) was formed into the sweat almond oil phase placed in an optical glass cuvette. All experiments were conducted at ambient temperature. A CCD camera was programmed to capture the variation of drop shape for 5000 s at frame rate of 25 images per s. The captured images were used to calculate the interfacial tension by the drop shape analysis resulting from the balance of gravitational forces and tension forces, wherein the contour of drop was fitted with the DS/DE method to determine the interfacial tension. Each measurement was performed over 5000 s in triplicate and data are presented as means ± SD.

2.4.5. Interfacial rheology

Stress-controlled rheometer Discovery HR 3 (TA instruments, USA) equipped with the Double Wall-Ring (DWR) device was used in this work. The sample was placed in a Peltier Cell made of Teflon with an inner radius of 31 mm and an outer radius of 39.5 mm. The height of the compartment where the first liquid dispersion could be introduced is 10 mm. A double wall-ring DWR made of Pt/Ir connected to the rheometer was used. The cross section of the ring is square shaped to create a planar interface. The inner ring radius is 34.5 mm, the outer ring radius is 35.5 mm. The exact protocol for the use of this device is described as follow: first, the platinum ring is cleaned intensively after use, and systemically flame-treated before any further measurement to remove organic contaminants. The aqueous phase corresponding to FL dispersions was then placed in the Peltier Cell and the DWR was accurately positioned at the air/water interface, after which oil phase (sweet almond oil) was carefully poured onto the aqueous phase until the whole ring was covered. Once ready, an oscillatory amplitude sweep experiment was used with applying an increasing strain, ranging from 0.1 to 100% to determine the linear viscoelastic domain (LVED). Finally, oscillatory time sweep experiments with a frequency of 1 Hz were performed by using a constant strain within the LVED to determine the interfacial properties changing over 15 h. All experiments were performed in triplicate and data are presented as means ± standard deviation (SD).

2.5. Stability monitoring

Emulsions were defined as stable since no coalescence phenomena occurred (merging of droplets inducing an increase of droplets size overtime) and emulsions exhibit no or few lignins precipitation phenomena (sedimentation).

For the stability evaluation, lignins emulsions were kept at 25 °C in 15 mL Eppendorfs (Corning Centristar™). Emulsions stabilities were monitored over time through visual aspect analysis, optical microscopy observations and SLS measurements. Visual aspect stability was studied after 1 day and 3 months at 25 °C. Optical microscopy, and granulometry analysis were measured after 1 day and 3 months at 25 °C. Analysis were done for the dense emulsified layer of each emulsion. The dense emulsified layer was measured in % v/v of emulsion after 1 day and 3 months at 25 °C. Sedimentation was measured in % v/v of emulsion after 1 day and 3 months at 25 °C.

3. Results and discussion

First, in order to relate pH variation of FL dispersions with their solubility state, the fraction (% w/w) of insoluble lignins have been calculated after centrifugation and lyophilization of the FL dispersions. The results are given in Table 1.

When the intermediate pH of FL aqueous dispersions increases, the fraction (%) of insoluble lignins decreases (Table 1). Therefore, by increasing the intermediate pH, optimized solubility was achieved and still maintained when reacidifying at pH 6.0 to obtain a pH appropriate for skin formulations.

In order to understand the stabilization mechanisms of lignins depending on the pH and therefore on their solubility state, the whole work was based on the characterization of lignins dispersions and corresponding emulsions depending on their pH.

Table 1

% of insoluble lignins within dispersions depending on the pH treatment.

Lignin dispersion		pH3-D	pH6-D	pH8.5–6-D	pH11-6-D
pH treatment process	Initial pH	2.9			
	Intermediate pH	No pH adjustment	N/A	8.5	11.0
	Final pH		6.0		
% insoluble lignins		55.1 ± 3.7	18.4 ± 0.7	7.2 ± 1.8	0.3 ± 0.1

3.1. Interfacial tension and interfacial rheology for deeper understanding of the interfacial behavior of lignins aqueous dispersions

3.1.1. Interfacial tension

The adsorption mechanisms of lignins at the interface according to pH history were investigated through interface tension experiments (Fig. 1 and Table 2). A drop of FL dispersion was formed in sweat almond oil at ambient temperature; then the recording of the interfacial tension started immediately and was continued for a period of 5000 s. Interfacial tension of the pure system, i.e. between sweat almond oil and water/propanediol 90/10 was also measured as "blank" reference.

For all lignins aqueous dispersions the interfacial tension was reduced compared to the water/propanediol system, thus illustrating the effect of lignins on the interface properties which was also demonstrated by Czaikoski et al [13] and Ghavidel and Fatehi [23]. In addition, for all lignins systems, a period of time with a gradual decrease in interfacial tension was observed compared to the water/propanediol 90/10 system where a rapid decrease was observed, establishment of a constant interfacial tension for all systems. This evidences a kinetic for the migration of the lignins to the interface depending on the lignins aqueous dispersions (from around 1500 s to 1 h); therefore, it appears that the interfacial film structure was established after a certain delay. Zhang et al [30] as well as Simon et al. [44] also observed a progressive adsorption of lignins at the interface with interfacial tension reaching a steady value. According to Fig. 1 and reported in Table 2, it took 1 h for pH3-D and pH8.5–6-D to structure the interface, whereas a bit less than an hour (3000 s) for pH11-6 D, and it appears that the interfacial film was organized much earlier for pH6-D, at 1500 s.

