

**FINAL REPORT**

# Formation of Detergent Stabilized Oil-Water Emulsion in Bilge Water and a Method to Thwart the Same

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Manoj K. Chaudhury  
Monicka Kullappan  
*Lehigh University*

**April 2023**

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| <b>REPORT DOCUMENTATION PAGE</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                               |                                             |                                                  |                                         | <i>Form Approved</i><br>OMB No. 0704-0188                        |  |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------|---------------------------------------------|--------------------------------------------------|-----------------------------------------|------------------------------------------------------------------|--|
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| <b>1. REPORT DATE (DD-MM-YYYY)</b><br>22/04/2023                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                               | <b>2. REPORT TYPE</b><br>SERDP Final Report |                                                  |                                         | <b>3. DATES COVERED (From - To)</b><br>4/4/2018 - 12/30/2022     |  |
| <b>4. TITLE AND SUBTITLE</b><br><br>Formation of Detergent Stabilized Oil-Water Emulsion in Bilge Water and a Method to Thwart the Same                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                               |                                             |                                                  | <b>5a. CONTRACT NUMBER</b><br>18-C-0011 |                                                                  |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                               |                                             |                                                  | <b>5b. GRANT NUMBER</b>                 |                                                                  |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                               |                                             |                                                  | <b>5c. PROGRAM ELEMENT NUMBER</b>       |                                                                  |  |
| <b>6. AUTHOR(S)</b><br>Manoj Chaudhury<br>Monicka Kullappan                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                               |                                             |                                                  | <b>5d. PROJECT NUMBER</b><br>WP18-1074  |                                                                  |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                               |                                             |                                                  | <b>5e. TASK NUMBER</b>                  |                                                                  |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                               |                                             |                                                  | <b>5f. WORK UNIT NUMBER</b>             |                                                                  |  |
| <b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b><br>Lehigh University<br>Chemical and Biomolecular Engineering<br>111 Research drive, Iacocca Hall<br>Bethlehem, PA 18015                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                               |                                             |                                                  |                                         | <b>8. PERFORMING ORGANIZATION REPORT NUMBER</b><br><br>WP18-1074 |  |
| <b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b><br>Strategic Environmental Research and Development Program (SERDP)<br>4800 Mark Center Drive, Suite 16F16<br>Alexandria, VA 22350-3605                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                               |                                             |                                                  |                                         | <b>10. SPONSOR/MONITOR'S ACRONYM(S)</b><br>SERDP                 |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                               |                                             |                                                  |                                         | <b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b><br>WP18-1074       |  |
| <b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b><br>DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                               |                                             |                                                  |                                         |                                                                  |  |
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| <b>16. SECURITY CLASSIFICATION OF:</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                               |                                             | <b>17. LIMITATION OF ABSTRACT</b><br><br>UNCLASS | <b>18. NUMBER OF PAGES</b><br><br>71    | <b>19a. NAME OF RESPONSIBLE PERSON</b><br>Manoj Chaudhury        |  |
| <b>a. REPORT</b><br><br>UNCLASS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | <b>b. ABSTRACT</b><br>UNCLASS | <b>c. THIS PAGE</b><br>UNCLASS              |                                                  |                                         | <b>19b. TELEPHONE NUMBER (Include area code)</b><br>610-739-1932 |  |

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## Acronyms (and symbols):

OW: refers to Oil in Water emulsion

PTBS: Poly-4 tert(butyl)styrene

PAM: Polyacrylamide

HLB: Hydrophilic Lyophilic balance

DLVO: Derjaguin-Landau-Verwey-Overbeek

pH : Potential of hydrogen

pKa: Dissociation constant

UV : Ultraviolet

pdf: Probability distribution function

Surfactants: Dodecanoic acid and Brij 35 mixture

Alkanes: Decane, Dodecane, Octane.

Aromatics: Xylenes, toluene, styrene, benzene

Nectar: saturated sugar solution (fructose and glucose mixture in water)

COOH: Carboxylic acid group

Et Oxide: Ethylene oxide

W : Water

O : Oil

CH : Hydrocarbon

D: Experimental diffusivity,  $\text{m}^2/\text{s}$

$D_e$ : Theoretical diffusivity,  $\text{m}^2/\text{s}$

$\kappa$  = the inverse Debye length

$\psi$  = electrical potential near a surface

$\psi_0$  = surface potential

$E = \psi_0 \kappa$  is the electrostatic field at the surface

$\langle \Delta P \rangle$  = root mean square of hydrodynamic pressure fluctuation

$\gamma$  = interfacial tension

$d$  = size of emulsion droplet

$d_{mk}$  = emulsion drop size in the inertial turbulent region

$d_{mV}$  = emulsion drop size in the viscous turbulent region

$\rho_C$  = the density of the continuous phase.

$\varepsilon$  = turbulent energy dissipation rate.

pdf - probability distribution function for pressure fluctuation  $[P(\Delta p)]$

$\pi$  = the surface pressure of a spread monolayer

$a$  = the area per molecule of a spread

monolayer  $E_s$  = interfacial elasticity

$G(k)$  = displacement spectrum with respect to wavenumber  $k$ .

## Extended Abstract

Emulsification of an oil in salinized water was studied under turbulent and agitation-free conditions in the presence of a mixture of an ionic and a non-ionic surfactant. The properties of the air-water and the oil-water interfaces were investigated using the methods of du-Nouy ring, drop resonance vibrometry and Langmuir film balance that allowed pinpointing the relevance of certain interfacial properties in emulsification. Estimation of the droplet size and its distribution from the nanometer to micrometer range was carried out with optical microscopy, acoustic attenuation spectroscopy and continuous hydrodynamic flow fractionation. These measurements provided the platform for the comparison of the emulsion droplet size with those predicted from the fluctuation of the dynamic stress in the turbulent water via a capillary-hydrodynamic model. While such a comparison was reasonably meaningful for micron size emulsion droplets, production of nanometer size droplets was beyond such a rudimentary expectation. We thus carried out systematic investigations into other factors that contribute to emulsification under both agitated and agitation free conditions. An important finding of these studies is that the infusion of air bubbles that profoundly enhance the hydrodynamic fluctuation produce mainly submicroscopic emulsion droplets, while a fluctuation inhibiting water-soluble polymer has the opposite effect. Furthermore, while a hydrophilic polymer dissolved in water enhances the ripening of the droplets with time, hydrophobic polymer in oil thwarts aging, plausibly by osmotic backpressure and interfacial stiffening, which, upon compression, acts against surface tension, thereby decreasing the chemical potential of the trapped oil molecules inside the droplet. These effects are similarly observed in spontaneous emulsifications, that is when a layer of oil containing the additives is deposited upon the surface of the aqueous phase in the absence of any external work input. Micro and/or Nano emulsions are formed when an organic liquid gently comes in contact with water in the presence of a surfactant, even with a positive interfacial tension. Many years of research made

it clear that the driving force for spontaneous emulsification arises from the differences of the bulk chemical potentials of various components, which triggers various non-equilibrium coupled transport processes, such as diffusion and hydrodynamic fluctuation. While extraordinary theoretical developments have taken place that attempt to describe the emulsification processes within the formalisms of global equilibrium and non-equilibrium thermodynamics, the local processes underlying the spontaneous emulsification, however, still remain elusive. In this research, we attempt to shed light on some of the local processes that involve the transfer of surfactant as well as molecular water from one phase to another (i.e. water to oil), subsequent formation of inverted emulsion and its evolution to oil-in- water emulsion as they cross the phase boundary. These processes lead to either strong or weak fluctuation of component concentration just below the interface that announces fast (athermal) diffusion of the emulsion droplets farther into the bulk of water. These studies have been able to identify the relevant interfacial and hydrodynamic parameters, careful controls of which should be valuable in thwarting emulsification in various practical settings.

## Objectives

Detergent stabilized oil in water (OW) emulsions are ubiquitous. While in certain applications, long time stability of these emulsions is desired, it can also be a nuisance in other situations. Stable emulsions cause concerns in various Armed Forces bilgewater applications as the extraction of water from the oily wastewater is expensive and becomes technically challenging. Understanding the causes underlying the formation of such emulsions should provide strategies to suppress the formation of such emulsions altogether. Furthermore, when they are formed, water can be extracted from the emulsion inexpensively, and efficiently. While the main objective of this research is to develop the fundamental understanding of OW emulsification under turbulent and agitation free conditions, we will also develop methods to thwart such emulsifications by taking advantage of the knowledge gained from the same studies.

## Technical Approach

The approach of this research is guided by the two sciences: surface chemistry and fluctuating hydrodynamics. specifically focusing on two important mechanisms of emulsification identified by us, as discussed below.

### Turbulence induced emulsification

Emulsification under turbulent hydrodynamics is, seemingly, easiest to understand. Here, the size of the emulsion is bounded between two length scales. The smallest length scale corresponds to the dimension of the smallest eddie:  $d_K \sim \nu^{3/4} \varepsilon^{-1/4}$ ,  $\nu$  being the kinematic viscosity of the continuous phase, while  $\varepsilon$  is the rate of work supplied to the fluid in to order to keep it in a turbulent state. This is the Kolmogorov scale, the role of which in emulsification process has undergone various degrees of evolution. In the Hinze scale, the size (diameter,  $d$ ) of the droplet arises from the balance between the root mean square fluctuation of the hydrodynamic  $\langle \Delta P \rangle$  and

the capillary ( $P_C$ ) pressures, i.e.  $\langle \Delta P \rangle \sim P_C$ ; where,  $\gamma$  is the oil-water interfacial tension,  $\langle \Delta P \rangle \sim \rho_c (\varepsilon d)^{2/3}$ ,  $P_C = 4\gamma/d$ , and  $\rho_c$  is the density of the continuous phase. The above scaling leads to a diameter of the droplet as  $d_H \sim \gamma^{3/5} / (\varepsilon^{2/5} \rho_c^{3/5})$ . The pressure fluctuation driven emulsification is the first step to the process, which is taken over by the viscous stress at the smallest scale of the turbulent eddies. The average droplet size is expected to lie between the Hinze and Kolmogorov scales,  $d_K$  and  $d_H$ , which has received ample supports in various studies.

### **Spontaneous Emulsification**

While the above process in an agitated fluid is conceptually appealing, the science of emulsification without an external agitation is quite rich. Without going into an extensive discussion of the vast literature existing on the subject, we point out only a few noted contributions. Sterling and Scriven suggested that certain Fourier modes of the interface excited by thermal fluctuation could be unstable in conjunction with diffusion across the interface and the Marangoni effects caused by the spatial variation of concentration of a surfactant. The ensuing instability leads to an interfacial turbulence that is further accentuated by a chemical reaction occurring in one of the phases. Another predominant viewpoint is that a surfactant could supersaturate if the bulk phases intermix via mutual diffusion, which would alter the standard chemical potential of the surfactant near the interface thus prompting the formation of emulsified phases. The above brief survey indicates that various non-equilibrium dynamics are expected to prevail at the interface, before all the chemical potential are equilibrated in the entire system. Thus, if the science of emulsification is to be advanced beyond its current status, we need to pay special attention to what happens at the borderline of equilibrium and non-equilibrium physics.

## Phase I

### **Thermodynamic and Kinetic Pathways to Agitated and Spontaneous Emulsification**

Monicka Kullappan and Manoj K. Chaudhury\*

Department of Chemical and Biomolecular Engineering

Department of Materials Science and Engineering, Lehigh University

Bethlehem, Pennsylvania 18015, United States

**Abstract** Emulsification of an oil (Dodecane and Diesel fuel) in salinized water was studied under turbulent and agitation-free conditions in the presence of a mixture of an ionic and a non-ionic surfactant. The properties of the air-water and the oil-water interfaces were investigated using the methods of du-Nouy ring, drop resonance vibrometry and Langmuir film balance that allowed pinpointing the relevance of certain interfacial properties in emulsification. Estimation of the droplet size and its distribution from the nanometer to micrometer range was carried out with optical microscopy, acoustic attenuation spectroscopy and continuous hydrodynamic flow fractionation. These measurements provided the platform for the comparison of the emulsion droplet size with those predicted from the fluctuation of the dynamic stress in the turbulent water via a capillary-hydrodynamic model. While such a comparison was reasonably meaningful for micron size emulsion droplets, production of nanometer size droplets was beyond such a rudimentary expectation. We thus carried out systematic investigations into other factors that contribute to emulsification under both agitated and agitation free conditions. An important finding of these studies is that the infusion of air bubbles that profoundly enhance the hydrodynamic fluctuation produce mainly submicroscopic emulsion droplets, while a fluctuation inhibiting water-soluble polymer has the opposite effect. Furthermore, while a hydrophilic polymer dissolved in water enhances the ripening of the droplets with time, hydrophobic polymer in oil thwarts aging, plausibly by osmotic backpressure and interfacial stiffening, which, upon compression, acts

against surface tension, thereby decreasing the chemical potential of the trapped oil molecules inside the droplet. These effects are similarly observed in spontaneous emulsifications, that is when a layer of oil containing the additives is deposited upon the surface of the aqueous phase in the absence of any external work input.

