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# Phase separation and spreading dynamics of French vinaigrette

H. Benabdelhalim<sup>1, a)</sup> and D. Brutin<sup>1, b)</sup>  
*Aix Marseille Univ, CNRS, IUSTI, Marseille, France.*

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Phase separation can be observed when vinaigrette is poured on a kitchen plate under certain conditions. The phase separation in vinaigrette, which comprises olive oil, vinegar, and mustard for stabilization and taste, is characterized by the outward spreading of olive oil from the main film. This phase separation and the phenomena that trigger it were investigated in this study. Moreover, the spreading dynamics of the vinaigrette were examined by analyzing the spreading factor and its rate. The spreading of different formulations of the vinaigrette was probed in this regard by varying the mass concentration of vinegar from 10 % to 40 % and the amount of mustard from 0.1 g to 0.5 g. The emulsion films were placed on a white tile substrate with similar characteristics to those of a kitchen plate at 21 °C and a relative humidity of 50 %. The spreading dynamics followed two distinct regimes; increasing the vinegar concentration of mustard-free formulations led to decreases in the spreading factor of the first regime and the spreading rate. The addition of mustard had a similar effect on the spreading factor of the first regime. The variations in these two parameters were related to changes in the system viscosity. The latter was found to be a function of the mustard and vinegar concentrations. Phase separation occurred at vinegar concentrations below 30 % because of a competition between the spreading and the existing instabilities in the vinaigrette. This phenomenon did not affect spreading dynamics.

## I. INTRODUCTION

The formulation and preparation of salad dressings and sauces are of crucial importance on various scales ranging from industry to kitchens. These processes play a role in product performance parameters, such as stability, viscosity, texture, appearance, taste, and flavor. Generally, food mixtures are emulsions of two or more immiscible liquids in continuous and dispersed phases, with the dispersed phase consisting of small droplets. The thermodynamic instability of these emulsions necessitates the addition of a chemical or natural stabilizer (emulsifier) to suppress or impede phase separation. Emulsion science combines different disciplines such as physics, chemistry, biology, and engineering<sup>1</sup>, and is primarily concerned with ensuring the stability and handling of emulsions, and optimization of formulations. The processes and technologies related to the preparation and characterization of salad dressings and sauces have been thoroughly described by Ford et al.<sup>2</sup>, Sikora et al.<sup>3</sup>, and Campbell<sup>4</sup>. Several researchers have exhaustively reviewed food emulsions<sup>1,5,6</sup> and emulsions in a general manner in terms of their formation, stabilization, and various properties<sup>7-9</sup>.

The complex composition, structure, and dynamics of emulsions present various challenges that should be addressed by research; this has led to significant interest in understanding their properties. Food emulsions can be classified according to their distributions: oil droplets dispersed in an aqueous phase (denoted as O/W emulsions) or water droplets dispersed in oil (W/O emulsions). The distribution of W/O emulsions is similar to that of the salad dressing investigated in this study (vinaigrette), in that vinegar

can be viewed as a substitute for water (denoted as V/O herein).

The conversion of two immiscible liquids into an emulsion can be achieved by providing mechanical energy manually or via a high-speed mixer. In his book<sup>1</sup>, McClements has provided details regarding the selection of the mixing method in terms of the energy required to disperse droplets in the continuous phase. However, straightforward mixing of two immiscible liquids and ensuring their long-term homogeneity are difficult, because of the rapid phase-separation tendency of the two phases into two distinct areas with different densities for minimizing the system energy and migrating to a stable thermodynamic state.

In these systems, the droplets tend to merge with their neighbors. The driving force behind this process pertains to the thermodynamically unfavorable contact between the water and oil molecules, resulting in unstable emulsions. The physical mechanisms responsible for this instability after homogenization are flocculation, coalescence, creaming or sedimentation, and Ostwald ripening<sup>1</sup>. Chemical mechanisms that react to the nature of the components also exist.

A kinetically stable (metastable) emulsion can be created for a specific period by adding an emulsifier, a surface-active molecule with an amphiphilic character, that is, polar and non-polar regions in the same molecule. The role of the emulsifier is to adsorb to the droplets of the dispersed phase formed during homogenization to create a film that prevents direct contact between the droplets. Emulsifiers are characterized by the hydrophilic-lipophilic balance (HLB), which represents their ability to dissolve in water (low HLB), oil (high HLB), or both (medium HLB). Emulsifiers are typically added to improve the stability of a product and provide a satisfactory shelf life. Moreover, other ingredients such as thickening agents, gelling agents, weighting agents, and ripening inhibitors can be employed to stabilize emulsions. The use of one or more stabilizers depends on the instability of the emulsion and the desired texture of the product.

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<sup>a)</sup>Electronic mail: [houssine.benabdelhalim@gmail.com](mailto:houssine.benabdelhalim@gmail.com)

<sup>b)</sup>Electronic mail: [david.brutin@univ-amu.fr](mailto:david.brutin@univ-amu.fr)

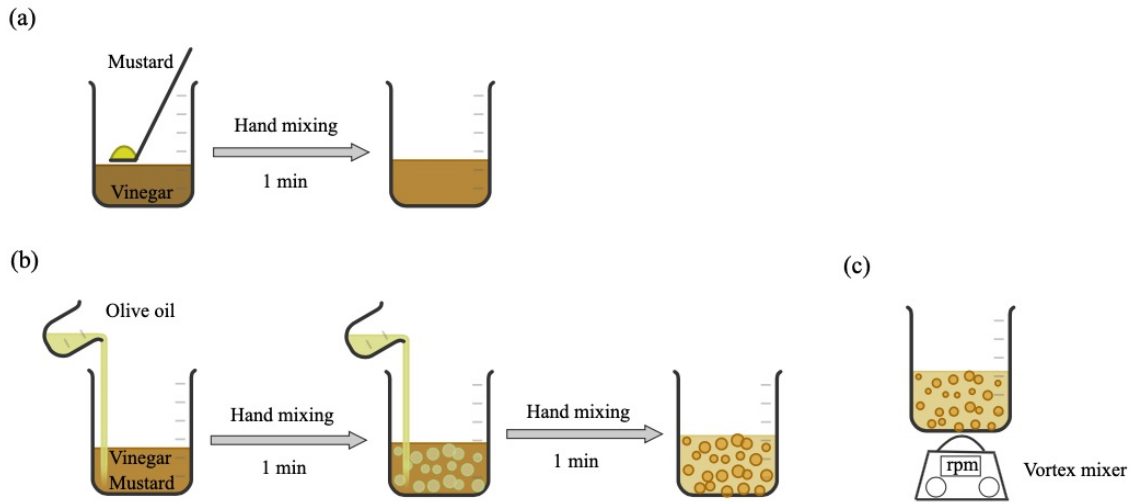


FIG. 1: Experimental formulation protocol featuring the (a) first, (b) second, and (c) third steps.