According to Fig. 1 and to Table 2, different interfacial tension values at plateau were reached, depending on the pH history of lignins dispersions; the higher the intermediate pH of the lignins dispersion the lower the interfacial tension once equilibrium was reached. This holds true and was more marked for the pH11-6-D where lignins were almost completely soluble. Therefore, it can be concluded that strong interactions through π-π stacking between the hydrophobic aromatic moieties of lignin surfactants and oil occur on one side and between their hydrophilic moieties and water on the other side decreasing the initial interfacial tension of water/propanediol 90/10 from 18.32 Nm/m (interfacial tension at plateau; Table 2) up to 1.85 mN/m, showing the amphiphilic nature of lignins.

When considering the other dispersions tested, it appears that the higher the intermediate pH of the aqueous dispersion, the higher was the decrease of the interfacial tension. According to Pichot et al. [29] and to Binks et al. [45] when combining silica particles with high concentration of surfactants, interfacial tension was dictated only by the surfactants. According to Drelich et al. [46], even when hydrophilic or hydrophobic particles were strongly adsorbed at the interface, there was no reduction of the interfacial tension values and they remained high compared to the values obtained in presence of surfactants. From present interfacial tension results, it is obvious that when lignins solubility in the dispersion is decreased, less lignin surfactants are present, and the interfacial tension is less decreased. Furthermore, the presence of lignin particles in aqueous dispersion affects the lignin surfactants efficiency in reducing the interfacial tension. This suggests that when lignins are not completely solubilized in the aqueous dispersion, both lignin particles and lignin surfactants are present at the interface. Lignin particles adsorb at the oil/water interface reducing the interfacial area covered by the lignin surfactants, therefore lowering the effective surface coverage and giving a higher interfacial tension. For the pH6-D, the amount of lignin particles and lignin surfactants is well balanced. In this case, lignin surfactants rapidly migrate thus reaching the interface and structuring it. The slower structuration of the interface which is observed for pH8.5–6-D and pH11-6-D (Fig. 1) could be explained by the fact that due to the high presence of lignin surfactants, more interactions could occur between lignin particles and lignin surfactants, thus slowing down the migration and adsorption of these latter at the interface. On the contrary, the slower structuration of the interface observed for pH3-D may result from the presence of numerous lignin particles which interfere with the adsorption of the few lignin surfactants present in this dispersion.

To summarize, the lignins species ability to modify the Oil/Water interface is directly linked to a competition between lignin surfactants and particles, the latter having a much slower diffusion and no ability to decrease rapidly the interfacial tension.

Based on our results obtained by interfacial tension, and in order to have a deeper understanding of the manner the interfacial film is formed and stabilized and of its mechanical properties, its viscoelastic properties were investigated through interfacial shear rheology.
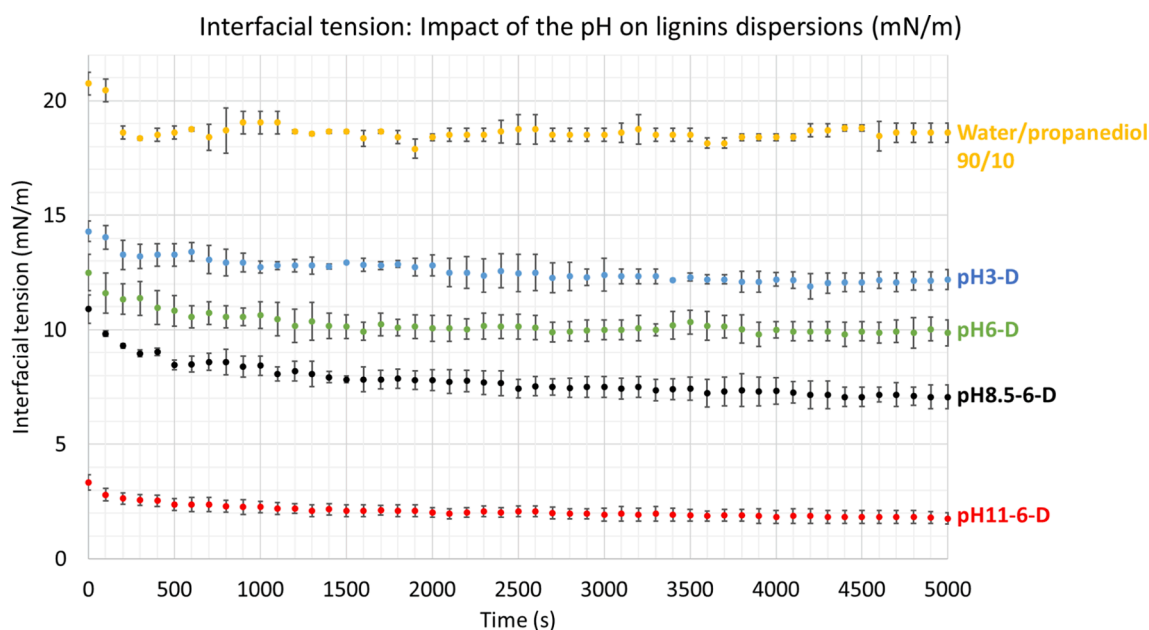

Fig. 1. Interfacial tension kinetics of lignins aqueous dispersions obtained by the pendant drop method in sweat almond oil at ambient temperature over 5000 s with legends: water/propanediol 90/10 (in yellow), pH3-D (in blue), pH6-D (in green), pH8.5–6-D (in black), pH11-6-D (in red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2

Lignins dispersions analyzed by interfacial tension and interfacial rheology and their corresponding interfacial tension at plateau (mN/m) and LVED limit (%strain).