## **1. Introduction**

Detergent stabilized oil in water emulsions are ubiquitous. While in certain applications, long time stability of these emulsions is desired, it can also be a nuisance in other situations. Stable emulsions cause concerns<sup>1-10</sup> in various wastewater treatments as the removal of oil-free water is expensive and becomes technically challenging. Understanding the causes underlying the formation of such emulsions should provide strategies to counter it, thus relieving some of the efforts required to purify oil-contaminated water.

From the point of view of surface thermodynamics, an oil-water interface spontaneously disintegrates to form stable emulsion if there is any tendency for its interfacial tension to be negative.<sup>11</sup> This could result from strong hydrophilicity of one of the functionalities and/or strong electrostatic charging<sup>12</sup> of the interface. On the other hand, if an oil water interface possesses a positive interfacial tension, conventional wisdom dictates that emulsification should not be a spontaneous process, as the system energy would increase at the cost of creating numerous new interfaces. This scenario is valid if the entire system evolves quasistatically towards equilibrium, and when the free energy of dispersion compensates for the increase of interfacial free energy. In reality, emulsification occurs, largely, under non-equilibrium conditions assisted by the difference of the chemical potentials between the initial and final states.<sup>3, 14</sup> While the chemical potentials are equilibrated, various diffusive, chaotic and dissipative transports are induced, which lead to the formation of various kinetically stable morphologies.<sup>13-31</sup> When oil is dispersed in water, or

vice versa, with a surfactant dissolved in one of the phases, emulsification occurs readily<sup>32-44</sup> with agitation even when the interfacial tension is positive. The issues of agitated and agitation-less emulsification are highly relevant to bilge water that is transferred to a central oily waste holding tank from the point of generation through sliding-shoe and cavity feed pumps.<sup>4</sup> As the bilge water is transferred, there are splashes into the tank and sloshing with ship motion that often lead to non-negligible agitation.<sup>4-77</sup> The oily water in the bilge also ages with time, where emulsification can proceed, seemingly, in the absence of any external agitation.

There are many facets to the problem, the first one being the stability of emulsion. The emulsion droplets undergo random motion in the aqueous phase via thermal and turbulence<sup>39</sup> induced diffusion; thus colliding and often fusing with each other with a concomitant ripening mediated by the well-known Ostwald process.<sup>45-50</sup> As the droplets grow large enough, they float on the surface of water.<sup>31</sup> One of the primary forces that destabilizes an emulsion is of the Van der Waals type. The stabilizing repulsive forces arise from the electrical, structural and thermal fluctuation forces.<sup>48-50</sup> While many decades of research have shed considerable light on the above issues, one problem that is still shrouded with mysteries is spontaneous emulsification, which occurs in systems with positive interfacial tension in the absence of external agitation. Considering the age of this field, it is not surprising that the underlying science has gained substantial amount of maturity at various levels. Yet, a comprehensive portfolio is still missing with which to make unequivocal predictions of the distribution of the droplet size and the stability of the emulsions formed under different conditions. The scientific understanding should be such that the droplet size, its distribution and its aging kinetics could be tempered with the control of few molecular, kinetic and thermodynamic parameters. Such a knowledge is of paramount importance in minimizing the incorporation of oil in water in the presence of surfactant under various settings. Before we provide an outline of the

research presented here, we survey briefly the main physico-chemical status of emulsion science that has developed upon the foundations of numerous pioneering studies.

### **1.1 Roadmap**

The objective of the overall research is to bridge the gap between surface science and fluctuating hydrodynamics in the science of emulsification and to identify new questions for further studies. In order to achieve this goal, we address two seemingly different aspects of emulsification, with and without agitation.

The literature is replete with excellent studies on the turbulence induced emulsification, in which the Kolmogorov-Hinze models are the starting points in predicting the size of the droplets and its distribution. While the field is substantially enriched with these studies,<sup>32-44</sup> further research is warranted for various reasons. For example, we do not find convincing evidence with such a seemingly trivial issue as whether the aqueous phases in the previous experiments were always free of dissolved air. This is an important point to consider, as we know that air bubbles produced during agitation could generate secondary waves,<sup>55-57</sup> including the shock waves upon collapse that could have profound implications in emulsion formation. Furthermore, the oil droplets produced via hydrodynamic fluctuation could also interact with the original fluctuation, thus modifying the state of turbulence itself. All these could lead to an interesting scenario in which the parent fluctuation and the kinematics of what is produced are coupled to some extent. Our specific study is directed towards predicting the distribution of droplet size, for which what is needed is a method that would allow measurements of the statistical distribution of dynamic stress fluctuation while the emulsification takes place. Dynamic pressure fluctuations in turbulence have been measured previously.<sup>58,59</sup> We intended to accomplish a similar objective with meticulous controls of several input parameters using a home-built reactor to be discussed below.

One key parameter that enters in the emulsification process is the interfacial tension of the oil and water in the presence of a surfactant, which can be measured using one of many standard methods.

<sup>1-9,11,22,25,29,66-68</sup> In the absence of agitation, the interfacial tension progresses slowly to a stable value, which is attributed to the diffusion and surface reorganization kinetics. While such type of data is useful for the properties of emulsions in an undisturbed situation, dynamic interfacial tension should play an important role when the interface fluctuates rapidly, as in turbulence. We thus resorted to a method in which a liquid drop is rapidly oscillated by forcing a pressure fluctuation inside it. At a critical volume, the drop exhibits resonance oscillation, which, in conjunction with the frequency of excitation, allows estimation of interfacial tension in a dynamic condition (Appendix 1.2).

The model system used in this study consisted of an oil (e.g. dodecane and diesel fuel) dispersed in water. Water was salinized to a seawater level concentration (0.6 M of salt, NaCl) in the presence of a mixture of surfactants consisting of an anionic (Dodecanoic acid) and a non-ionic (Brij-35 amphiphilic) surfactant. The compositions of water, oil, salt and surfactant are typical and consistent with the recommendation for the simulation of bilgewater.<sup>4</sup> From the surface tension measurements, as will be described below, the concentration of surfactant was slightly below the critical micellar concentration. Nevertheless, the resulting emulsion was rather stable, i.e. it did not exhibit any visible separation of oil from the emulsion over a period of one to two months.

In order to further elucidate the properties of these surfactants, they were spread over the surface of salinized water, following which the surface pressure-area plots<sup>60-63</sup> were constructed using a Langmuir Trough. Experiments conducted in the quiescent and slightly agitated conditions along with certain polymeric additives provided valuable insights into the stability of surfactant

monolayers, which were also useful in understanding their roles in the formation and the aging of the emulsion droplets (Appendix 3.4).

The emulsions prepared at different turbulent strengths were analyzed using three different methods: optical microscopy that allowed a visual examination of the emulsion droplets, acoustic attenuation spectroscopy<sup>64-66</sup> (APS) and capillary hydrodynamic fractionation<sup>65</sup> (CHDF) that allowed, in tandem, estimation<sup>66</sup> of the droplet size from about 5 nm to 100  $\mu$ m. These distributions were then compared with the predictions based on turbulent stress fluctuation (Appendix 3.6).

One unique observation of these studies was that nanosized emulsions are always formed, even though their formation would require more intense hydrodynamic fluctuations than those found experimentally. This observation led us to interrogate the process of emulsification in the absence of any external agitation. Even here, irrespective of the degree of care taken to avoid spurious agitation, nano-sized emulsions were always formed; however, their formation and evolution could be tempered with the control of their interfacial properties. At the end, we find that both emulsifications under agitation and without it share several common features, so much so, that the word “agitation-less” may not have any real meaning in emulsion science. The paper is organized as follows. The Results and Discussion section presents the summary of all the experiments performed in this research, with adequate introduction and analysis. Elaborate descriptions of the experimental methods are provided in the Appendix (A). After consolidating the main points of this research, several references are cited. As the literature is vast, we had no choice, but to omit, regretfully, many important references.

## 1.2. Results and Discussions

### 1.2.1. Surface Tension of the Oil-Water Interfaces

We measured the interfacial tension of salinized water against air, dodecane and diesel fuel using the well-known du Nouy ring method in the presence and absence of the mixed surfactants dissolved in the aqueous phase. Dodecane was used as received, whereas diesel oil was used after passing it through a column packed with activated alumina.

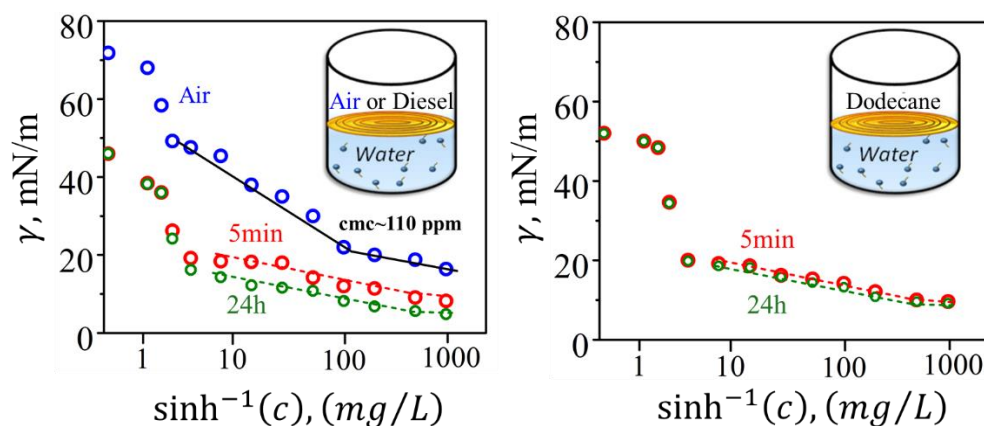


**Figure 1.1.** Interfacial tensions of two oil-water interfaces are shown as a function of the concentration ( $c$  in mg/L) of the mixed surfactant (Dodecanoic acid and Brij-35, equal weight ratios) in the aqueous phase. The dashed lines are meant to guide the eyes.

Dodecanoic acid and Brij-35 were dissolved in water at equal weight ratios, but at different net concentrations, before a layer of oil was deposited over it. In all cases, the du Nouy ring was first immersed in the aqueous phase, which was gradually pulled out of the oil-water interface to measure the surface or interfacial tension. The surface tensions of the air-water and oil-water interfaces were 72 mN/m, 52 mN/m (with dodecane<sup>67, 69</sup>) and 45 mN/m (with diesel<sup>7, 66-68</sup>) respectively, which decreased, as expected with the increase of the concentration of surfactant in the aqueous phase. In some cases, the interfacial tension reached a stable value quickly (i.e. in air and dodecane), whereas in some other cases, these values changed even after a day (Figure 1.1).

Dynamic evolution of interfacial tension is a ubiquitous phenomenon, which has been nicely elucidated in the recent studies<sup>7,8</sup> highlighting the roles of diffusion and interfacial adsorption kinetics.

All the surface tension values are plotted against concentration ( $c$ ) using the inverse sine hyperbolic function (i.e.  $\sinh^{-1}(c)$ ) for the reason that it captures the zero values, which is not possible with a logarithmic function. As this function converges to  $\ln c$  at high concentration, cmc and surface excess quantities can be estimated without any loss of generality. From the surface tensions measured in air, the cmc is estimated to be about 110 ppm. Similar measurements made against the two oils did not permit us to estimate the cmc in unequivocal way, although it appears that the cmc is shifted to higher values. The measurements with the oil water interfaces were limited by the fact that the surfactants separate from water if concentrations were higher than 1000 ppm. While a detailed analysis of the various scenarios expected of the oil-water interface are beyond the scope of and the need for the current work, a crucial point is that the concentration of surfactant used here is such that the formation of emulsion mediated by the solvation of the micelles would be minimized, thereby allowing us to focus on other relevant mechanisms.