Vinaigrette is a mixture of oil, vinegar, mustard, and various spices. Olive oil and vinegar typically represent the continuous and dispersed phases, respectively, with mustard being added to ensure stabilization of the emulsion and to provide a slightly spicy taste. The emulsifying character of yellow mustard, which is used in industry as a stabilizer or emulsifier, is due to mucilaginous materials<sup>10</sup>. Mustard mucilage reduces the surface tension of water molecules. Moreover, the consistency of vinaigrette is attributed to these materials<sup>11</sup>. Cui et al.<sup>12</sup> showed that this mucilage behaves as a shear-thinning fluid. Milani et al.<sup>13</sup> examined the influence of yellow mustard on the viscosity and stability of mayonnaise sauce, and found that increasing the mustard concentration led to an increase in the mixture viscosity and an improvement in stability.

Lozano-Gendreau et al.<sup>14</sup> characterized and analyzed the physicochemical properties and flow behavior of a new vinaigrette formulation. The concentrations of oil and mustard, and storage time were found to significantly affect the stability and rheological behavior of the emulsion. The rheological behavior was described using a modified Herschel–Bulkley model, and the vinaigrette was determined to be a yield stress fluid whose threshold was a function of the three studied parameters. These results, in particular, can be used to develop new formulations with longer shelf lives for satisfying customer requirements.

As mentioned earlier, the preparation of an emulsion requires the contribution of agitation-induced mechanical energy. The speed and duration of agitation influence the stability of the emulsion; these aspects were examined by Chen et al.<sup>15</sup>, who found that stable emulsions could be achieved at high mixing speeds. This can lead to the dispersion of more droplets via minimization of their size, thus suppressing (or hindering) coalescence and flocculation. In addition, exceeding a particular limit was noted to result in detachment of the emulsifier from the droplets; this behavior also applied to the mixing time<sup>15</sup>.

The phase separation of V/O emulsions during their spreading on a horizontal substrate was investigated in this study. Phase separation occurs when one component stops spreading, and the other continues. Pouring a given quantity of vinaigrette leads to the outward spread of the oil from the main film. This phase separation occurs under specific formulation conditions depending on the concentration of vinegar and the presence or absence of mustard. Therefore, spreading experiments of vinaigrette with different formulations were performed on a substrate with identical characteristics to that of a plate at 21 °C and a relative humidity of 50 %. Humidity control was targeted because of its considerable influence on the spreading dynamics and the final surface at equilibrium<sup>16,17</sup>.

Although the spreading dynamics of fluids and emulsions have been rigorously investigated, certain issues persist. This phenomenon is omnipresent in the culinary, cosmetic, and construction materials industries, as well as in biomedical and forensic sciences. The spreading dynamics of food sauces and salad dressings have not been reported to date. Elucidation of this phenomenon can enable the development of new formulations and the optimization of the process of preparation on an industrial scale and in kitchens.

Classically, the spreading of a fluid on a horizontal and non-porous substrate can be described by the balance of the existing inertial, gravitational, capillary, and viscous forces. Several regimes appear during this spreading, with each regime being described by the competition between two dominant forces: a driving force and a dissipative one. The balance of these two forces yields a power-law evolution of the radius,  $R(t) = ct^n$ , where the spreading factor,  $n$ , is a function of the driving force and the nature of the dissipation. In addition to these forces, several instabilities that intervene depending on the nature of the fluid and the external parameters must be considered because of the complicated nature of the spreading dynamics.

Cazabat and Stuart<sup>18</sup> notably examined the spreading

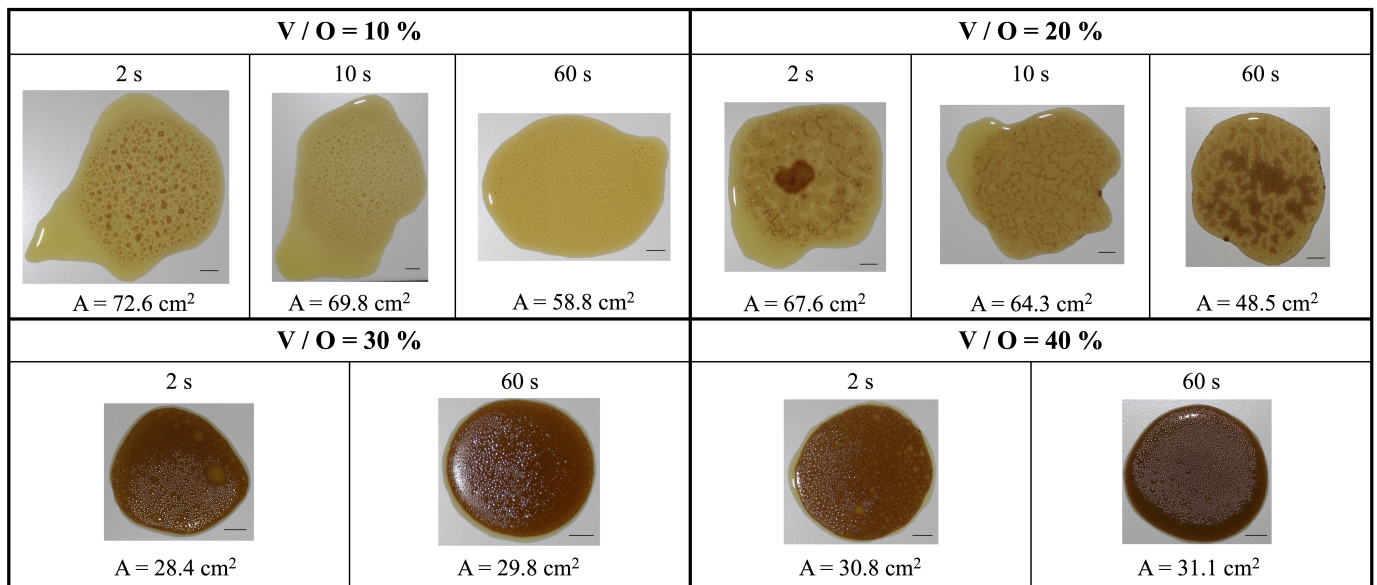


FIG. 2: Effects of mixing time and vinegar concentration on the spreading, phase separation, and homogeneity of vinaigrette films ( $4.16 \text{ g} \pm 2.2 \%$ ) on a white tile substrate at  $21 \text{ }^\circ\text{C}$  and a relative humidity of 50 %. "A" represents the final spreading area. (The scale bar represent 1 cm)