Lignin dispersion		Water/propanediol 90/10	pH3-D	pH6-D	pH8.5–6-D	pH11-6-D
Interfacial tension	Plateau (mN/m)	18.52 ± 0.15	12.12 ± 0.33	9.95 ± 0.49	7.19 ± 0.51	1.85 ± 0.28
	Time for stabilization (s)	300	3600	1500	3600	3000
Interfacial rheology	LVED Limit (%strain)	112.2	11.9	1.6	0.4	0.6

3.1.2. Interfacial rheology

Interfacial shear rheology has been used in order to study lignins emulsifying mechanisms depending on the pH history of the different lignins dispersions. Applying shear strain to interfacial layers gives indirect access to information on interactions occuring at interfaces [31]. Therefore, the interfacial moduli could provide important information about the build-up of the interface, kinetics and interactions either between lignin particles either between lignin particles and lignin surfactants. Firstly, an oscillatory amplitude sweep experiment was performed with applying an increasing strain, ranging from 0.1 to 100% in order to determine the linear viscoelastic domain (LVED). For every lignins dispersion, the linear viscoelastic domain limit as expressed in %strain
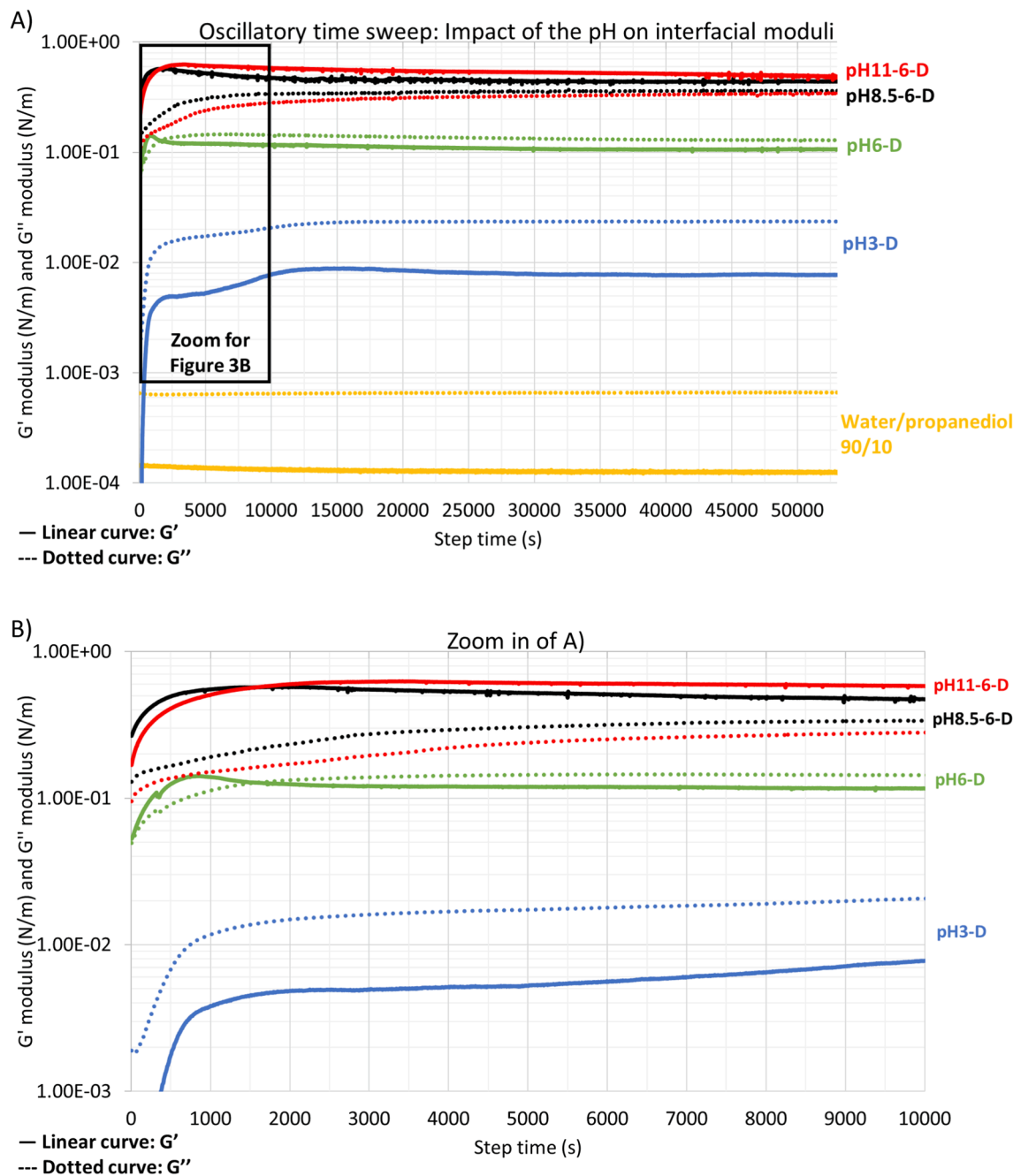