### **1.2.2. Rapidly fluctuating interface**

The slow evolution of the interfacial tension as observed with the above method does not say much of what happens when an interface fluctuates rapidly, as in turbulence, where fast bulk and interfacial dynamics drive the system to reach a stable state rapidly. In order to gain information of a rapidly fluctuating interface, we opted for a method based on drop vibrometry. The general method is to vibrate a drop with an external time varying force, in which either the volume or the frequency is kept fixed. The drop exhibits a resonance vibration when the excitation frequency matches with one of the spherical harmonics of the drop.<sup>71-76</sup> At that condition, the frequency ( $\square$ )

of vibration is proportional to  $(\gamma/m)^{1/2}$ , where  $m$  is the effective mass of the drop. The proportionality factor depends upon the eigen mode of spherical harmonics, which, according to Rayleigh scheme, is  $\ell = 2$  in the current experiments. Previous studies showed that the role of the contact angle<sup>72</sup> of the drop can be successfully described by defining an effective mass as in equation 1:

$$m = \frac{4\rho V}{(2-3\cos\theta-\cos^3\theta)} \quad (1)$$

Where,  $V$  is the volume of the resonating droplet,  $\theta$  is the contact angle of the liquid droplet on the support, and  $\rho$  is the density the liquid drop that is oscillated by inducing a sinusoidal pressure fluctuation inside it, as described schematically in Figure 1.2. Briefly, a drop of a given

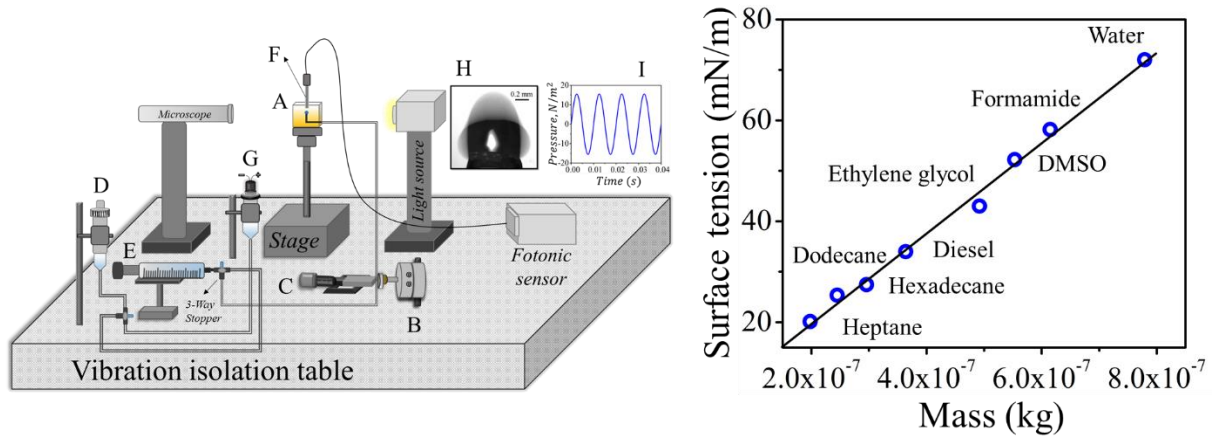


**Figure 1.2. (Left)** Schematic representation of the drop resonance experiment for studying the properties of the dynamic interface of an aqueous liquid droplet in the pool of oil. The drop is inflated at the tip of the needle, which is attached to a sample cell (A) filled with oil. The drop is subjected to a sinusoidal fluctuation of pressure, generated by a mechanical oscillator (B), the tip of which periodically squeezes and relaxes a flexible rubber tube against a solid block, which can be advanced or receded by a micromanipulator (C). The injection system consists of a Gilmont syringe (D) with a capacity of 1 mL. When the liquid is depleted inside this syringe, it can be backfilled through another normal glass syringe (E) through a three-point junction. The fluctuation of the surface of the drop is monitored with either a Foton probe or an accelerometer (F) placed above the drop. The dynamic pressure fluctuation is recorded using an accelerometer (G) that is glued against a thin rubber film covering the end of one of the tubes. A static microscopic image (H) of an aqueous drop containing the surfactant in a pool of dodecane. Next to it, a typical pressure pulse is shown (I). **(Right)** The critical mass of a liquid drop that exhibits resonance at a driving frequency of 100 Hz in air is proportional to its surface tension.

liquid was formed at the tip of a needle and then inflated while a pressure fluctuation of amplitude 15 Pa and frequency 100 Hz was already imposed upon it. The drop was allowed to grow until it exhibited a resonance, corresponding to the  $\ell = 2$  spherical harmonic mode (Figure 1.2). This mode is referred to as the first pumping mode, in comparison to the  $\ell = 0, 1$  modes, which correspond to symmetric deformation and the translation of the drop. Although the resonance condition could easily be identified using an ordinary video microscopy, it could be ascertained more accurately using a displacement sensor (an optical probe or an accelerometer) placed slightly above the drop, the response of which was displayed on a computer screen. When the drop was slightly inflated or deflated from its visually observed resonant state, the sensor above it exhibited maximum output at a critical droplet volume. Experiments performed with various liquid drops in air ascertained that the critical mass of drop of a given liquid at resonance is indeed proportional to its surface tension (Figure 1.2).

**Table 1.1.** Interfacial Tensions of Oil-Water Interfaces

| Oil phase | Salt water phase | Volume of the droplet ( $\mu\text{L}$ ) | Dynamic Interfacial Tension ( $\text{mN/m}$ ) |
|-----------|------------------|-----------------------------------------|-----------------------------------------------|
| Diesel    | - Surfactant     | 1.6                                     | 44.4                                          |
| Diesel    | + Surfactant     | 0.2                                     | 4.1                                           |
| Dodecane  | - Surfactant     | 2.2                                     | 52.0                                          |
| Dodecane  | + Surfactant     | 0.3                                     | 6.7                                           |

While similar experiments could be carried out with water drop in a pool of oil (Table 1.1), interpretations of these results are not as straightforward as for the pure liquids, since the frequency of vibration depends on the viscosities of two phases and the Eigen modes in a rather complex

way. Fortunately, however, when these parameters are held fixed, the interfacial tension is proportional to only the volume of the droplet.<sup>74-76</sup> Since the interfacial tension of given oil-water interface is known *a priori*, the interfacial tensions of the same system with surfactant added in water could be determined using the above consideration.

The cases of immediate interests are the dodecane-water and diesel-water interfaces with 100 ppm of the mixed surfactant (dodecanoic acid and Brij-35) present in water. We note that the dynamic interfacial tensions of the oil-water interfaces are somewhat lower than the values estimated from the du-Nouy ring method. The former values have been used for the analysis of some of the results described below.

### **1.2.3. Studies on the stability of the dynamic surfaces**

Surface pressure-area constructs provide useful information<sup>60-63</sup> about the properties of a monomolecular film of a surfactant spread at air-water interface. The particular property of interest to us is the stability of the monolayer while its interfacial area decreases, as, such a scenario is expected in a typical emulsification process. The existing literature<sup>29, 30</sup> suggests that the competition of various forces (hydrodynamic, Marangoni and osmotic stresses) resulting from the transient gradients of concentrations of various species could lead to the formation of regions of local compression and expansion of the interface. Various biophysical studies with lipid membrane suggest that compression of a lipid monolayer beyond a critical value leads to folding instability,<sup>63</sup> which, as discussed later in this text, should encourage formation of nano-sized emulsions.

We studied the  $\pi$ - $A$  isotherms of the surfactants on a Langmuir trough (Figure 1.3), in the presence and absence of two high molecular weight hydrophobic polymers: PDMS (polydimethylsiloxane, MW= 308,000 Da) and PTBS (Poly(4-tert-butylstyrene), MW= 1,500,000 Da). In a separate

experiment, the  $\pi$ - $A$  isotherm was also measured by mildly agitating the surface of water with the help of a slowly rotating disk in contact with it.

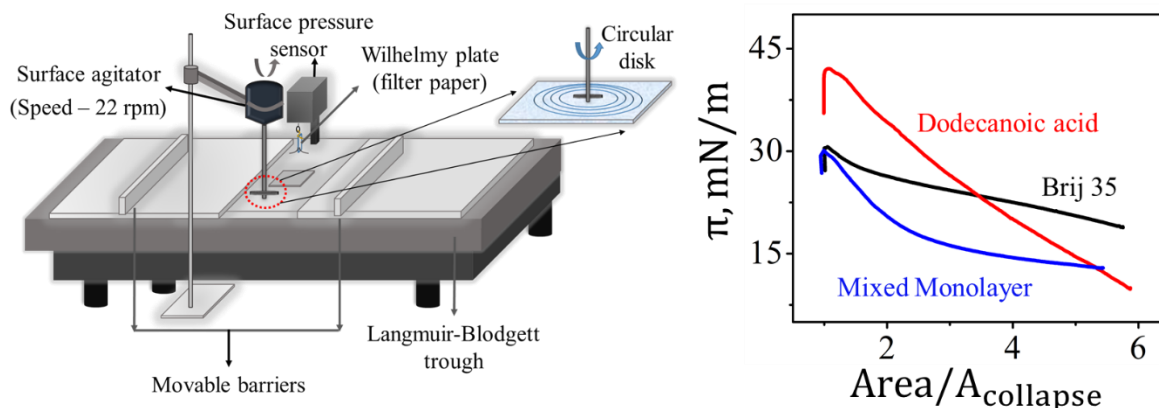


**Figure 1.3. (Left)** Schematic of a Langmuir-Blodgett trough used for the surface pressure area constructs in the presence and absence of surface agitation by depositing a small amount of the surfactant on the surface of water and compressing it using two Teflon bars. The surface tension was measured using a Wilhelmy plate method, where a pre-wetted blotting paper was used as the measuring plate. In this setup, the surface can be agitated by gently rotating a small aluminum disk contacting the surface of water. **(Right)** Surface pressure-Area constructs obtained with Dodecanoic acid, Brij-35 and their mixture. All the monolayers collapse when the surface is sufficiently compressed.

These surface pressure-area ( $\pi$ - $A$ ) constructs were made using the standard procedure, i.e. starting with a surfactant dispersed on the surface of the salinized water at an initial surface pressure of about 10 mN/m, it was compressed using two sliding bars till the monolayer collapsed.

However, unlike the standard method, in which the monolayer is compressed very slowly to approximate a quasistatic condition, we compressed the monolayer at a moderate rate of 250 cm<sup>2</sup>/min in order to minimize the problem of surfactant dissolution, particularly with the more soluble non-ionic surfactant.

The results summarized in Figure 1.3 show that  $\pi - A$  construct (note: from here onward, we will use the term “construct” instead of “isotherm” as the later implies a thermodynamically stable state, which is not necessarily the case with some of the experiments described here) depends upon

the composition of the monolayer. In particular, the construct of the mixed monolayer in the expanded state is parallel to that observed with the non-ionic surfactant (Brij-35), while it is parallel to that of the ionic surfactant (Dodecanoic acid) in the compressed state. This pattern of behavior is further accentuated when the interface is mildly agitated by rotating a small disk in contact with the surface. Qualitatively, these results indicate that the composition of the mixed surfactant changes as it is progressively compressed, in that the non-ionic surfactant is depleted with the decrease of interfacial area. While such an experiment could not be performed with an oil-water interface, we may surmise that both the ionic and non-ionic surfactants would be depleted from the surface accompanied with the dissolution of the less polar dodecanoic acid in oil and the polar Brij in water.

All the monolayers collapsed beyond a certain level of compression as evidenced by a rapid decrease of surface pressure. The surface pressure and the corresponding area per molecule at the critical compression differed from one surfactant to another, which for dodecanoic acid, Brij 35, and their mixture are as follows: 0.1, 0.6 and 0.2 nm<sup>2</sup>, respectively. These values should not be construed as the real area per molecule of the surfactants in the most compressed state, as one expects that the monolayers may already have undergone a crumpling transition or other modifications before they are on the verge of collapse. It was interesting to note that when a small amount of a long chain polymer (PDMS or PTBS) is premixed with the surfactant mixture, the constructs are less concave than that observed with the mixed surfactant alone, coupled with the fact that the monolayer did not collapse. When the surface was agitated by rotating a disk in contact with the liquid surface, these constructs were only slightly shifted from those without agitation, although a collapse of the monolayer is evident in the presence of agitation (Figure 1.4 (a) and (b)).

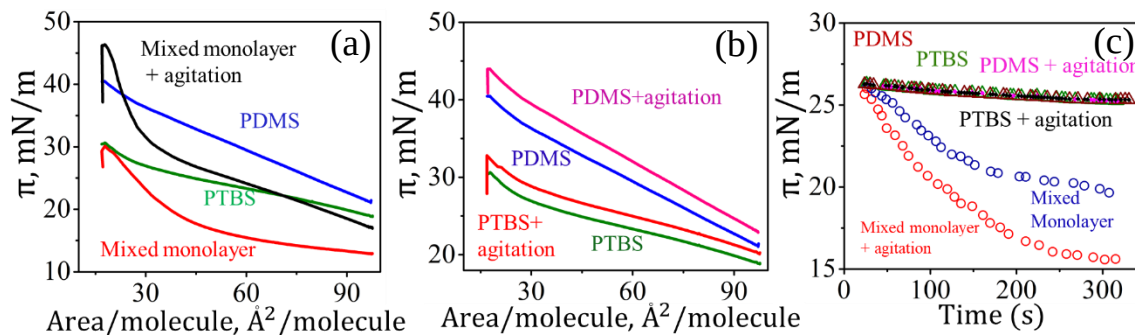


**Figure 1.4.** (a) Surface Pressure-Area constructs of the mixed surfactant monolayer containing small amounts of PTBS and PDMS. (b) Same as in figure a, but with the surface of water gently agitated by rotating a disc in contact with it. (c) When each of these monolayers is compressed to yield a surface pressure of about 26 mN/m and is allowed to relax, the surface pressure decreases with time. Very little decrease of surface pressure is observed with the monolayer containing a hydrophobic polymeric additive.