dynamics of silicone oil, and their dependence on the volume and roughness of the surface. Two power-law regimes were observed: a capillary regime with  $n = 1/10$  and a gravity regime with  $n = 1/8$ . Deblais et al.<sup>19</sup> examined the spreading of an O/W emulsion with two different formulations and surfactant-induced stabilization. The deposition of the emulsion on a glass substrate was performed using a rigid inclined slide to vary the speed and height of the slide. Several phenomena such as the inversion of the emulsion, coalescence, and the formation of a complex pattern were observed therein. Phase inversion and destabilization are related to the rate of spread and non-Newtonian behavior of emulsions.

The emulsion droplets impact and spreading have already been investigated by considering the surface energy at the liquid-liquid interface and rheological characteristic<sup>20</sup>. Piskunov et al.<sup>21</sup> showed in their study on Bingham emulsions, that the relationship between the effects of viscoplasticity, yield stress, and capillarity plays a major role in the description of the maximum spreading diameter. Kumar et al.<sup>22</sup> found that the emulsion viscosity increases with the percentage of water, which leads to a decrease in the final spreading diameter. Also, they reported an increase in the droplet contact angle at equilibrium.

This study was aimed at elucidating the spreading dynamics of vinaigrette as a function of vinegar and mustard concentrations. The spreading dynamics were analyzed at a fixed room temperature and relative humidity on a white tile substrate. The phase separation and the spreading factor,  $n$ , of the vinaigrette were probed under similar conditions.

## II. METHODS AND MATERIALS

Experiments were performed using a vinaigrette composed of extra virgin olive oil ( $\rho_o = 820 \text{ kg/m}^3$ ), balsamic vinegar of Modena ( $\rho_v = 964 \text{ kg/m}^3$ ), and Dijon mustard ( $\rho_o = 1124 \text{ kg/m}^3$ ), which were purchased from a supermarket. The high-quality balsamic vinegar of Modena is a Newtonian fluid with constant viscosity. It is mainly composed of sugars (glucose and fructose), organic acids, and volatile components. Its rheological behavior was exhaustively studied by Falcon et al.<sup>23,24</sup>. Emulsions were prepared using different formulations by varying the mass concentration of vinegar from 10 % to 40 % with a step of 5 %, and changing the amount of mustard from 0 g to 0.5 g with a step of 0.1 g. Spreading and phase separation behavior were examined on a white tile substrate with similar properties to those of a kitchen plate (roughness of  $0.93 \pm 12 \%$   $\mu\text{m}$ ). This substrate was selected because of difficulties involved in procuring a perfectly horizontal kitchen plate. All experiments were performed inside a glove box at a relative humidity of 50 %, which was regulated using a built-in system, and at room temperature ( $21 \text{ }^\circ\text{C}$ ). For white tile conditions, we have an equilibrium contact angle of:  $\theta_{oil} = 43.2^\circ \pm 5 \%$  and  $\theta_{vinegar} = 40.1^\circ \pm 8 \%$ . Consequently, both liquids have similar wetting proprieties.

Three steps were followed to prepare the vinaigrette. The first step involved manually mixing the vinegar and mustard with a spatula for 1 min. The mustard was well dissolved in the vinegar in this step. The second step involved progressive addition of the olive oil while manually mixing to disperse the vinegar droplets in the continuous phase (oil). In the third step, the vinaigrette was mixed at 4500 rpm using a vortex mixer for 10 s. The selection of the mixing time is discussed

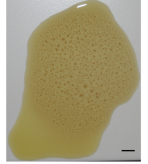
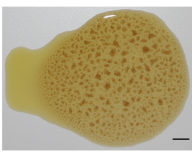
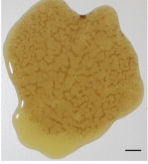
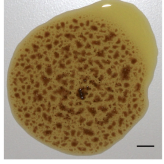
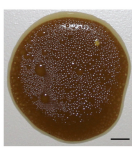