Fig. 2. A) Interfacial rheological curves obtained by oscillation time sweep measurements at a steady % of deformation at controlled temperature of 25 °C over 15 h Legends: G′ full line and G″ dotted line: water/propanediol 90/10 (in yellow); pH3-D (in blue); pH6-D (in green); pH8.5–6-D (in black); pH11-6-D (in red) B) Zoom In of A) from 0 to 10000 s. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

was identified as corresponding to 10% loss of G′ (Table 2). For each dispersion, a % strain within the LVED domain was chosen and used for the oscillatory time sweep experiments. Thereafter, oscillatory time sweep experiments, at a steady % of deformation, corresponding to the linear viscoelastic zone determined from oscillatory amplitude sweep experiments for each lignins dispersion were performed over 15 h at controlled temperature of 25 °C (Fig. 2A).

Whatever the mixtures tested, the presence of lignins in the dispersion significantly increases the viscoelastic moduli G′ and G″ in all cases, thus demonstrating that lignins induce interfacial organization (Fig. 2). On one hand results evidence a sharp changing of viscoelastic moduli over the first hours and, on the other hand, a plateau corresponding to moduli stabilization is observed after few hours thus illustrating stabilization of the interfacial film. Another striking point is that interfacial viscoelastic properties also differ from one system to another, some systems keeping loss modulus predominant over time while others show a higher storage modulus thus illustrating highly different viscoelastic structure at the liquid–liquid interface.

There is a strong impact of the pH history on the rheological interfacial properties of lignins dispersions; meanwhile, the G′ and G″ modulus behavior as a function of the intermediate pH of the dispersions is linked to the lignins solubility. Consequently, present interfacial rheological results do indicate that the more soluble lignins fraction within the dispersion, the higher the G′ and G″ moduli which reflects the higher rigidity of the interfacial film formed by lignins.

For the dispersions that underwent back-acid procedure, pH8.5–6-D and pH11-6-D, lignins being mostly soluble, a rapid migration at the interface is achieved, and according to literature, when highly solvated, polymer chains tend to spread at the interface [47]. The interfacial storage modulus G′ rapidly increases and exceeds the interfacial loss modulus G″ which does not decrease over time under deformation. After a fairly short period of time - less than 1 h - both moduli reach a constant value, thus suggesting that lignin surfactants rapidly adsorb at the interface and form an interfacial layer without desorption. Therefore, the whole results for lignins dispersion submitted to back-acid process indicate the occurrence of an interface owing strong associative interfacial network structure, with a solid-like structure [33] formed with a prevailed elastic behavior. In such a scenario, strong physico-chemical interactions may occur between lignin surfactants at the interface, leading to high interfacial modulus resistant against deformation of the contacting phases [32]. In addition, lignin surfactants allow maintaining dense interfacial cohesion since adsorption is stronger than sedimentation related to their high kinetics (Fig. 2A).

On the contrary, if considering pH3-D, a viscous predominant behavior was observed. This means that deformation of the interfacial layer displaces the particles out of their equilibrium position, which do not resist deformation, the interfacial structure induces energy dissipation [48]. Furthermore, the interfacial localization of particles is determined by their wetting properties between the contacting fluids [49]. Thus, due to insolubility and in spite of their high wetting surface properties, there is probably a significant portion of lignin particles not localized at the interface of the two immiscible fluids, then, because of gravity forces occurrence, no stabilization of the interface occurs thus both G′ and G″ moduli do not increase as much as when more lignins are solubilized. In addition, lignin particles owing strong chemical affinity with each other's, aggregates could be formed leading to more pronounced sedimentation and their adsorption at the interface may be therefore limited. For the pH3-D, which is mainly composed of lignin particles, a purely viscous fluid-like response of the interfacial film is obtained directly from the beginning, since no crossover point is observed [37].

For pH6-D, a rapid increase of the storage modulus G′ which is higher than the G″ modulus is first observed (Fig. 2B), showing a solid-like response. In a second step, after around 15 min, a small drop of the G′ modulus is observed thus becoming lower than the G″ modulus showing a transition from elastic to viscous behavior; this phenomenon evidences

the occurrence of a definitive fluid-like response [36]. This may be explained by the fact that there are less lignin surfactants at the interface and there is desorption of lignin particles from the interface conducting to sedimentation caused by gravity forces. For pH6-D, where lignin surfactants and lignin particles coexist, two emulsifying regimes are therefore present: firstly lignin surfactants do migrate very fastly at the interface, then, particles do not spontaneously adsorb to the interface, although they do adsorb but exert only weak repulsive forces at the interfaces [35].

3.2. Study of lignins emulsifying capacity of O/W emulsions

In order to enrich the observations resulting from interfacial rheology and interfacial tension investigations on the mechanisms occurring at the O/W interface depending on the pH history of the aqueous phase, a study of the emulsification capacity of lignins within O/W emulsions was envisaged. To this purpose, the continuous phase of formulations containing the lignin species was varied accordingly to their pH history, and the evolution of the emulsions' stability was studied and characterized to evaluate the lignins emulsifying capacities. The emulsions were prepared with the same pH variation process as the dispersions, but with a concentration in lignins of 2.5% w/w, corresponding to pH3-E, pH6-E, pH8.5–6-E, and pH11-6-E.