In another experiment, the mixed monolayers were compressed to yield a surface pressure of about 26 mN/m following which the time evolution of the surface pressure was monitored (Figure 1.4 (c)). Here, the surface pressure continued to decrease with time, which was accelerated when the surface was continuously agitated with the rotating disc. By contrast, the surface pressure of the monolayer decreased only slightly when it was prepared with a small amount of a hydrophobic polymer (PDMS or PTBS), both in the presence and absence of agitation. Taken together, these results strongly suggest that the stability of the monolayer is enhanced in the presence of a long chain polymer, which, presumably is due to the increased connectivity of the surfactant molecules with the backbones of the long chain polymers. This enhanced durability, as discussed below, plays an important role in the stability of the micro and nano sized emulsion droplets.

#### 1.2.4. Effect of Turbulence power in droplet size distribution

Having characterized the surface and interfacial properties of oil-water interfaces and gaining useful insights into the stability of the surfactant monolayer deposited on the surface of water, we now explore the role of hydrodynamic pressure fluctuations originating in turbulence on the generation of micro and nano size droplets of oil when it is emulsified in water. These turbulences

induced emulsification experiments were carried out with a home-built apparatus, as depicted in Figure 1.5 in which the salinized water entered through one end of a thick-walled plastic conduit and exited from the other end aided by a positive displacement pump. As invasion of air is unwanted inside the conduit for most of the studies, it was made as airtight as possible. Furthermore, a net positive pressure inside the conduit ensured that air could not invade the system from outside. Air could, however, be infused in the conduit during agitation when desired. As discussed above, in order to simulate the salinity of seawater, salt is added to freshly prepared distilled water at the concentration of 0.6 M. In a typical experiment, surfactant (100 ppm) was dissolved in the salinized water starting with a concentrated solution in the presence of gentle stirring in a holding tank placed above the conduit. The difference between the levels of the conduit

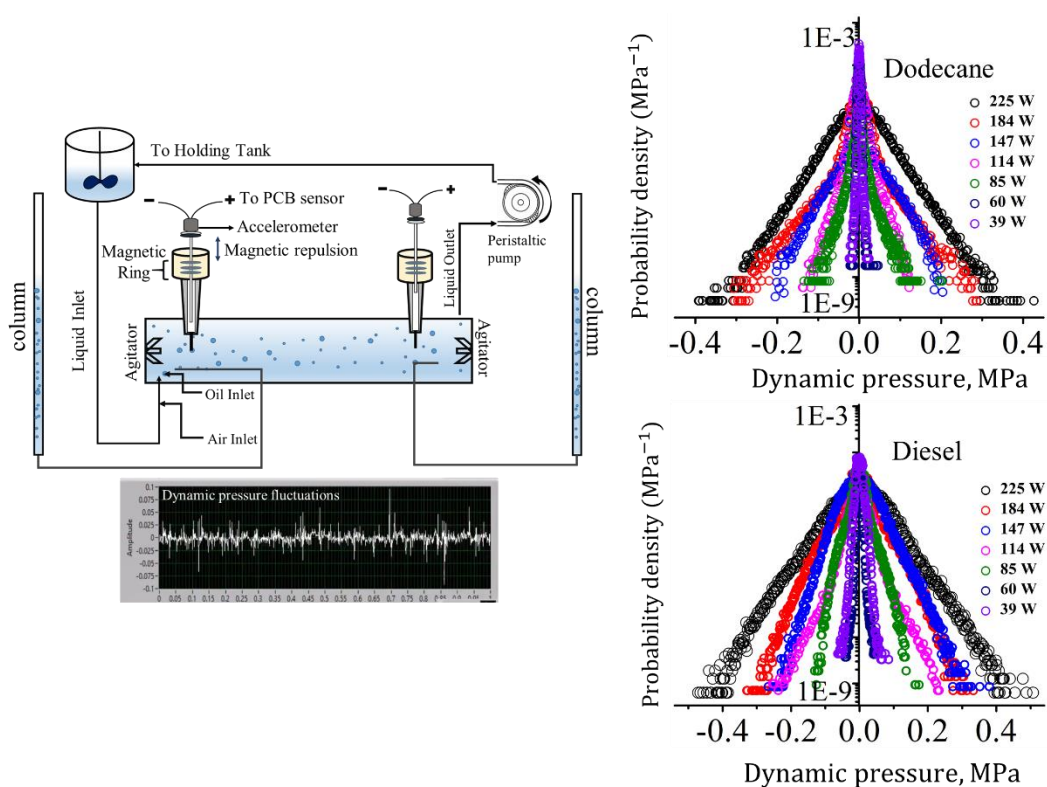


**Figure 1.5. (Left)** A (self-explanatory) schematic of the apparatus used to generate turbulence. While the hydrodynamic spectra can be measured with the magnetically levitated accelerometers, the one close to the entrance was used. The two tall columns placed at the entrance and exit sides of the conduit are filled with water. The difference in the heights of water allow an estimation of the pressure difference between entrance and exit points. A typical time series of the dynamic

pressure fluctuation measured by the accelerometer is shown below this schematic. **(Right)** Probability distribution function of dynamic pressure fluctuations during the formation of emulsion at various nominal power inputs.

and the holding tank created a hydrostatic pressure head thereby ensuring a smooth influx of water in the conduit. A peristaltic pump was used to remove the water from the conduit to either backfill the holding tank or to divert it to a collection tank. Oil was pumped into the turbulent water using a syringe pump, the flow rate of which was set to such a value that the concentrations of oil and surfactant were maintained at 1000 ppm to 100 ppm in the emulsion.

Turbulence was produced by the rotation of an impeller close to the entrance of water. There is another impeller on the other end of the conduit. When both the impellers spin, strong von Karman vortex can be produced inside the conduit. However, for all the studies described here, turbulence was generated by one impeller, while the other one was slowly rotated to induce a gentle mixing of the emulsion as it exits the conduit. The nominal power (40 W to 225 W) input to the turbulence generating impeller was estimated from the product of the voltage applied to the motor running the impeller and the corresponding current flowing through the electrical circuit.

In order to characterize the hydrodynamic fluctuation in the turbulent water, we measured the dynamic pressure of the fluid transmitted to an accelerometer through a capillary of diameter 0.4 mm. In order to avoid wall effect, the accelerometer was magnetically levitated. A small tungsten rod as attached to the accelerometer was inserted vertically inside a capillary tube, which vibrated randomly in response to the dynamic pressure fluctuation of the liquid near the capillary tube. From the mass of the rod and its acceleration obtained from the calibrated accelerometer, we obtained the dynamic force. By dividing this force by the open base area of the rod, we obtained the dynamic pressure that rapidly fluctuated with time as turbulence was set up inside the conduit.

The probability density function (pdf) of the dynamic pressure fluctuation as obtained from the time series of the voltage fluctuation of the calibrated accelerometer is shown in Figure 1.5. What is clear is that these pdf's (Figure 1.5) are highly non-Gaussian, with large fluctuations exhibiting nearly exponential or stretched exponential distributions. The probability of occurrence of large fluctuations is therefore higher than that would be the case with a Gaussian distribution, which plays important roles in breaking up large droplets. Such type of information cannot be obtained from the value of the root mean square pressure used in classical scaling methods<sup>33</sup> to predict droplet size, which provides no information about the fluctuations at different scales. Previous attempts to obtain this information was based upon a presumed<sup>33</sup> Kolmogorov energy spectrum. In our research, our objective is that no prior assumption regarding energy spectra or a presumed distribution would be necessary. The emulsions, as analyzed using three methods (microscopic analysis using differential interference contrast (Figure 1.6), acoustic attenuation spectroscopy (or the Acoustic Particle Sizer, APS) and capillary hydrodynamic fractionation, CHDF) exhibited a distribution of droplet size ranging from nanometer to micrometer length scales.

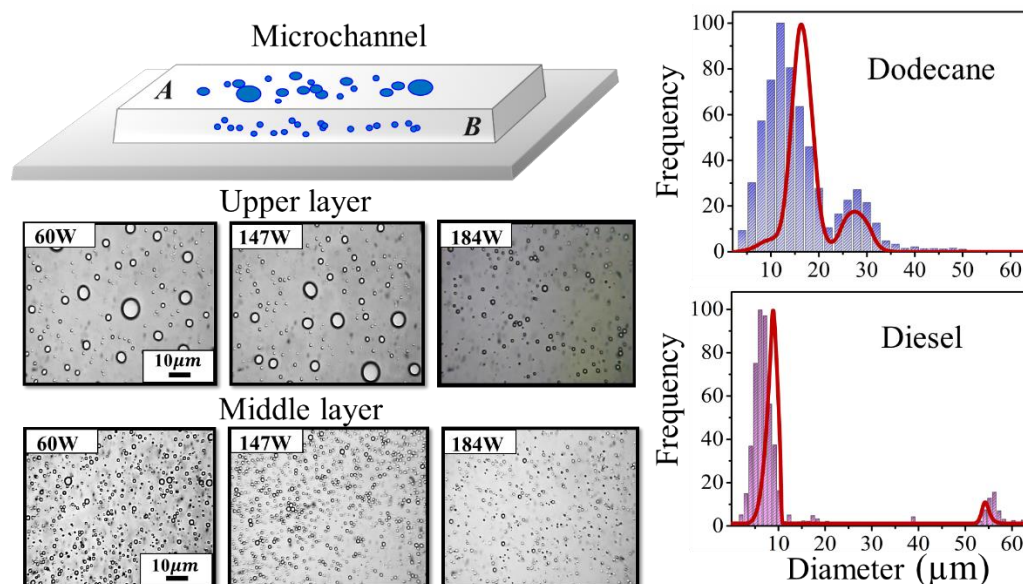


**Figure 1.6. (Left)** DIC microscopic images of emulsions formed with the Dodecane-salt water-surfactant system at three different input powers. The larger droplets float on the upper surface of the channel (shown above the micrographs), whereas the middle layer shows the smaller droplets. **(Right)** Typical pdfs of the droplet size distributions examined from the microscopic images are compared with those obtained from acoustic attenuation spectroscopy.

### 1.2.5. Optical and spectroscopic analysis of the emulsion

Optical microscopy has the advantage that the droplets are directly visualized. One disadvantage this method suffers from is the fact that the numbers of droplets used for the analysis is rather small, notwithstanding that the method is also very time consuming. Another disadvantage stems from the fact that the suspension progressively gets depleted of the larger droplets, which tend to float upward in the microscopic cell where a small volume of the emulsion was sandwiched between two glass slides with a gap of about 200 μm. The upper part of this sandwiched structure showed mostly the larger droplets, whereas the middle part showed the presence of smaller droplets. Even though we made efforts to use images from both the upper and middle part of the cell, there is a propensity of the population to be biased towards the smaller droplet size as the middle part of the geometry contains a larger population of droplets. The acoustic attenuation spectroscopy, on the

other hand, uses a much larger population of the droplets, where its segregation is not an issue as the suspension is gently and continuously stirred according to the protocol of this method. In spite of the limitations of the analysis of droplet size using optical imaging (Figure 1.6), the overall distribution obtained using this method closely parallels to what is observed with the acoustic attenuation spectroscopy. In the rest of the paper, we mainly report the data obtained from APS for the droplets in the range of  $0.1 \mu\text{m}$  to  $100 \mu\text{m}$ , whereas CHDF data are reported for droplets of diameter in the sub-micron range.

#### 1.2.6. Analysis of the droplet size distribution

What is trivially evident with the results summarized in Figure 1.7 is that the droplets of smaller size are produced with the increase of the power input. The distribution, however, is not monomodal indicating, that the initially formed droplets might undergo coalescence with each other and also grow via Ostwald ripening to certain degrees. We were tempted to make an approximate prediction of the droplet size distribution using the spectral distribution of the dynamic pressure as summarized in Figure 1.6 by making the simple assumption that the size of a droplet of size  $r_i$  can be correlated with the dynamic pressure  $P_i$  by equating the Laplace pressure and the fluctuation of dynamic pressure as  $2\gamma / r_i = |P_i|$ . Here  $\gamma$  is the interfacial tension between oil and the surfactant containing salt water as measured using the drop resonance method described above. These results are effectively treated by constructing first a cumulative distribution of the droplet size distribution and then taking its derivative for constructing a plot in the spectral domain to be compared with the data obtained from acoustic attenuation spectroscopy.