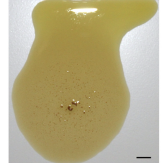
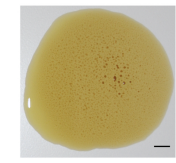
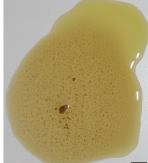
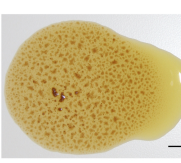
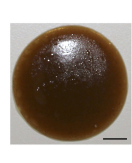
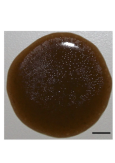
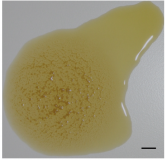
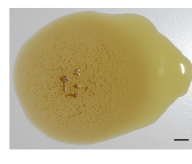
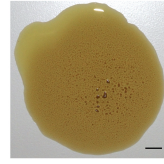
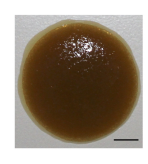
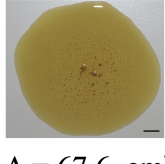
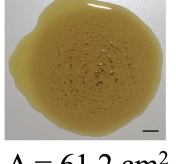
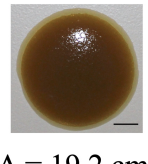
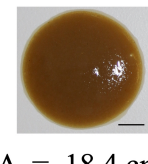
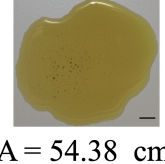
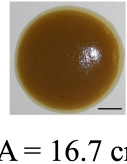
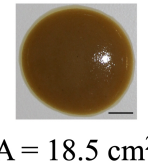
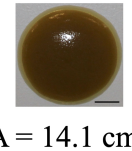
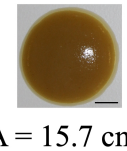
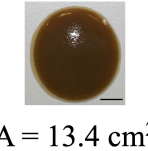
|             |     | V / O (%)  |   |   |   |   |   |
|-------------|-----|--|---|---|---|---|---|
|             |     | 10   | 15  | 20  | 25  | 30  | 40  |
| Mustard (g) | 0   | <br>A = 69.8 cm <sup>2</sup>    | <br>A = 73.1 cm <sup>2</sup>   | <br>A = 67.6 cm <sup>2</sup>   | <br>A = 61.3 cm <sup>2</sup>  | <br>A = 35.3 cm <sup>2</sup> | <br>A = 28.5 cm <sup>2</sup> |
|             | 0.1 | <br>A = 70.1 cm <sup>2</sup>    | <br>A = 70.8 cm <sup>2</sup>   | <br>A = 88.5 cm <sup>2</sup>   | <br>A = 68.2 cm <sup>2</sup>  | <br>A = 22.9 cm <sup>2</sup> | <br>A = 18.8 cm <sup>2</sup> |
|             | 0.2 | <br>A = 82.2 cm <sup>2</sup>    | <br>A = 84.9 cm <sup>2</sup>   | <br>A = 65.3 cm <sup>2</sup>   | <br>A = 20.4 cm <sup>2</sup>  |   |   |
|             | 0.3 | <br>A = 67.6 cm <sup>2</sup>   | <br>A = 61.2 cm <sup>2</sup>  | <br>A = 19.2 cm <sup>2</sup>  | <br>A = 18.4 cm <sup>2</sup> |   |   |
|             | 0.4 | <br>A = 54.38 cm <sup>2</sup> | <br>A = 16.7 cm <sup>2</sup> | <br>A = 18.5 cm <sup>2</sup> |   |   |   |
|             | 0.5 | <br>A = 14.1 cm <sup>2</sup>  | <br>A = 15.7 cm <sup>2</sup> | <br>A = 13.4 cm <sup>2</sup> |   |   |   |

FIG. 3: Effects of mustard and vinegar concentrations on the spreading and phase separation of French vinaigrette films ( $4.16 \text{ g} \pm 2.2 \%$ ) on a white tile at  $21 \text{ }^\circ\text{C}$  and a relative humidity of  $50 \%$ . (The scale bar represent  $1 \text{ cm}$ )

in the following section. Fig. 1 shows a schematic of the emulsion preparation protocol.

Immediately after its preparation,  $4.16 \text{ g} \pm 2.2 \%$  of the emulsion was poured on the substrate, which was placed on a balance (Mettler Toledo, MS6002TS) to ensure the use of identical initial amounts in the experiments. A fresh emulsion was prepared for each experiment ( $5 \text{ g}$  of oil and

vinegar + mustard). The spreading and phase separation behavior were monitored using a digital camera (Canon EOS 7D), with photographs being acquired every  $5 \text{ s}$  during the first  $5 \text{ min}$  and every  $1 \text{ min}$  until the end of the two-hour-long experiment. This experimental duration was selected to ensure that the equilibrium regime, during which the film stops spreading, was achieved. We chose components

concentrations and films area that enable a clear phase separation. The separation phenomena would have been observed for smaller or larger films. The film size is not the main parameter of this paper.

#### A. Effects of mixing time on phase separation during spreading

The first set of experiments was performed to determine the influence of the mixing time (third step) on the texture and phase separation of a mustard-free emulsion. Various mixing times—2, 4, 8, 10, 20, and 60 s—were employed with four V/O mass concentrations: 10 %, 20 %, 30 %, and 40 %.

Fig. 2 shows photos of an emulsion poured on the white tile substrate, which were acquired 2 h after their placement. The effects of the mixing time were monitored at concentrations of 10 % and 20 %. Phase separation decreased with time until it disappeared at 60 s. Longer durations of mixing clearly led to superior dispersion of vinegar as small droplets, which mitigated or impeded the instabilities that resist the flow (flocculation and coalescence), resulting in the oil readily dragging the droplets during its spread. The coalescence achieved at a concentration of 20 % was more pronounced than that at 10 %, because of the presence of more vinegar. Verbish et al.<sup>25</sup> reported that increasing the homogenization period leads to a decrease in the droplet diameter of the dispersed phase, which improves the emulsion stability. Phase separation was not observed at vinegar concentrations of 30 % and 40 %, because of close packing of the droplets. The excess oil that was not encapsulated spread outward, forming a crown at the edges of the emulsion. This effect appeared in all the experiments conducted with varying mixing times.

Similar emulsions containing the emulsifier (mustard) were subsequently examined. Mustard is used for stabilization in the classic vinaigrette recipe. A mixing time of 10 s was selected based on previous studies. Chen et al.<sup>15</sup> examined the stability of a W/O emulsion with an emulsifier, and noted the existence of a possible risk related to the detachment of the emulsifier from the oil–water interface at long mixing times. However, the stability of the emulsion increased with time below a threshold homogenization time<sup>15</sup>. Although emulsion stability was not directly analyzed, phase separation was related to it. This is comprehensively described in the next section.

### III. RESULTS AND DISCUSSIONS

The effects of vinegar and mustard concentrations on phase separation during the spreading of vinaigrette are discussed herein. First, the visual aspect of this separation is analyzed and linked to the emulsion stability. The second part describes the characterization of the spreading dynamics of the vinaigrette.

#### A. Visualization of the phase separation

Emulsions such as vinaigrette are often prepared domestically. These products are also prepared on an industrial scale following precise formulation protocols to obtain stable emulsions. Mustard was used in this study to stabilize the vinaigrette. Recipes of this product was designed to provide an excellent taste, desired texture, and stable emulsions for specific periods.