3.2.1. Visual aspect variation of FL-emulsions depending on the pH history of lignins emulsions' continuous phase

Firstly, a visual assessment of the emulsions aspect was conducted for different pH history of lignins within the continuous aqueous phase dispersions (Table 3).

According to Table 3, pH3-E corresponding to a dispersion prepared with lignins incorporated in the aqueous phase without any pH readjustment, was totally unstable as oil demixed after only 1 day.

Otherwise, after 1 day, one can observe that all emulsions with a final pH of 6 exhibited a creaming phenomenon of emulsified phase with no oil exudate, thus evidencing a certain emulsifying ability but a lack of suspending capacity. A schematized evolution of the lignins emulsions is

Table 3

Visual aspect and sedimentation amount by varying the pH history of the continuous phase of emulsions containing 2.5% of lignins.

Emulsion	Visual aspect		Sedimentation (% v/v of emulsion)	
	After 1 day	After 3 months	After 1 day	After 3 months
pH3-E	Unstable Complete demixing of water and oil	UnstableComplete demixing	N/A	N/A
pH6-E	Light concentrated emulsified layer (15% v/v of emulsion), brown diluted emulsified layer	No evolution	0.3	0.4
pH8.5–6-E	Concentrated emulsified layer (15% v/v of emulsion) becoming darker at the surface, dark brown diluted emulsified layer	No evolution	Slight sediment (<0.1)	0.6
pH11-6-E	Concentrated emulsified layer (15% v/v of emulsion) becoming darker at the surface, black diluted emulsified layer	No evolution	No sediment	2

shown in Fig. 3. The creaming effect resulted in two phases: a lower aqueous phase so-called diluted emulsified layer, and an upper one so-called concentrated emulsified layer. This latter phase showed a gel-like cream aspect much thicker, and much lighter color than the diluted emulsified layer; in addition, the bottom is composed of sediments depending on the pH history of lignins used within the preparation of the continuous aqueous phase dispersions. It is important to note that after 3 months, no significant evolution was observed for all these latter emulsions. Consequently, such a creaming phenomenon may result from the migration of oil droplets but without impacting the stabilization potential of lignins; besides, it may easily be solved by the addition of suspending agent.

No or only a trace of sedimentation was initially observed after 1 day for pH11-6-Eand pH8.5–6-E respectively, while it was more pronounced for pH6-E. Then, after 3 months of stability monitoring, the highest % of sedimentation was observed for pH11-6-E and the lowest for pH6-E. A kinetic effect was observed on the evolution of the sedimentation amount: there was marked changing for the sedimentation when lignins sediment from the beginning.

3.2.2. Microstructure and granulometry characterization of the concentrated emulsified layer of lignins emulsions

For the characterization of lignins emulsions, only the concentrated emulsified layer was characterized since the diluted emulsified layer was mostly composed of solubilized lignins species together with few oil droplets. Therefore, studying this latter upper phase was the most appropriate manner to allow assessing lignins emulsifying properties. To this end, both optical microscopy and granulometry distribution of the concentrated emulsified layer corresponding to the emulsions prepared at different pH treatments of lignins are shown in Table 4.

Firstly, one can observe an initial marked heterogeneous microstructure for pH3-E, with lignins dispersed unevenly in the emulsion and not at the interface (Table 4A). For the other 3 emulsions where a final pH of 6 was adjusted, stable oil droplets are formed with a similar microstructure after 1 day of ageing, evidencing a high content of oil droplets stabilized by lignins in the concentrated emulsified layer corresponding to a rigid network of oil droplets (Table 4A). In addition, for the pH3-E, no accurate granulometry analysis could be achieved as no stable droplets were formed; this is the reason why no curve is shown on the figure. This may be due to lignin aggregates heterogeneously dispersed in the system instead of lignin species stabilizing the interfaces. Conversely, the granulometry distribution by volume of the emulsified upper phase corresponding to the three other pH-dependent emulsions after 1 day of ageing are shown in Table 4C. A first population of droplets owing a diameter around 1 μm was observed for the 3 emulsions, while a clearly predominant droplets population ranging from 5 to 50 μm diameter was evidenced for the 3 systems. In addition, it is interesting to note that a slight tendency to lower droplet size when lower intermediate pH of the continuous phase of emulsion could be observed.

After 3 months of ageing, an unstable and heterogeneous microstructure was observed by optical microscopy for pH3-E (Table 4B) with lignins dispersed unevenly in the emulsion with no much evolution observed between 1 day and 3 months of stability. On one hand,
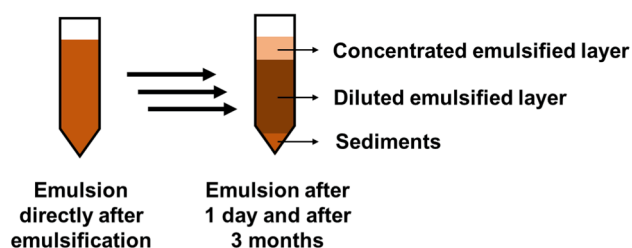
microscopy images evidenced no significant evolution of the microstructure for the pH6-emulsion (Table 4B). On the opposite, a marked coalescence was observed for the pH11-6-E, while a limited, intermediate, coalescence was observed for the pH8.5–6-E (Table 4A). The granulometry distribution by volume of the pH-dependent emulsions after 3 months of ageing are shown in Table 4D. A more pronounced population of thin droplets of diameter size between 0.5 and 3 μm was observed for pH6-E compared to pH8.5–6-E and pH11-6-E (Table 4D), which confirms the optical microscopy observations for the pH6-emulsion (Table 4B). A second population of droplets was observed for the 3 emulsions: between 3 and 30 μm for the pH6-E and between 3 and 50 μm for the emulsions where a back-acid was performed. Coalescence occurred for both emulsions obtained with lignins treated through back-acid process.