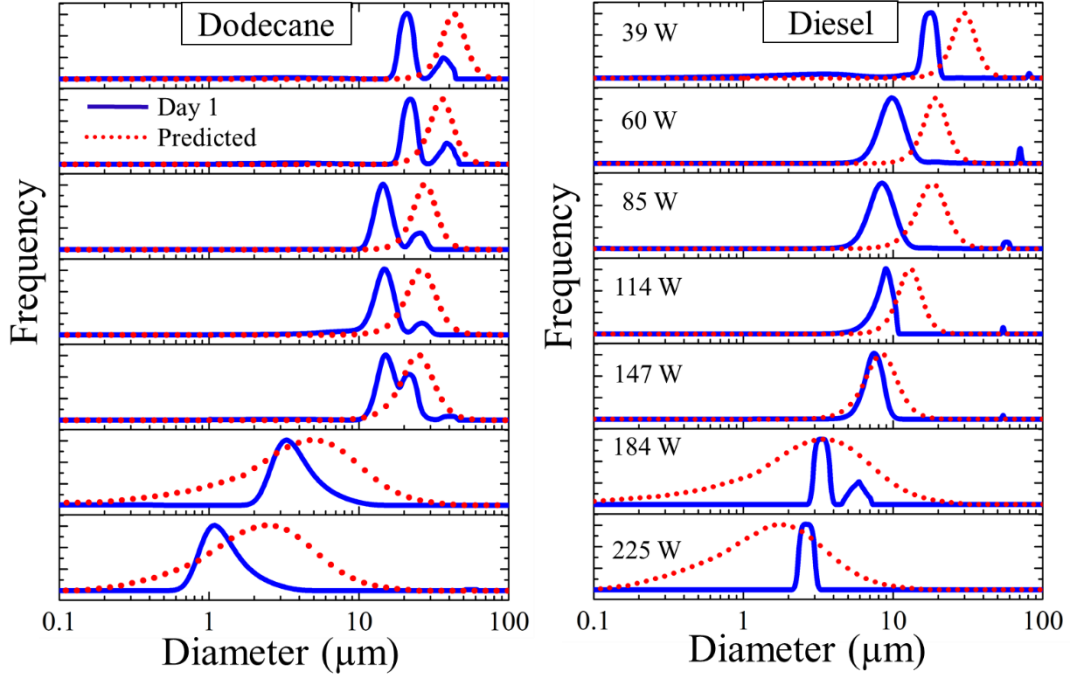


**Figure 1.7.** Comparison of the droplet size distributions obtained from (—) APS and those (···) predicted from the hydrodynamic fluctuation spectra at different input powers. The left and right panels are for dodecane and diesel, respectively.

These results summarized in Figure 1.7 show that the distributions expected from the analysis of the pressure fluctuations follow, more or less, the same trends observed experimentally with the peak diameter of any given distribution being off by a factor of about two to three in predictions and observations. This discrepancy reveals some limitations of this rudimentary analysis. Long ago, Sevik and Park<sup>41</sup> proposed that the breakup of a droplet is not describable by simply balancing the Turbulence and the Laplace pressures. They noted that when a drop is subjected to a fluctuating field, its resonance modes are excited, which result in a violent breakup of the droplet. To motivate this discussion, let us remind ourselves that the frequency of the first pumping mode of a spherical drop corresponds to ,  $\omega_1 = \sqrt{48\gamma / [\pi^2 d^3 (2\rho_w + 3\rho_o)]}$  where w and o correspond to water (external phase) and oil (internal phase) respectively. The characteristic frequency for the hydrodynamic fluctuation corresponding to the dynamic pressure  $P_i$  is  $\omega_2 = \sqrt{2P_w / \rho} / d$ . Following Sevik and

Park,<sup>41</sup> when  $\omega_1 = \omega_2$ , the drop undergoes resonance fluctuation. Such a condition would be fulfilled if  $d = 0.6\gamma / P_i$ , which is considerably smaller than that ( $d = 4\gamma / P_i$ ) obtained by balancing the dynamic pressure with the Laplace pressure. The situation becomes interesting if we consider the simultaneous excitations of the higher spherical harmonics, that would be the case of a stochastic resonance, as was previously demonstrated by Mettu and Chaudhury.<sup>73</sup> The real situation, however, is even more complex. For example, we note that the assumption has been made in constructing the plots in Figure 1.7 that the droplet size has one to one correlation with the fluctuating pressure. This assumption may be justified if the liquid flows at a high rate, so that the residence time of the liquid within the volume being activated by the impeller is comparable, as a first approximation, to the period of turbulent fluctuation operating on the opposite sides of a drop. Within the parameters used in our experiments, the droplets are expected to break down in a cascade, as they are subjected to multiple pressure pulses. This is particularly evident with the liquid passing multiple times through the conduit in a close circuit mode, when the distribution of the droplet size is shifted to even smaller value (Appendix A: Figures S1 and S2). At the highest powers, the droplets experience the pressure pulses so frequently even with a brief residence time that the distribution becomes, more or less, independent of the number of passes of water through the conduit. While an adequate analysis of this problem would require a statistical level population balance analysis, which is postponed for future, it is intriguing to note that the distribution, while it is relatively independent of the number of passes, is narrower than those expected from the pressure fluctuations at the highest input power. At these high powers, water clearly cavitates, which can be visually perceived from the scattering of a beam of light directed towards the conduit. Based on past observations,<sup>55-57</sup> it is meaningful to speculate that the production and the collapse

of the bubbles during cavitation generate shock waves, which have profound implications on the droplet breakdown process.

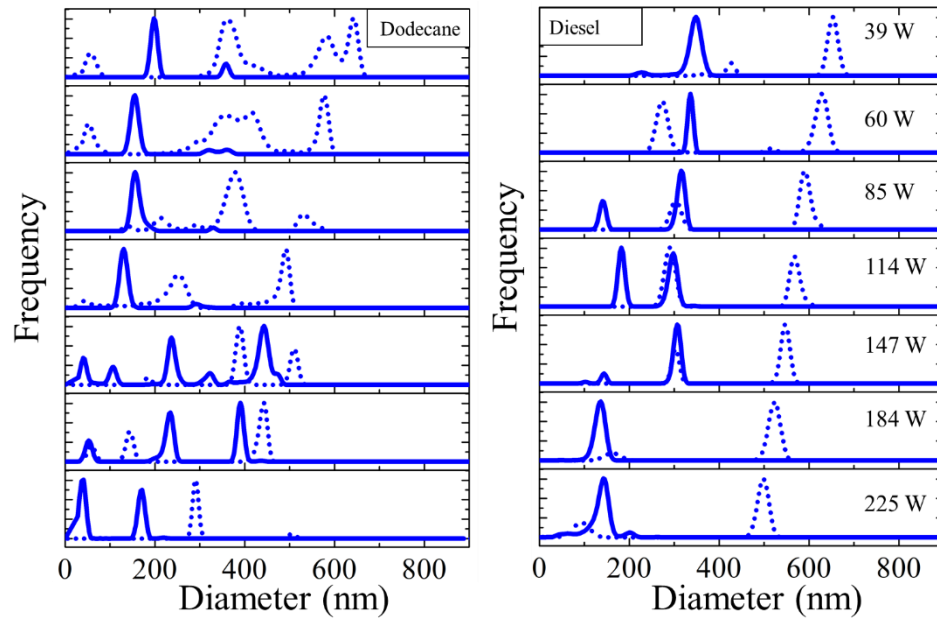


**Figure 1.8.** Droplet size distribution obtained using CHDF at different input powers. All these droplets grow in size as they age. The blue curves correspond to the emulsions when they were freshly formed, whereas the dotted curves (■ ■ ■) correspond to 28 days. The left and right panels are for dodecane and diesel, respectively.

More than the discrepancy observed between the predicted and the observed droplet size distributions, what is intriguing is the fact that nano-sized emulsions (10 nm to 300 nm) are formed (Figure 1.8) at all the input powers for both dodecane and diesel. Formation of such nano-sized emulsions are not warranted from the intensity of the dynamic pressure fluctuations. Thus, their formation points out certain, yet to be identified, factors that the conventional model of emulsification does not capture.

The number density of the nano-sized fractions of the emulsions, as measured in CHDF, increases systematically with the nominal input power, irrespective of which of the Hinze or Kolmogorov scales is used (Figure 1.9). What is evident from the non-zero intercepts of these plots is that nano-

sized emulsions can potentially form even in the absence of any agitation. This particular observation points towards the important role of another hidden process that is coupled with the hydrodynamic stress induced break up of droplets.

When a drop is in a turbulent field, it would not only experience a fluctuation of normal stress, as is assumed in the Kolmogorov-Hinze droplet break up model, but also a fluctuating shear stress especially as the surfactant adsorbed interface is somewhat rigidified. With a shear stress acting on a drop's surface, surfactant molecules are expected to densify on some regions on the surface and rarify in the surrounding regions. When the compaction of the surfactants reaches a critical value, it could collapse resulting in a folding transition, which become precursors to nano-meter size droplets. This is somewhat akin to what has been described in the literature as tip streaming,<sup>82-86</sup> where it is assumed that the interfacial tension could be negative under extreme compression.

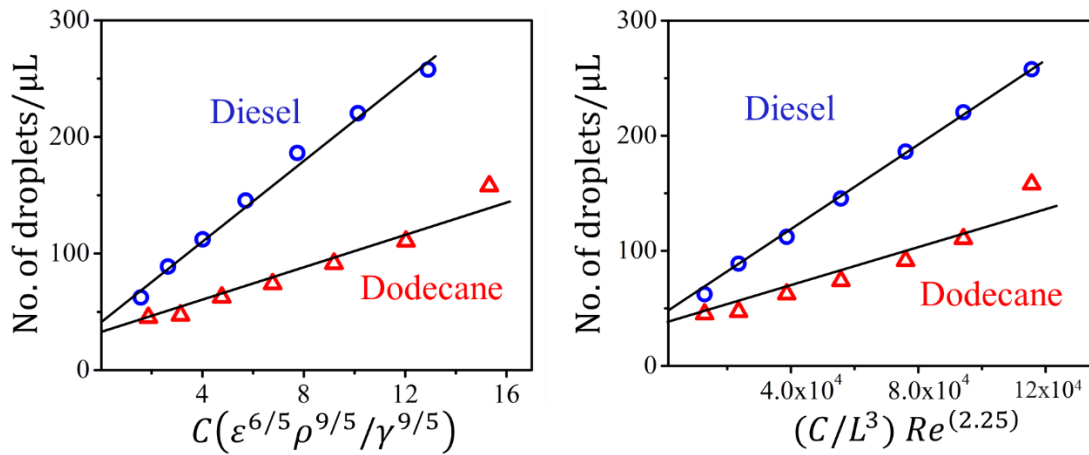


**Figure 1.9.** Comparison of the number density of droplets as obtained from CHDF with those estimated from Hinze and Kolmogorov scaling.

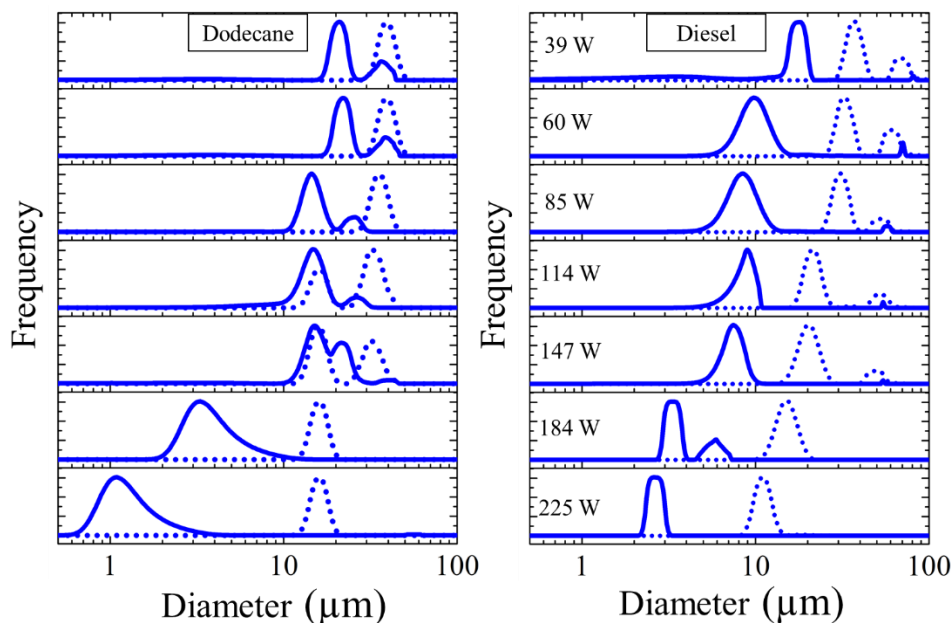


**Figure 1.10.** Droplet size distribution obtained using APS at different input powers. All these droplets grow in size. The blue curves (—) are obtained soon after the emulsions were formed. The dotted curves (···) are obtained after 28 days. The left and right panels are for dodecane and diesel, respectively

All the droplets of sizes ranging from nanometer to micrometer dimensions aged with time (Figure 1.10), presumably due to the combinations of such events as coalescence and Ostwald ripening. Diesel fuel containing droplets have the propensity to grow faster than dodecane. This would be expected, as the solubility of dodecane (0.001 mg/L) is much lower than that of diesel (40 mg/L) in water, which is an important contributor to the Ostwald ripening process.