Pouring a vinaigrette (homemade or industrial) onto a plate results in its spreading until it reaches an equilibrium state. During this spreading, the two phases that constitute the dressing can separate depending on the concentrations of vinegar and mustard. The formulations investigated in this study were designed to explain this phenomenon and prevent phase separation. Fig. 3 shows the different emulsion films obtained after equilibrium, which represents the complete stoppage of spreading. Emulsions with V/O concentrations of 35 % were not presented because they behaved similarly to those with concentrations of 30 % and 40 %. Fig. 4 shows the spreading of a vinaigrette prepared using 25 % vinegar and 0.1 g of mustard on the white tile substrate. The plate was horizontal with an accuracy of  $\pm 0.05^\circ$ . The anisotropy of the film spreading come from the inherent irregularities on the plate. Phase separation occurred 1 min after the formation of the film. The vinegar droplets formed aggregates and sediments during spreading. In addition, the spreading velocity decreased over time, and the flow could no longer drag the vinegar. Consequently, olive oil separated and spread outward from the main film.

This phase separation can be explained based on the competition between the spreading flow and the characteristic instabilities of emulsions (flocculation, coalescence, and sedimentation or creaming); the latter factors cannot be appropriately visualized on a thin film, which varied between 0.55 mm and 3.4 mm in thickness in this study. Sedimentation is a common instability that is encountered in food emulsions<sup>26</sup> because of differences in the densities of the dispersed and continuous phases. The densities of oil and vinegar used in this study were  $820 \text{ kg/m}^3$  and  $964 \text{ kg/m}^3$ , respectively. The vinegar droplets with their higher densities move downward via "sedimentation" because of gravitational forces acting on them<sup>27</sup>. The speed at which an isolated drop of vinegar moves can be expressed using Stokes' law:

$$v_{Stokes} = \frac{2gr^2(\rho_{vinegar} - \rho_{oil})}{9\eta} \quad (1)$$

where  $\eta$  is the continuous phase viscosity and  $r$  is the droplet radius. Equation [1] is obtained by balancing the downward force owing to gravity,  $F_g = 4/3\pi r^3(\rho_v - \rho_o)g$ , and the upward force due to hydrodynamic friction,  $F_f = -6\pi\eta rv$ , acting on the droplet. As a rule of thumb, an emulsion with a sedimentation rate lower than  $0.5 \text{ mm.day}^{-1}$  is considered stable<sup>1</sup>. Stokes' law indicates that sedimentation can be impeded by decreasing the droplet size, which could result in a longer shelf life and stability. It should be noted that equation [1] is an approximation, and the experimental measurements of sedimentation likely exhibit considerable

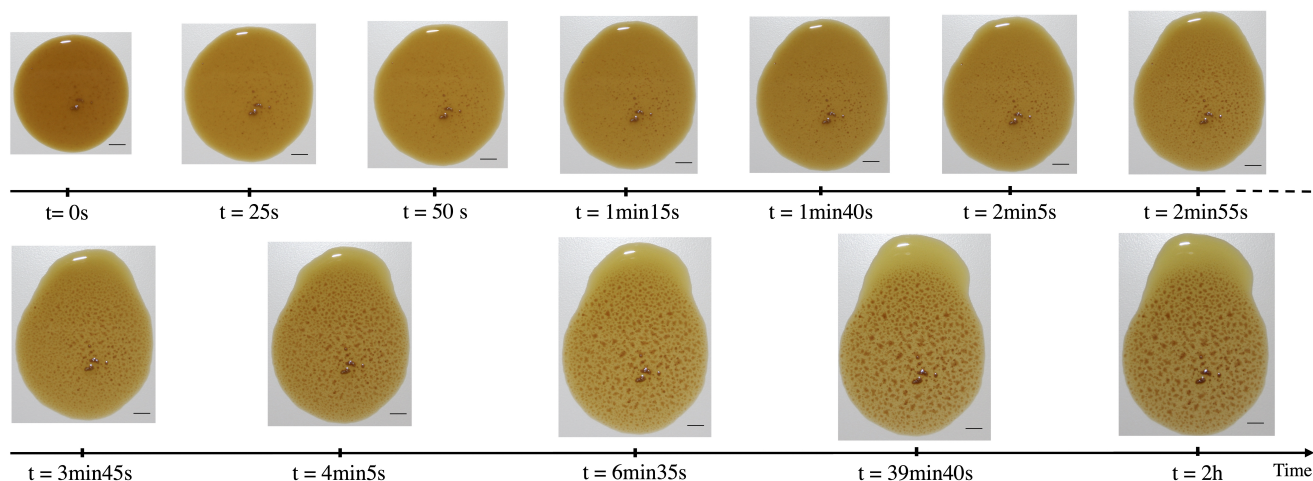


FIG. 4: Time lapse of the spreading of a vinaigrette film ( $4.16 \text{ g} \pm 2.2 \%$ ,  $V/O = 25 \%$ ,  $m_{\text{mustard}} = 0.1 \text{ g}$ ) on a white tile substrate at  $21 \text{ }^\circ\text{C}$  and a relative humidity of  $50 \%$ , showing spreading and phase separation. (The scale bar represent  $1 \text{ cm}$ )

differences in this regard. This is because of the omission of droplet fluidity and the no-slip assumption of the Stokes' equation with respect to the interface between the droplet and the surrounding fluid<sup>28</sup>. In addition, dilution of the system leads to a higher sedimentation or creaming velocity than that of a concentrated emulsion<sup>29</sup>. The decreasing sedimentation velocity in concentrated emulsions is due to the droplet–droplet interactions and the crowding effect<sup>30</sup>.

Flocculation, which refers to the association of two or more droplets in the dispersed phase, can be either advantageous or disadvantageous in terms of emulsion stability. In vinaigrette, flocculation accelerates the process of sedimentation by the creation of larger aggregates, which increases the viscosity. However, a vinaigrette with desirable texture can be achieved by controlling this phenomenon. Droplet collisions occur owing to the presence of movements that are induced by Brownian motion, gravitational separation, or an applied mechanical force<sup>1</sup>.