Regarding visual aspect, sedimentation amount, microstructure and granulometry results, pH6-E showed the most promising results in terms of emulsion formation and stabilization.

3.3. Stabilization mechanisms dependency on the pH history of lignins emulsions

By aligning interfacial rheology and interfacial tension results with emulsions' stability, it appears that different stabilizing mechanisms could occur at the oil/water interface depending on the pH history of the aqueous lignin preparation.
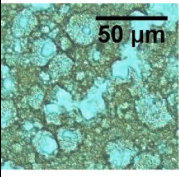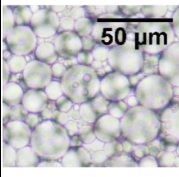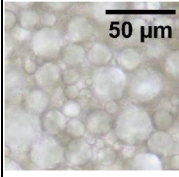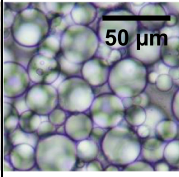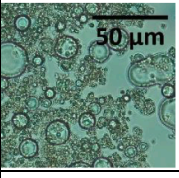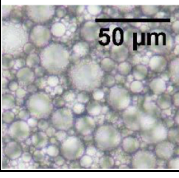
It is clear that pH3-E is composed of lignins particles which end-up forming aggregates and prevent stabilization of oil droplets. The incapacity of lignins particles in pH3-E to emulsify oil may be caused by their self-aggregation. This could be explained by the occurrence of hydrophobic interactions, Van Der Walls 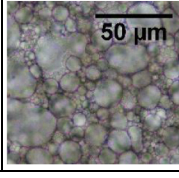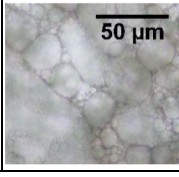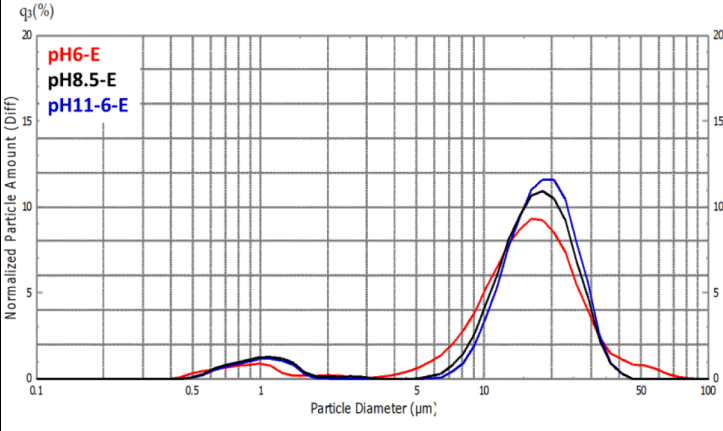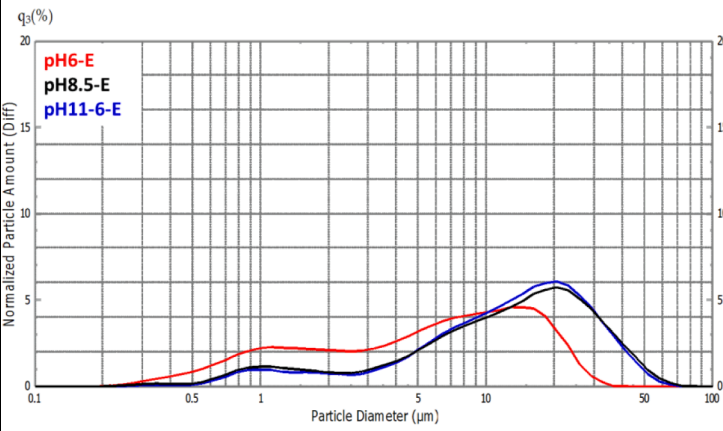or π- π stacking leading to a higher hydrodynamic volume because of the electrostatic repulsion between lignins [23]. According to both pendant drop measurements and to interfacial rheology, not much decrease was observed of the interfacial tension, nor increase of the rheological moduli for this dispersion, obviously indicating that in such a case lignins poorly impact the interface. Lignins dispersed in the aqueous phase with no intermediate pH readjustment and with a final pH of 6 are in the form of both particles and surfactants. Thus, during emulsification process lignin particles might position themselves around oil droplets, thus forming Pickering emulsions. It is currently reported that Pickering emulsions are more stable than O/W emulsions stabilized with surfactants because solid particles at the interface form a rigid film around the dispersed droplets increasing the kinetic stability of the emulsions [16]. In addition, particle adsorption at the oil/water interface is irreversible [50], once adsorption has occurred, therefore they are more resistant to Ostwald ripening and coalescence [21]. On the opposite, lignins dispersions with intermediate pH of 8.5 or 11 are mostly composed of lignin surfactants. Consequently, once emulsified, their adsorption at the interface is weaker and reversible, therefore presents less efficient emulsifying properties than Pickering emulsions leading to more sedimentation. This aligns with the work of Ghavidel and Fatehi [27] who demonstrated that depending on the pH of the emulsions, sulfoethylated lignins could be in the form of nanoparticles or surfactants thus targeting Pickering or non-Pickering emulsions could be achieved.