Ostwald ripening appears to be an important mechanism underlying the droplet aging process in which the oil first dissolves in water, before it is absorbed by a larger droplet followed by the diffusion of the oil molecules in water. Surprisingly, however, some droplets of sizes even smaller than the original sample become visible as time progresses, for which there are three possibilities to consider. Firstly, this could be the result of the growth of even smaller droplets that were not detected when the emulsion was prepared on the first day. Secondly, there is the possibility that they are the byproducts

of the coalescence of larger droplets. Various spherical harmonics could be excited following the coalescence of two or more drops that could result in the generation of shock waves leading to multiple fragmentations of the larger drops.<sup>87</sup>

The third possibility is motivated by an interesting experiment reported by Dabros et al,<sup>88</sup> who deflated a micrometer size drop of water immersed in an oil in the presence of a surfactant. The deflation resulted in the formation of small droplets ejecting out of the surface of the original drop as the surface area of the drop decreased. The phenomenon, again, is linked to the classical instability resulting from the competition of the bending and compression of the interface. It is conceivable that interfacial instability of nanometer length scale could be formed when the surface of a drop continues to shrink by sacrificing its inner phase during an Ostwald ripening process, thus reaching a state of critical compression and then collapse. The plausibility of such a scenario can be illustrated with a rudimentary model by considering three components to the interfacial energy, which is motivated by previous seminal works,<sup>52,89,90</sup> but with more rudimentary assumptions.

One component arises from the usual interfacial free energy. The second component arises from the elastic compression of surfactant monolayer, which results from the confinement of the various degrees of freedom of the surfactant molecules and its segments. A third component arises from the bending energy. We consider the scenario in which a drop has already been shrunk; thus, an elastic compression has stored some elastic strain energy. At a critical state, the drop could relieve this strain energy by fragmenting into multiple smaller droplets, if such a process decreases the total interfacial energy. We write the total energy (equation 2) of a compressed monolayer with the drop of current radius  $r$  as follows:

$$U_1 = 4\pi r^2 \gamma + 2\pi r_o^2 E \delta_0 \varepsilon^2 + 8\pi k \quad (2)$$

Where, the three terms on the right side represent the surface, elastic and bending energies respectively. Here,  $\delta_0$  is the thickness of the film in the uncompressed state, which increases to  $\delta$  as the film is compressed;  $E$  is the surface elasticity;  $k$  is the bending modulus, and  $\varepsilon = (r - r_0)/r_0$  is the strain as the radius of the sphere decreases from  $r_0$  to  $r$ . We assume that the film is incompressible so that the volume of the monolayer remains constant  $r^2\delta = r_0^2\delta_0$ , where  $\delta_0$  and  $\delta$  are the initial and the compressed monolayer thickness, respectively. This assumption may not be rigorously correct; nevertheless, this does not obfuscate the essential physics at the cost of simplifying the problem. We also make use of the small deformation approximation here in order to elucidate the basic physics of the problem; it also simplifies the calculation. For a more rigorous calculation, a large deformation theory can certainly be used; however, the generality of the results would not be denied by the assumptions made here. Now, let us consider that such a strained drop fragment into multiple ( $N$ ) smaller drops of radius  $r_1$ . The total energy of the fragmented drops (ignoring the change of the chemical potential of the liquid inside the drop) is shown in equation 2:

$$U_2 = 4\pi N r_1^2 \gamma + 2\pi r_0^2 E \delta_0 \varepsilon_1^2 + 8\pi N k \quad (3)$$

where, each small drop is in state of strain as  $\varepsilon_1 = (r_1 - r_{01})/r_{01}$ ,  $r_{01}$  being the radius of the drop in the relaxed state. By using the constancy of the total volume of the fragmented drops and that of the monolayer film, we have:  $r^3 = N r_1^3$  and  $N r_1^2 \delta_1 = r_0^2 \delta_0$ , which leads to:  $\delta_1 = r_0^2 \delta_0 / (N r_1^2)$  and  $r_{01} = r_0 / \sqrt{N}$ . We can thus estimate the difference of the total energy (equation 4) of the fragmented drops and the original drop as:

$$\Delta U = U_2 - U_1 = 4\pi r_o^2 \gamma (1 + \varepsilon)^2 (N^{\frac{1}{3}} - 1) + 2\pi r_o^2 E \delta_0 (((1 + \varepsilon) N^{\frac{1}{6}} - 1)^2 - \varepsilon^2) + 8\pi (N - 1)k \quad (4)$$

$\Delta U$  has a minimum for a given number (N) of the daughter droplets, which is obtained by setting  $\partial(\Delta U) / \partial N = 0$ , which yields equation 5:

$$(1 + \varepsilon) N^{\frac{1}{6}} (2\gamma + E\delta_0) - E\delta_0 + \frac{12kN^{\frac{5}{6}}}{(1 + \varepsilon)r_o^2} = 0 \quad (5)$$

The contribution of the bending modulus becomes important for very small drop sizes. Using a typical value of  $\gamma$  as 5 mN/m and  $k$  as  $100 k_B T$ , and typical values of  $|\varepsilon|$  and  $N$  on the order of unity, we note that the contribution of bending elasticity becomes important when the size of the droplet is in the range of 50 nm. The value of  $k \sim 100 k_B T$  is typical of a lipid bilayer. In a pioneering paper, de Meglio et al<sup>91</sup> reported that the bending rigidity of a surfactant monolayer ( $\sim k_B T$ ) adsorbed at an oil-water interface is much smaller than that this value<sup>62</sup>. In any event, as bending energy discourages formation of small droplets, it is possible that very small droplets would be stabilized at some low length scale. However, then, we need to consider the enhancement of the chemical potential of the surfactants themselves that would promote its dissolution in the aqueous phase. Furthermore, the role of spontaneous curvature of the monolayer would temper the effect of bending energy to some extent. For the imminent problem in hand, we can ignore the bending energy term for micron size droplets (equation 5), when the number of fragmented drops would be  $N = (E\delta_0 / (1 + \varepsilon)(2\gamma + E\delta_0))^6$ .

For multiple fragmentation,  $N > 1$ , this condition should be met:  $-\frac{\varepsilon E \delta_0}{1 + \varepsilon} > 2\gamma$  for  $\varepsilon < 0$  (i.e.

compression). For a rough illustration of what entails, if we assume  $E\delta_0 = \gamma$ , the above energy minimization leads us to conclude that a droplet would begin to disintegrate as soon as it shrinks to

one third of its original size, following which, disintegration would proceed rapidly. The fragmented drops, would, after some time, disintegrate themselves, thereby triggering a critical speeding up catastrophe. Note that the effective surface tension  $\gamma + \varepsilon E \delta_o$  can remain positive during the entire droplet fragmentation regime. Thus, the conclusion is that the original work needed to create the emulsions are stored as excess chemical potential in the drop, which drives the entire process, while, ultimately converting to irrecoverable (dissipated) energy.

While these ideas are tentative, additional experiments, to be reported below, indicate that the stiffness of the surface does play an important role in the droplet generation as well as the aging processes, which has already been discussed in the literature.<sup>22, 28</sup> However, before reverting to this point, we describe what happens when the hydrodynamic fluctuation is accentuated with air infusion, or quenched with long chain hydrophilic polymers added to water.

We speculated above that the narrow distribution of the droplet size produced at the high agitation power inputs is a consequence of the concomitant cavitation of water. A collapsing bubble is known to generate shock wave thus giving rise to additional impetus for drop to break up. In order to test this hypothesis, air was injected inside the conduit at a low flow rate ( $\sim 5.2$  mL/min) at various power inputs (114 W and higher). What transpired owing to the air infusion was that a more vigorous fluctuation of the dynamic pressure developed in the turbulent water, which was readily picked up by the accelerometer (Figure 1.11).

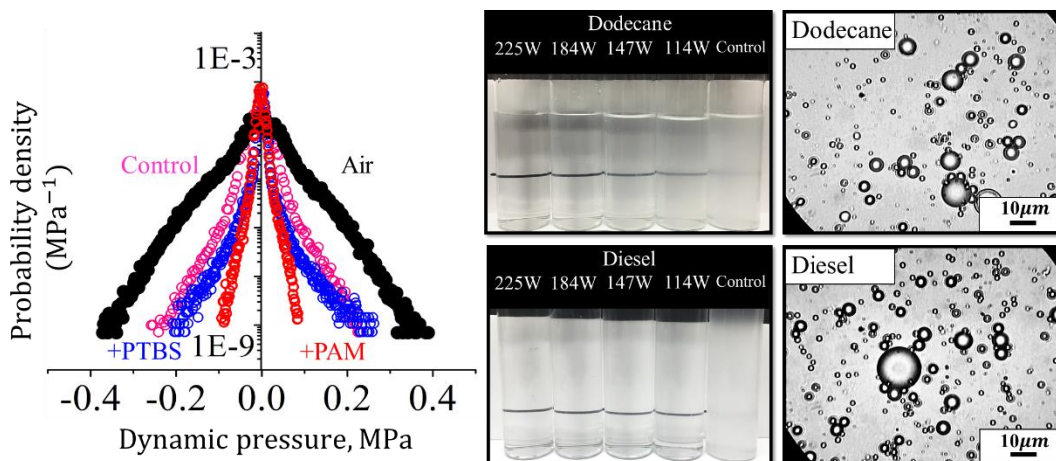


**Figure 1.11. (Left)** Hydrodynamic fluctuation spectrum is enhanced with the infusion of air, but suppressed by the addition of 20 ppm of polyacrylamide in the aqueous phase. The spectrum is relatively uninfluenced when a hydrophobic polymer is present in oil. These results are obtained with Diesel. Similar behaviors were also observed with dodecane (not shown here). **(Middle)** With air infusion, so fine emulsions are produced that the suspension is transparent, which is evident here when a thin marked line is placed behind the glass vials containing the surfactant, they become visible. **(Right)** The microscopic images show that the droplets cluster when polyacrylamide is added to water, presumably due to depletion induced force. All these experiments were carried out at a power input of 114 W.

The emulsion droplets formed during air infusion were so small and the emulsion was so transparent (Figure 1.11) that they could not be detected either using optical microscopy or the acoustic attenuation spectroscopy. CHDF, on the other hand, detected the production of droplets of size less than 100 nm. This particular experiment with air infusion is intriguing in the sense that turbulence that generates the air bubbles also affects the hydrodynamic fluctuations that produced those in the first place. This fluctuation-response coupling is an interesting feature of this unique far from an equilibrium process dominated by large fluctuations that deserve future studies on its own merit.

Another way to modify the turbulence spectrum and thus the emulsification process is to take advantage of an effect discovered, previously by Mysels<sup>92</sup> and later, more succinctly, by Toms.<sup>93</sup> The latter study culminated into what is called the Toms effect, according to which even a trace amount of a long chain hydrophilic polymer in a fluid reduces the turbulent frictional drag. We

expected that the addition of such a polymer in water could thwart the formation of droplets by quenching the large fluctuations. Indeed, when a large molecular weight (1MM) polyacrylamide was premixed in the aqueous phase even at a concentration of 20 ppm, the large hydrodynamic fluctuations were significantly frustrated; consequently, the overall distribution of the emulsion droplets were also shifted to larger size. At this juncture, we report an intriguing observation that low concentration of polyacrylamide not only quenches turbulence, possibly by killing the eddies that is commonly perceived to be a known yet not well understood effect, we observed that it is also quite effective in thwarting pressure waves. When a pressure wave is induced inside a conduit (Appendix, Figure 3), by suddenly arresting the flow of water inside it, a dynamic pressure signal is detected by the accelerometer, which is quenched even with a trace (20 ppm) amount of the polymer, but exacerbated systematically by further increasing its concentration.