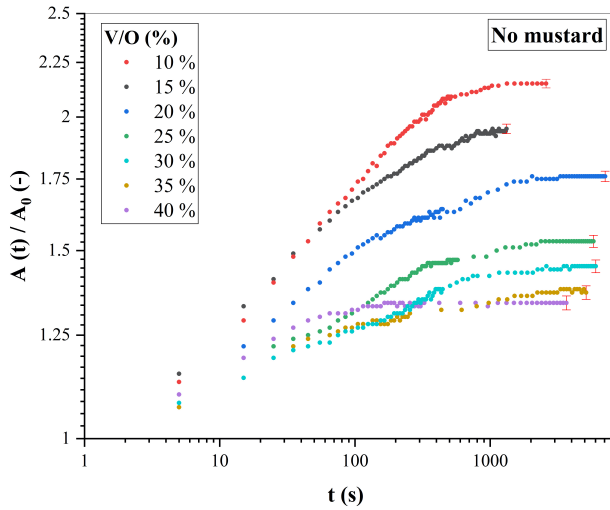
Coalescence, a process during which one or more droplets merge<sup>31,32</sup>, is considered to be the primary phenomenon by which emulsions achieve their thermodynamically stable states, owing to a reduction in the contact area between vinegar and oil. Similar to flocculation, coalescence accelerates sedimentation. Moreover, coalescence can occur only when the droplets are sufficiently close, and the film that separates them is broken.

The use of an emulsifier, the generation of small droplets, and the selection of an appropriate concentration can assist in the prevention of sedimentation or creaming, flocculation, and coalescence. These phenomena were not characterized and measured according to the different formulations. However, their definitions were used to explain the phase separation that occurred during the spreading of vinaigrette.

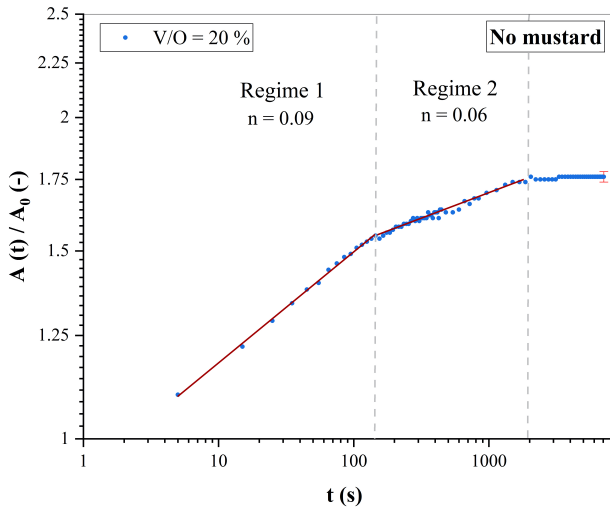
At  $V/O$  mass concentrations below  $30 \%$ , phase separation was pronounced and started disappearing above a specific mustard concentration threshold Fig. 3. Increasing the concentration of mustard (emulsifier) hindered the forces

generated by flocculation and coalescence, leading to the disappearance of the resistant forces, and straightforward dragging of vinegar by the oil. Toward the end of these experiments, that is  $2 \text{ h}$  after the preparation of the vinaigrette, the vinegar was noted to adhere to the substrate in scenarios involving low concentrations of mustard. This adhesion is related to sedimentation; hence, this particular instability affects phase separation. An additional morphological change was induced by the increase in mustard concentration, which is related to changes in texture and an increase in viscosity. These resulted in a creamy emulsion in which the excess oil spread outward and formed a crown at the edge of the emulsion, similar to scenarios involving  $V/O$  concentrations above  $30 \%$ . This phenomenon was previously observed by Forester et al.<sup>33</sup> and was explained by the fact that the droplets diameter of the dispersed phase is larger than the thickness of the precursor film, which causes the precursor film to spread out ahead of the interline demarcating the dispersed phase. At vinegar concentrations above  $30 \%$ , phase separation no longer occurred in the mustard-free samples. However, the addition of mustard prevented the formation of the crown during the spreading because of the sufficient amount of vinegar for encapsulating the oil and the high viscosity due to the presence of the mustard.

Fig. 3 enables visualization of the effects of mustard on the morphologies of the final films. In the mustard-free emulsions with low concentrations of vinegar, the vinegar droplets aggregated because of attractive forces related to coalescence and flocculation. At low vinegar concentrations and increasing mustard concentration, the lack of aggregates was observed owing to the emulsifying quality of mustard. However, the excess mustard that was not dissolved in the vinegar appeared as small fragments scattered in the thin films. Beyond a certain amount of mustard, its "thickening" quality was observed, which led to a change in texture, resulting in a creamy emulsion.



(a) Spreading kinetics



(b) Spreading dynamics

FIG. 5: (a) Spreading kinetics of vinegar–oil emulsions ( $m = 4.16 \text{ g} \pm 2.2 \%$ ) on a white tile substrate at  $21 \text{ }^\circ\text{C}$  and a relative humidity of  $50 \%$ . (b) Log–log plot featuring time evolution of the rescaled area of an equilibrated film at  $21 \text{ }^\circ\text{C}$  and a relative humidity of  $50 \%$ . The red lines represent visual guides for two different slopes. A typical error bar is shown at a single point in each curve.

## B. Vinaigrette spreading dynamics

Fig.5.a shows the evolution of the film area, "A," normalized by the initial area "A<sub>0</sub>" over time (that is, the spreading rate) of mustard-free formulations with different mass concentrations of vinegar ranging from  $10 \%$  to  $40 \%$  with a step of  $5 \%$ . Because the film area was not perfectly circular, the evolution of the surface was monitored instead of the radius. A<sub>0</sub> represents the initial area obtained immediately after pouring the emulsion. At equilibrium, an increase in the dispersed phase concentration led to a decrease in the spreading rate because of an increase in emulsion