Consequently, stabilization at the interfaces results from a combination of both coexisting phenomena: lignin particles forming Pickering emulsions on one hand, and lignin surfactants forming non-Pickering emulsions on the other hand. In both cases, steric and electrostatic repulsion occur at the interfaces.

To summarize, this work undoubtedly evidenced that stabilization mechanism of lignins differ depending on the pH history of the continuous phase of the lignin emulsion which impacts their solubility state. Pickering emulsions with lignins in the form of particles or non-Pickering emulsions with lignins in the form of surfactants, as well as emulsions with both lignin particles and surfactants were obtained. Both mechanisms may occur when lignin particles and lignin surfactants

Fig. 3. Evolution of lignins emulsions after1 day and after 3 months.

Table 4

Optical microscopy photos (G ×400, scale 50 μm) and granulometry distribution (by volume) of the concentrated emulsified layer of pH3-E, pH6-E, pH8.5–6-E, pH11-6-E, after 1 day and after 3 months of stability.

Entry			pH3-E	pH6-E	pH8.5-6-E	pH11-6-E
A	Optical Microscopy G x 400 Scale bar 50 μm	After 1 day				
B		After 3 months				
C	Granulometry Distribution (by volume)	After 1 day				
D	Granulometry Distribution (by volume)	After 3 months				

coexist in the same emulsion. The appropriate balance between lignin particles and lignin surfactants could lead to a synergy of both mechanisms and give rise to the most stable emulsion. A schematic representation of the different stabilization mechanisms occurring at the oil/water interface depending on the form of lignins governed by their pH history is proposed in Fig. 4.

4. Conclusions

The present work allowed explaining how fractionated alkali lignins FL adsorb and stabilize the interface, as well as how they change interface's physical properties, depending on their solubility state which was evidenced by various interfacial properties investigations. The pH history of the dispersions has a considerable impact on the colloidal form of FL and, consequently, on the resulting properties like interfacial shear rheology and interfacial tension of corresponding aqueous dispersions. This work demonstrated that the pH history could impact the long-time stability of the emulsions.

Lignin particles do not reduce the interfacial tension; the ability for lignins to reduce Oil/Water interfacial tension is mainly governed by lignins soluble species: the more the FL at soluble state in solution the lower the final interfacial tension; in the most efficient case, the interfacial tension value reaches a low value (1.85mN/m) thus illustrating high interface activity for lignins surfactant species. In addition, lignin surfactants efficiency in reducing the interfacial tension could be affected either (1) simply because less surfactants are present in the dispersion; either (2) by the presence of lignin particles which could adsorb at the interface thus lowering the effective surface coverage and/or interactions occurring between lignin particles and lignin surfactants, resulting to the adsorption of these latter on lignin particles. In all cases, the amount of lignin surfactants adsorbed at the oil/water interface is reduced. These observations clearly evidence a different kinetic for the