The predicted droplet size distributions in the turbulence induced emulsification experiments with both air and polyacrylamide is in accord with the experimental trend, although quantitative discrepancies exist. The effects produced by the additives discussed above are more clearly discernable in the submicron range of the emulsion droplet distribution as shown in Figure 1.12. Air infusion during emulsification produces the smallest size droplets ( $<100$  nm). On the other hand, the addition of polyacrylamide in water produces large droplets  $> 400$  nm to a substantial degree. By contrast, addition of a high molecular weight hydrophobic polymer in oil neither affects the shear viscosity of the oil nor does it alter the hydrodynamic fluctuation in a noticeable way.

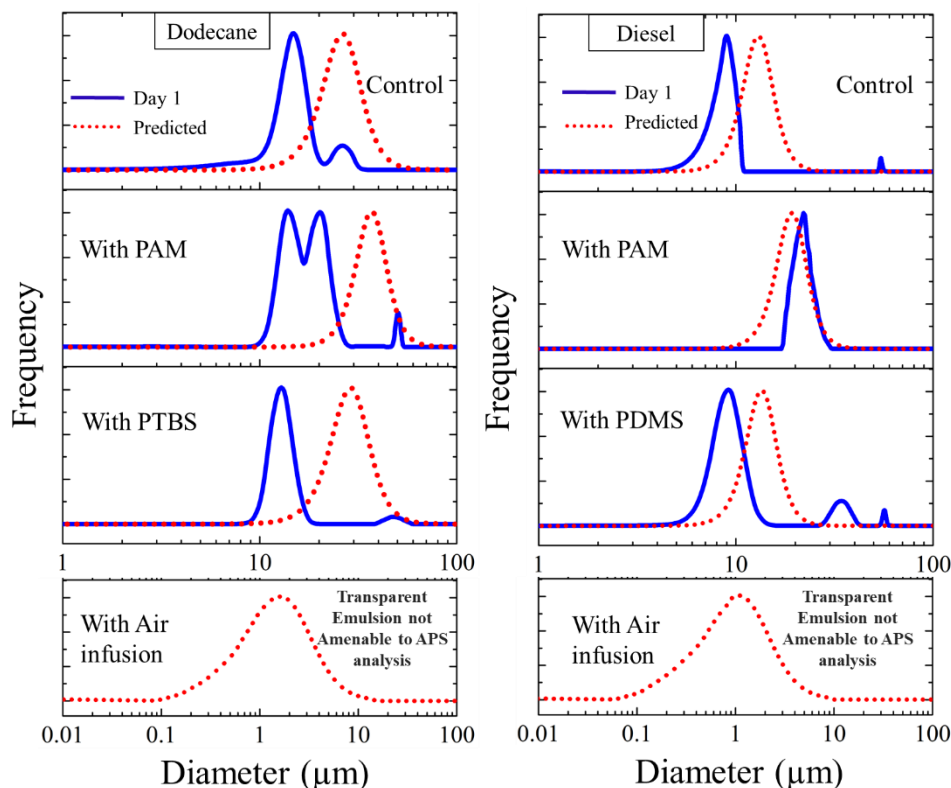


**Figure 1.12.** Comparison of the distributions of the sizes of droplets produced with polyacrylamide in water, or a hydrophobic polymer in oil, with those predicted from the analysis of the hydrodynamic fluctuation spectra. The droplets produced with air infusion are so small that they could not be analyzed with APS.

In order to motivate the discussion that is to follow, here we highlight the differences in the aging characteristics of the prepared emulsions particularly focusing on two cases: polyacrylamide in water and a hydrophobic polymer in the oil. Emulsions produced with polyacrylamide grow most rapidly. This may be intuitively ascribed to the formation of the droplet cluster (Figures 13 and 14) via depletion flocculation<sup>94</sup> induced force, which prevails when the long chain polymers are excluded from the intervening space of two droplets, thereby resulting in an osmotic force induced attraction of the droplets. As the droplets get close to each other, enhancement of fusion as well as Ostwald ripening are expected, which is evident in both the sub-micron (Figure 1.13) as well as micron (Figure

1.14) ranges of the emulsion droplets. By comparison, the droplets hardly age when a hydrophobic polymer is dissolved in oil. A possible explanation of this effect may be understood as follows.

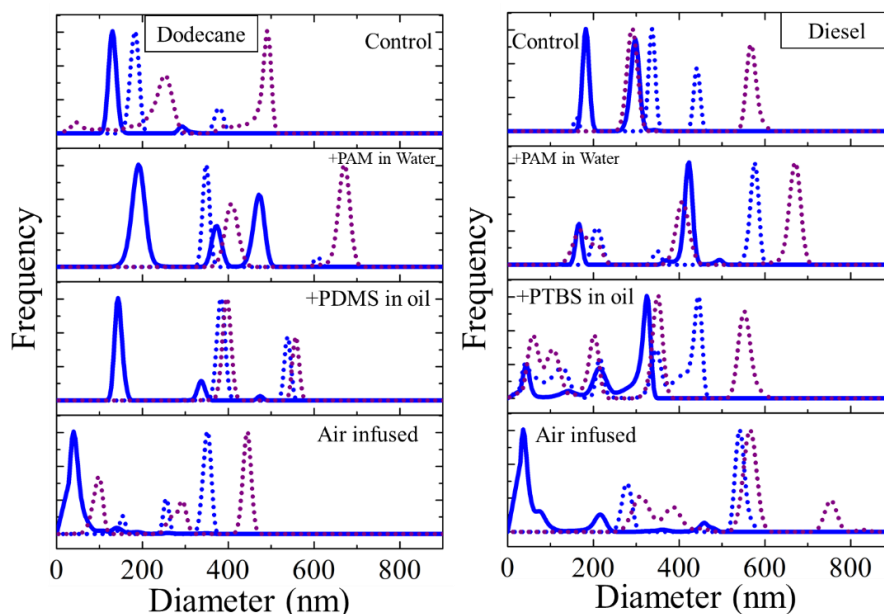


**Figure 1.13.** Aging of the nanometer size droplets produced in three cases: polyacrylamide in water, a hydrophobic polymer in oil, and with air infusion obtained using CHDF. The blue curves (—) are obtained soon after the emulsions were formed. The dotted curves (· · ·), (· · ·) are obtained after 7 and 28 days respectively.

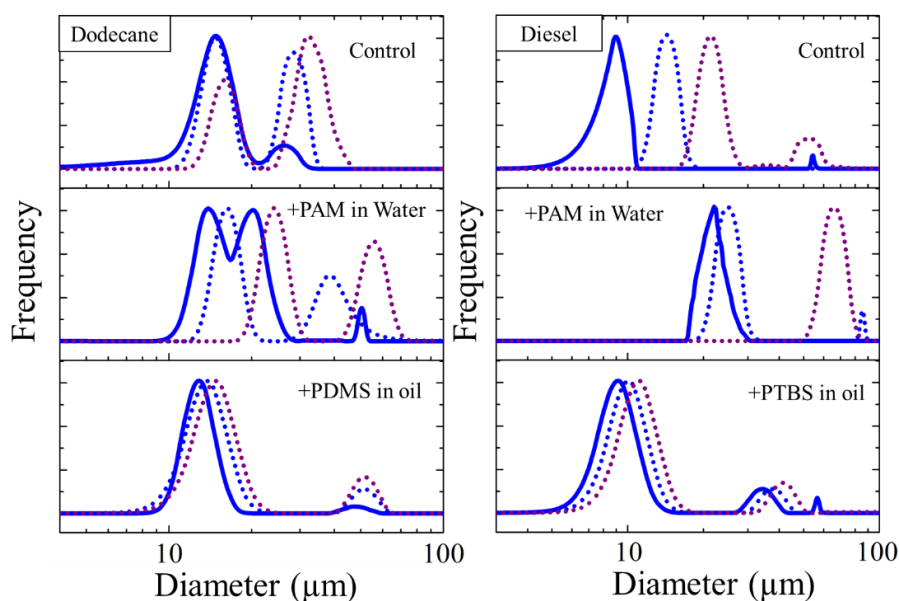


**Figure 1.14.** Aging of the micrometer size droplets produced in three cases: polyacrylamide in water, a hydrophobic polymer in oil, and with air infusion obtained using APS. The blue curves

(—) are obtained soon after the emulsions were formed. The dotted curves (---), (---) are obtained after 7 and 28 days respectively.

Ostwald ripening occurs due to the Laplace pressure mediated increase of the chemical potential of the liquid encapsulated inside an emulsion droplet. When the interfacial tension is the only primary force acting on the drop, the chemical potential of oil over that of its standard value is  $2v_m\gamma/r$ , where  $v_m$  is the molar volume of the liquid,  $\gamma$  is the interfacial tension and  $r$  is the radius of a droplet. Accordingly, the chemical potential of the liquid inside a smaller droplet is greater than that of a larger droplet, which increases the solubility of oil in water. The net result is that oil molecules migrate from the smaller droplet toward the larger droplet; thus the larger one grows and the smaller one shrinks. When a polymer is dissolved in the droplet, it would have two effects. First the chemical potential of oil would be decreased due to the entropy of mixing of the polymer and oil. This is similar to what was proposed by Walstra,<sup>95</sup> that Ostwald ripening would be slowed down or arrested if an osmotic pressure acts against the Laplace pressure. Meinders et al<sup>96</sup> suggested that Gibbs elasticity could play an important role in thwarting the Ostwald ripening process. In our case, while the polymer can be trapped inside the droplet contributing to Osmotic pressure along the line proposed by Walstra,<sup>95</sup> it can also associate with the surfactant monolayer thus stiffening the interface. This was somewhat evident in the  $\pi$ -A constructs that enhanced the stability of the monolayer at the air-water interface. The fact that the hydrophobic polymer modifies the oil water interface can also be discerned from the drop resonance experiments as described above (Figure 1.15). Being driven by a periodic pressure fluctuation, the response of the drop should also coincide with the forcing frequency.

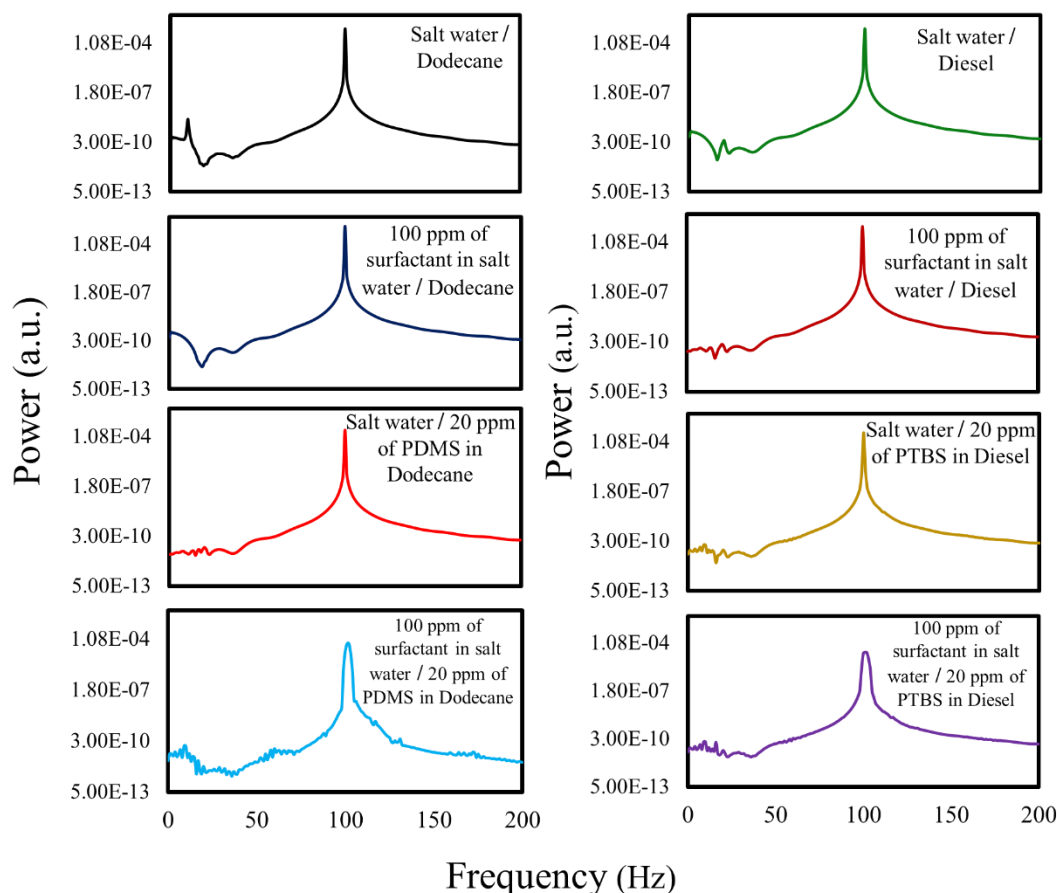


**Figure 1.15.** Power spectra of the oscillating drop at a frequency of 100 Hz are sharply centered around 100 Hz when the oil contains no additive. However, when a water soluble polymer (PDMS or PTBS) is added in oil, the peak is broader as it is composed of more than one response. These power spectra were obtained following the method described in Fig 2. However, instead of using the Foton probe, magnetically levitated accelerometer (see Fig 5 and the relevant text) was used, which vastly improved the time resolution.