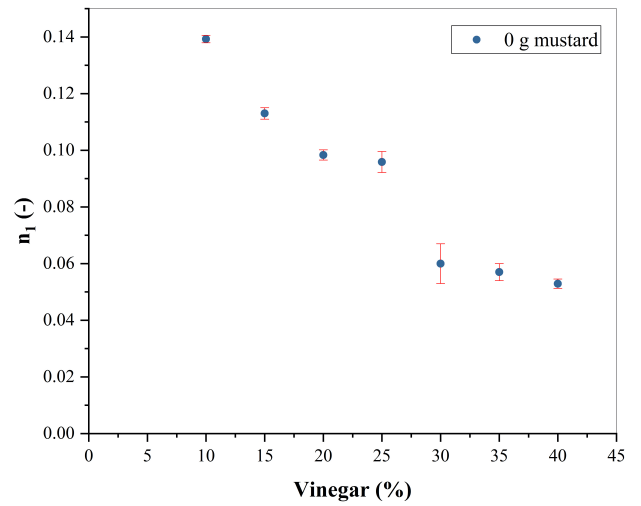


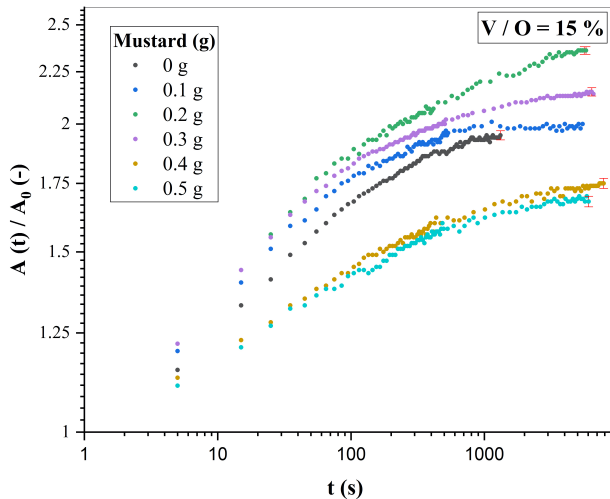
FIG. 6: Spreading factor of mustard-free vinegar–oil emulsions ( $m = 4.16 \text{ g} \pm 2.2 \%$ ) as a function of the vinegar concentration at  $21 \text{ }^\circ\text{C}$  and a relative humidity of  $50 \%$ .

viscosity. An increase in concentration implies the presence of more droplets, resulting in more friction with the continuous phase. R. Chanamai and D. McClements<sup>29</sup> have shown that the apparent viscosity of an O/W emulsion increases with increasing concentration of the dispersed phase, and that the viscosity of a diluted emulsion is independent of the shear rate, in contrast to that of a condensed emulsion. Additionally, emulsions with larger droplets were noted to exhibit low viscosities compared to those of emulsions with small droplets. E. Forester et al.<sup>33</sup> analyzed the spreading of an emulsion of water dispersed in silicone oil with an emulsifier, and observed a similar phenomenon in terms of a decrease in the spreading rate with increasing concentration of water droplets. However, the phase separation did not influence the spreading dynamics of these formulations, unlike that observed by H. Benabdelhalim and D. Brutin<sup>17</sup>, who examined the spreading of human blood pools. However, phase separation is influenced by the concentration of each component.

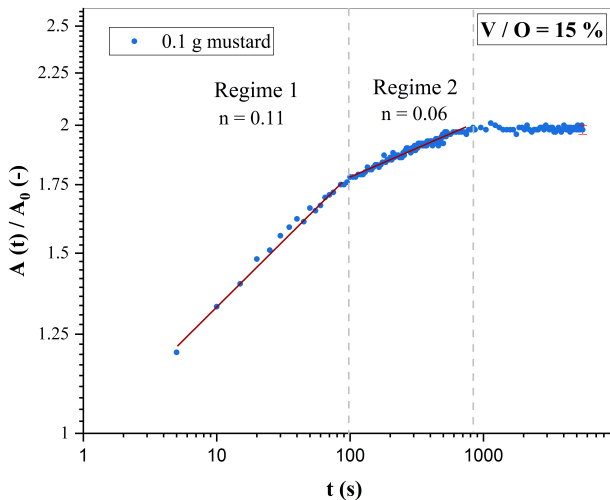
The spreading dynamics of the vinaigrette with or without mustard follow similar dynamics to those of pure fluids<sup>33</sup>; therefore, they can be described by a power law,  $A(t)/A_0 = ct^n$ . E. Forester et al.<sup>33</sup> examined emulsion drops with an emulsifier, and found that the radius of the drops varied with a spreading factor of  $1/10$ , as is often observed in pure fluids<sup>34,35</sup>. This value of  $1/10$  resulted from the absence of gravitational effects; moreover, the drops formed hemispheres at equilibrium. In the present scenario, the gravitational forces were not negligible, and the final shape was pancake-like instead of hemispherical. The spreading dynamics of an emulsion with  $20 \%$  vinegar were characterized by two distinct regimes, as shown in Fig.5.b; the first regime was driven by gravitational forces and countered by viscous forces with a spreading factor,  $n$ , of  $0.09$ , and the second capillary–viscous regime represented the termination of the spreading with a factor of  $0.06$ . The spreading factor



of the first regime was examined to analyze the spreading dynamics as a function of the vinegar concentrations, because it perfectly described the influence of viscosity. Fig.6 shows the evolution of the spreading factor as a function of the vinegar concentration. This factor was determined using a power-law fit. The error bars accounted for the uncertainty of the fit and the errors that occurred during image processing. A decrease in this factor with increasing vinegar concentration was observed. The increase in this concentration presumably delayed the spreading, similar to the spreading rate, because of changes in the viscosity. These results are consistent with those obtained by E. Forester et al.<sup>33</sup>.



(a) Spreading kinetics



(b) Spreading dynamics

FIG. 7: **(a)** Spreading kinetics of vinegar–oil emulsions with different amounts of mustard ( $m = 4.16 \text{ g} \pm 2.2 \%$ ,  $V/O = 15 \%$ ) on a white tile substrate at  $21 \text{ }^\circ\text{C}$  and a relative humidity of  $50 \%$ . **(b)** Log–log plot featuring time evolution of the rescaled area of an equilibrated film at  $21 \text{ }^\circ\text{C}$  and a relative humidity of  $50 \%$ . The red lines are visual guides that represent two different slopes. A typical error bar is shown at a single point in each curve.