pH3-E (*Initial*)
oil
water

pH3-E (*3 months*)
oil
water

pH6-E (*Initial*)
oil
water

pH6-E (*3 months*)
oil
water

pH8.5-6-E (*Initial*)
oil
water

pH8.5-6-E (*3 months*)
oil
water

pH11-6-E (*Initial*)
oil
water

pH11-6-E (*3 months*)
oil
water
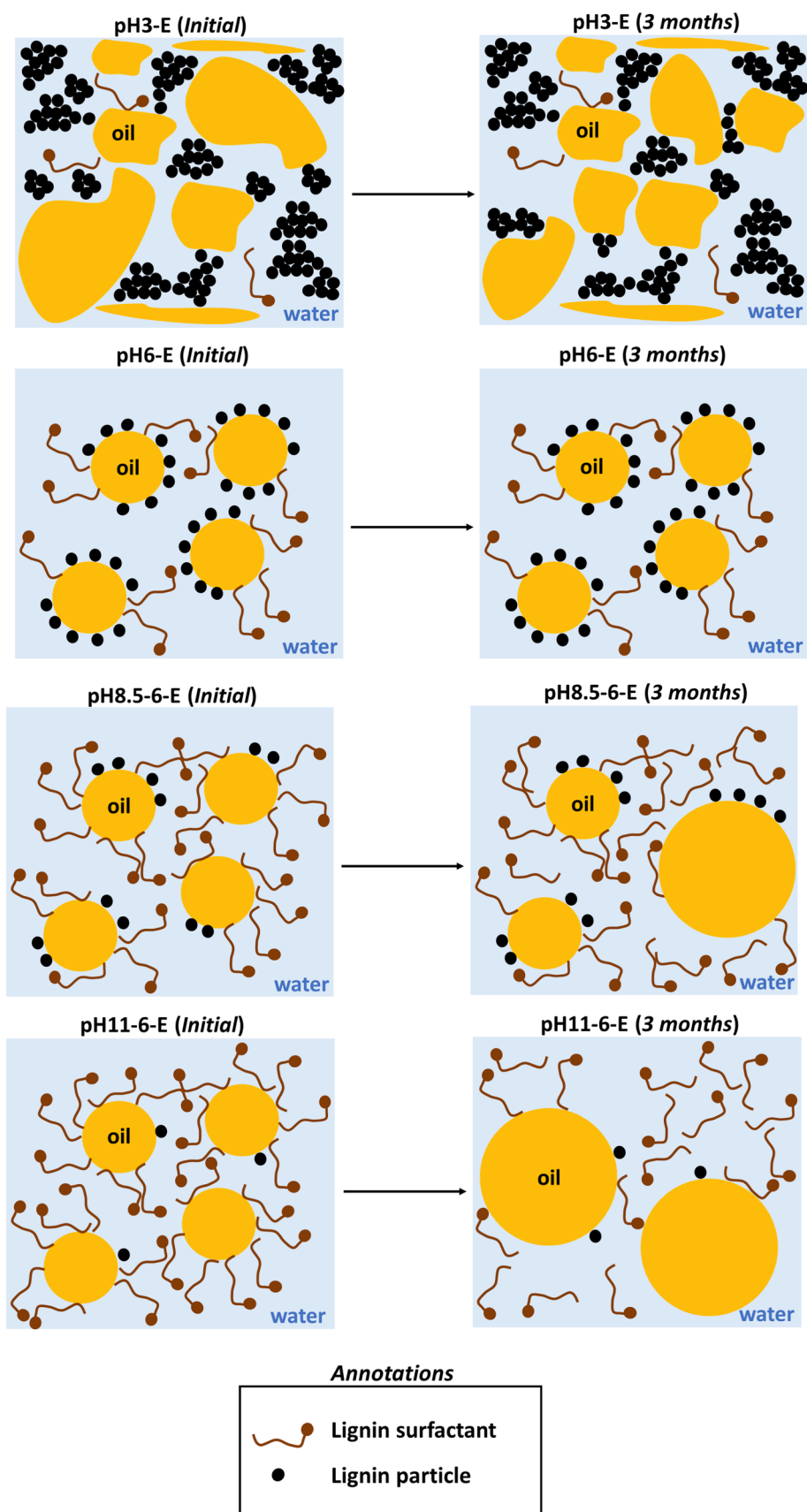
Annotations

Lignin surfactant

Lignin particle

Fig. 4. Proposed stabilization mechanism at the oil/water interface depending on the form of lignins governed by their pH history.

structuration of the interface depending on the form of lignins present in the dispersion: a suitable balance between the two forms of lignins in the initial aqueous dispersion evidences a rapid stabilization of the interface.

Different adsorption mechanisms are present at the interface depending on the pH history of lignins dispersions and therefore interfacial behavior and properties are governed by a combination of Pickering particles and surfactants species. The more soluble lignins within the dispersion, the more saturated the oil/water interface with lignin surfactants. Consequently, adsorption forces being higher than gravity forces, the interface rigidity is much stronger for lignin surfactants, thus becoming more favorable for resisting deformation and stabilizing the interface. In addition, the fast kinetic of lignin surfactants allows maintaining dense interfacial cohesion. On the contrary, when a high amount of lignin particles is present within the dispersion, stabilization of the interface is limited showing low viscoelastic properties; this may result from both the gravity forces occurrence, and the strong chemical affinity of particles with each others.

The stability monitoring over time demonstrated that the pH history of the lignins dispersion used for the preparation of emulsions had a great impact on the visual stability of the emulsions. No pH readjustment gave a phase shift because lignins were not adsorbed at the interface and couldn't efficiently stabilize oil droplets. The higher the intermediate pH of the dispersion the more soluble lignins in the continuous phase of emulsions, the higher the coalescence and the sedimentation of the emulsion, showing the decreased capacities of lignin surfactants to stabilize oil droplets. The competitive adsorption of lignins could change the emulsion's stability and promote different rates and degrees of coalescence depending on the prevailed form of lignins within the emulsion. We have shown that when a balance between both lignin forms, particles, and surfactants, was present in the continuous aqueous phase, the most stable emulsion was obtained regarding microstructure, oil droplets' diameter evolution and sedimentation.

The whole results proved that a competition between Pickering stabilization and non-Pickering stabilization occurs governed by pH history and that synergistic mechanisms with a well-balanced amount of lignin particles and lignin surfactants lead to enhanced stability of O/W emulsions. In the most favorable case, a strong interface providing a barrier against droplet coalescence and limiting sedimentation is interestingly evidenced. Emulsifying properties of lignins could therefore be modulated depending on their pH history and so their colloidal form.

CRediT authorship contribution statement

Caroline Hadjiefstathiou: Conceptualization, Methodology, Validation, Investigation, Writing – original draft, Visualization. **Audrey Manière:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Funding acquisition. **Joan Attia:** Supervision, Funding acquisition. **Florian Pion:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision. **Paul-Henri Ducrot:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision. **Ecaterina Gore:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision. **Michel Grisel:** Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2023.123030.

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