The spreading dynamics of formulations with mustard were subsequently analyzed. First, the influence of mustard on formulations with  $15 \%$  vinegar is considered (Fig.3), followed by a discussion of the other scenarios based on the spreading factor of the first regime. Their visual aspects have been discussed in the first sub-section. Fig.7.a shows the evolution of the spreading rates over time for different amounts of mustard. The arrangement of the curves does not appear to assist elucidation of the influence of mustard. The addition of mustard certainly creates a layer around the vinegar droplets, which suppresses (or delays) coalescence and flocculation, resulting in a smaller force that slows the flow, and the dragging of the droplets by the continuous phase. This explains the increase in the spreading rate in scenarios involving  $0.1 \text{ g}$  and  $0.2 \text{ g}$  of mustard and  $15 \%$  vinegar. The use of  $0.3 \text{ g}$  to  $0.5 \text{ g}$  of mustard led to a decrease in the spreading rate owing to the thickening character of the mustard (increase in viscosity). This critical mass of the mustard depends on the concentration of vinegar (Fig.3).

The spreading dynamics of these formulations were also described by two regimes, as shown in Fig.7.b. The use of  $0.1 \text{ g}$  of mustard led to the first regime with a spreading factor,  $n = 0.11$ , and a second, slower regime with  $n = 0.06$ . Therefore, both regimes exist in mustard-incorporated samples. As in the experiments conducted without mustard, the effects of the added mustard were elucidated by analyzing the first spreading factor corresponding to all vinegar concentrations. Fig.8 shows plots of the spreading factor as a function of vinegar and mustard concentrations. At a fixed amount of mustard, effects similar to those obtained without mustard were observed in terms of a decrease in the spreading factor with increasing vinegar concentration. The evolution of the spreading factor as a function of the quantity of mustard appears to be linear, and decreases with the quantity of mustard. This evolution was expressed using the two equations described below based on linear fitting.

For concentrations between  $10 \%$  and  $40 \%$ , the following relationship applies:

$$n_1 = \alpha_1 + \beta_1 \times m_{\text{Mustard}} \quad (2)$$

The two coefficients, which are a function of the vinegar concentration ( $C_v \%$ ), are expressed as follows:

$$\alpha_1(C_v \%) = \alpha_{11} + \alpha_{12} \times C_v \% \quad (3)$$

$$\beta_1(C_v \%) = \beta_{11} + \beta_{12} \times C_v \% \quad (4)$$

This modalization is an approximation of the observed evolution, which considers the variations occurring at low concentrations of vinegar. However, it enables the characterization and description of the emulsifying characteristics of mustard. The decrease in the spreading factor with the vinegar concentration and amount of mustard is linked to changes in texture and viscosity. Given that addition of mustard leads to a more homogeneous vinaigrette, the droplets remain well dispersed in the emulsion.

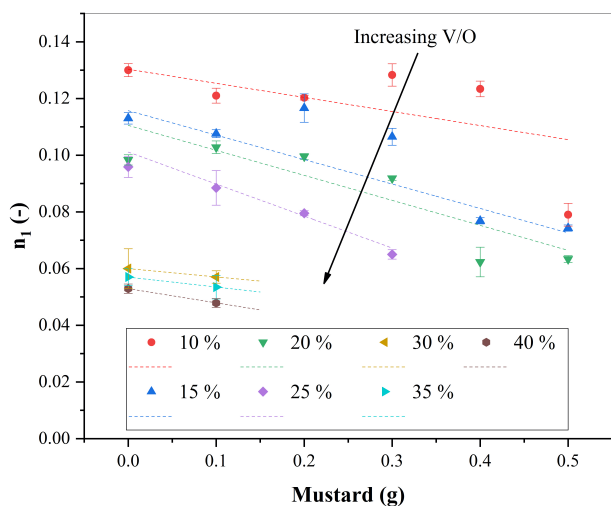


FIG. 8: Spreading factor of vinaigrette ( $m = 4.16 \text{ g} \pm 2.2 \%$ ) as a function of the vinegar and mustard concentrations at  $21 \text{ }^\circ\text{C}$  and a relative humidity of  $50 \%$  on a white tile substrate. The dashed lines represent linear fits.

These results suggest that spreading can be used to visualize the changes in the apparent viscosity of emulsions and their concentration-dependent variations. The spreading factor was selected as an indicator because the spreading rate is related to the nature of the substrate, which can provide more practical results. However, the analysis of the first spreading regime enabled mitigation of the effects of the slight difference in roughness observed on the different surfaces. In addition, phase separation during spreading can be a quick indicator of the presence or absence of certain instabilities.

#### IV. CONCLUSIONS

The spreading dynamics and phase separation of vinaigrette were investigated. These phenomena were described based on the outward spreading of a portion of olive oil from the main film. A formulation protocol was developed in this regard. Immediately after the preparation of the vinaigrette, films were placed on a white tile substrate inside a glove box with relative humidity and temperature control. All films had identical initial masses and were formed at  $21 \text{ }^\circ\text{C}$  and a relative humidity of  $50 \%$ . Different formulations were prepared by varying the mass concentration of vinegar from  $10 \%$  to  $40 \%$ , and the mass of mustard from  $0.1 \text{ g}$  to  $0.5 \text{ g}$ .

The spreading dynamics of the vinaigrette were analyzed based on the spreading rate and spreading factor of the first (gravitational–viscous) regime. In mustard-free formulations, the spreading rate and spreading factor decreased with increasing vinegar mass concentration because of an increase in the mixture viscosity, which was due to the droplet–droplet interactions and the friction between the dispersed and continuous phases. The addition of mustard primarily affected the emulsion stability and viscosity. At fixed mass concentrations of vinegar (less than  $30 \%$ ), the spreading rate

increased with the amount of mustard until a threshold was reached; the spreading rate decreased beyond this point. This threshold is a function of the vinegar concentration. However, the spreading factor appeared to decrease with the amount of mustard. This variation was attributed to the change in viscosity related to the thickening of the mustard.

Phase separation occurred because of the competition between the oil flow during the spreading of the vinaigrette and the interactions between the droplets of the dispersed phase (vinegar). These interactions are the origin of the instabilities that separate two-phase emulsions. The addition of mustard impeded these instabilities and prevented phase separation because of its emulsifying and thickening tendencies. This phase separation did not influence the spreading dynamics.

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#### AUTHOR CONTRIBUTIONS STATEMENT

H.B. performed the experiments, analyzed the data, and prepared the manuscript. D.B. supervised the research, analyzed the data, and reviewed the manuscript.

#### DATA AVAILABILITY

The data that support the findings of this study are available within the article or from the corresponding authors.

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