At all the oil-water interfaces, without a hydrophobic polymer, each drop exhibits one sharp peak in the power spectrum of the drop oscillation at a frequency corresponding to that of forcing. On the other hand, when a small amount of polymer is dissolved in the oil, and the surfactant is present in water, the corresponding power is reduced while the primary peak still appears at 100 Hz. This strongly indicates that the origin of the phenomenon is interfacial, which results from the adsorption of the polymer on the surfactant covered interface. Furthermore, the vibration energy seems to be dispersed to dissipation and noise to some extent, thus exciting a mode slightly higher

than 100 Hz. This can be clearly seen with PDMS added to dodecane, but somewhat less clearly with PTBS added to diesel. While these results are amenable to more detailed analysis, for the time being, we can be reasonably sure that the interface is showing two types of responses indicating, that one unique surface stress that is composed of surface tension and elasticity is not entirely adequate to describe the property of the interface.

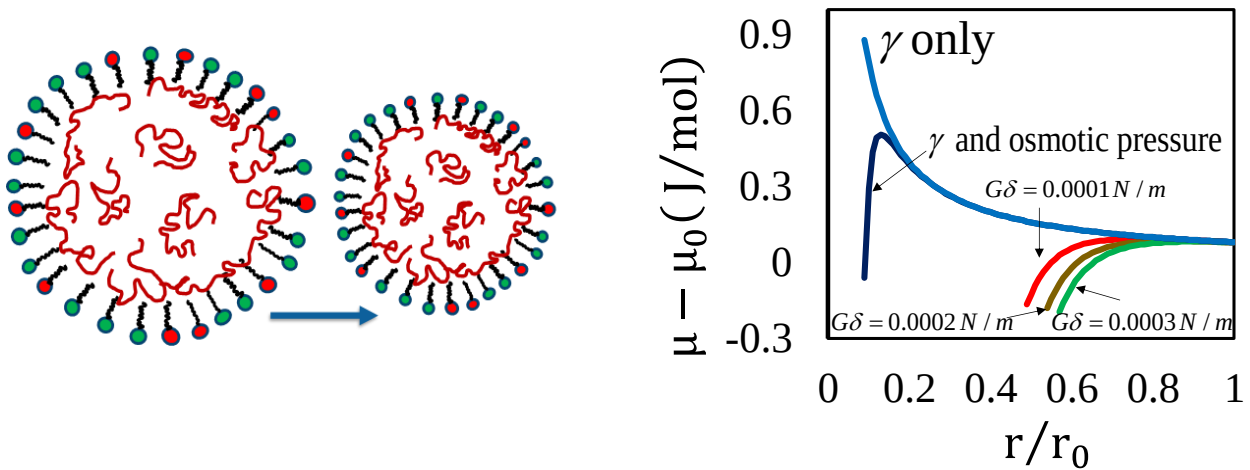


**Figure 1.16. (Left)** As a droplet containing a long chain polymer shrinks, the chemical potential increases for two reasons: entropy of mixing and the compression of the interface. **(Right)** When a droplet exhibits elastic response, the excess chemical potential can decrease with radius.

Long ago, Buff<sup>97</sup> considered a modification of Gibbs-Thomson equation as follows:

$$RT \ln S = V_m \left[ \frac{2\gamma}{r} + \left( \frac{\partial \gamma}{\partial r} \right)_T \right] \quad (6)$$

Where  $S$  is the degree of supersaturation, which is usually greater than unity. The second term inside the square bracket of equation 6 is usually interpreted as the curvature dependent surface tension, or bending modulus of the interface. Meinders et al,<sup>96</sup> on the other hand, expressed the second term in the formal definition of Gibbs elasticity, which is a continuation of a flat surface. There are various other important ramifications of the thermodynamics of curved surfaces, the

clearest exposition of which was first provided by Boruvka and Neumann,<sup>98</sup> and later by Ljunggren et al.<sup>99</sup>

In the backdrop of these developments, we present here a naive model, in which we consider the contributions of the interfacial tension and elastic compression of the surface of the drop separately, ( equation 7) . We assume that the polymeric molecules attached to the surfactant monolayer behaves as a thin elastomeric film of thickness  $\square$  and shear modulus  $G$ , so that its deformation is governed by a neo-Hookean model.<sup>100</sup>

The scenario we consider is that as the volume of a small emulsion droplet decreases, the elastic film is compressed, which acts against the tendency of the surface tension to reduce the surface area. The usual method of minimization of the Helmholtz free energy associated with a virtual increase of the volume of the drop yields the following equation:

$$\Delta P(4\pi r_o^3 \lambda^2) d\lambda = \gamma(8\pi r_o^2 \lambda) d\lambda + v \frac{dW}{d\lambda} d\lambda \quad (7)$$

Here,  $\Delta P$  is the pressure jump across the interface,  $v$  is the volume of the elastic film, which is assumed to remain invariant during the deformation of the drop of initial radius  $r_o$ ;  $\lambda (= r / r_o)$  is the radial compression of the drop.  $W$  is the strain energy density, which is expressed in terms of the scalar measure of strain  $J_1 = 2\lambda^2 + \lambda^{-4} - 3$  using the simplest neo-Hookean form as:

$$W = GJ_1 / 2 \quad (8)$$

Simplification of equation 7 lead to a Laplace equation (equation 8) comprising of the surface tension and elasticity terms:

$$\Delta P = \frac{2\gamma}{r_o \lambda} + \frac{2G\delta}{r_o} \left( \frac{1}{\lambda} - \frac{1}{\lambda^7} \right) \quad (9)$$

Multiplying the pressure jump with the molar volume ( $v_m$ ) of the internal phase of the emulsion droplet yields its chemical potential over that of its standard value. The polymer inside the droplet is also in the solvated state, which contributes to its chemical potential<sup>101</sup> the contribution of which increases as a droplet shrinks due to the concomitant increase of the polymer concentration inside it. Taken together all the terms, the chemical potential ( $\mu$ ) of the molecules in the dispersed phase can be written as follows:

$$\mu - \mu_o = -\frac{RT\phi_o^2}{2\lambda^6} + \frac{2v_m\gamma}{r_o\lambda} + \frac{2G\delta v_m}{r_o}\left(\frac{1}{\lambda} - \frac{1}{\lambda^7}\right) \quad (10)$$

where,  $\mu_o$  is the chemical potential of the pure solvent. The first term on the right arises from the free energy of mixing, the second term arises from the conventional surface tension effect and third term is due to elastic compression.  $\phi_o$  is the volume fraction of the solvated polymer in the drop of initial radius  $r_o$ . We have ignored the Foly-Huggins interaction parameter<sup>102</sup>  $\chi_{ps}$ , i.e. we assume that the polymer is dissolved in a good solvent.

The over chemical potential of oil is evaluated (equation 10) using the volume fraction of a typical 1 MM weight polymer at 20 ppm concentration (this is the lowest concentration used in our experiments) in oil. Since, we do not have the exact value of the Elasticity, we arbitrarily varied  $G$  lower than the interfacial tension and the Gibbs elasticity obtained from the surface pressure construct. The results summarized in Figure 1.16 show that the over chemical potential of oil increases as a droplet shrinks, which is the classic result in the absence of elasticity and osmotic pressure acting on the drop. However, with the contributions of all the terms taken together, the overchemical potential is much suppressed below the classical behavior even when the contribution of the elastic term is very small.

Ignoring the Osmotic pressure term, equation 10 predicts that the over chemical potential would at first increase as the droplet shrinks, reaching a maximum at  $\lambda = [7G\delta / (\gamma + G\delta)]^{1/6}$ , which corresponds to the radius of the shrunk droplet as  $3r_0 / 4$ ; from there, the chemical potential decreases further and reaches a zero value at  $\lambda = [G\delta / (\gamma + G\delta)]^{1/6}$ . Even in the absence of any elasticity, overchemical potential is affected by the osmotic pressure originating from the trace amount of the dissolved polymer. Thus, while the supersaturation of oil in water increases monotonically as the droplet shrinks in the absence of the polymer, the Ostwald ripening is frustrated owing to the roles of osmotic pressure and elasticity as suggested previously by Walstra,<sup>95</sup> Meinders et al,<sup>96</sup> Erni et al<sup>102</sup> and recently by Rosowski et al.<sup>103</sup> This expectation is indeed borne out with the observations made with both the PTBS and PDMS dissolved in Diesel and Dodecane (Figures 13 and 14, see also: Appendix, Figures S4 and S5) respectively at both the microscopic and sub-microscopic ranges of droplet sizes.

We make a note here that the ultra small drops may not be able to accommodate the polymer molecules to begin with, as it would have to pay penalty of entropic confinement in doing so. Thus, certain amount of Ostwald ripening may still occur with the nano-sized droplets, which are devoid of these polymers. We also note that elasticity of the surfactant monolayer would also play a role when it is critically compressed. However, the drop at that stage should be disintegrated, unless the surface adsorbed polymer stabilizes it, perhaps, by inducing a crumpled morphology<sup>88</sup> to the interface.

### 1.2.7. Emulsification without External Agitation

This study was initially motivated by the results of Figure 1.9, according to which nano-sized emulsions might be formed at zero Reynolds number (Re), i.e. in the absence of any external agitation. Secondly, the results with the turbulence induced emulsification, as described above,

prompt us to consider if a hydrophobic polymer dissolved in oil would affect spontaneous emulsification. While the above two questions were posed *a priori*, an issue arose *a posteriori* while analyzing the data, that is, if a small amount of a hydrophilic polymer dissolved in water would inhibit emulsification as it does in turbulence.

The subject under consideration belongs to the domain of what is called the “spontaneous emulsification” that continues to elude the surface chemists to date. Previously published studies<sup>13-22,29,30</sup> provided certain powerful rationales to suggest that the so-called spontaneous emulsification, by and large, is triggered by interfacial agitation. Such an agitation is a direct consequence of the fact that oil in contact with an aqueous phase is not at chemical equilibrium to begin with. Thereby, the differences of the chemical potentials of all the species in the oil and aqueous phases induce mass and momentum transports coupled with morphological transformations, all connected to each other.

As diffusion proceeds, each phase is enriched with the molecules of the other phase near the interface, thereby leading to a supersaturation of the surfactant in one of the phases. This is a non-equilibrium state, prompting spontaneous morphological transformation of the surfactants leading to lamellar, micellar or other phases as permitted by the phase diagram. Supersaturation could also lead to the precipitation of some of the surfactants as particulates. If such a particle meets the interface, very fast Marangoni force induced shock waves may even be expected to be ejected out randomly in space and time. Such a process is generally accompanied with random twitching of the interface and local bursts, which we observed (Figure 1.17); however, this phenomenon has a long prior history.<sup>103-105</sup>

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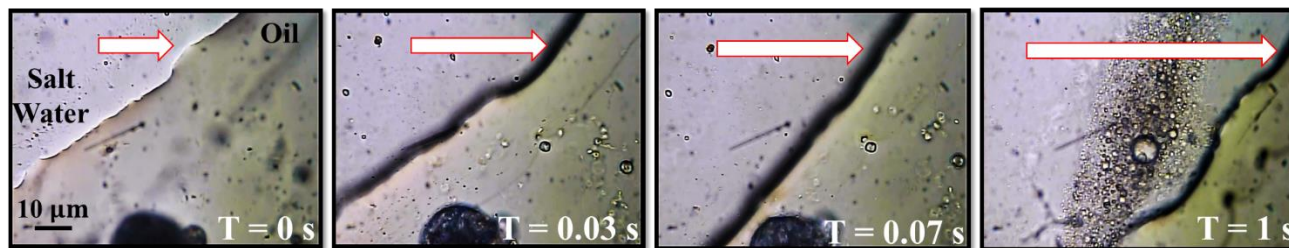


**Figure 1.17.** A drop of oil with 400 ppm of a mixture of Dodecanoic acid and Brij 35 is placed in close contact with a drop of 0.6 M of salt water on a microscope stage. An aggregate formed from the surfactant molecules appear as the dark particle. As soon as the oil-water interface reaches the particle, it spontaneously disintegrates to form oil in water emulsions. See also (Appendix: Movie 1)

If the interfacial region gets enriched or depleted of certain components due to diffusion and the concomitant phase transformation, osmotic flow of the bulk phases would also develop near the interface. These coupled dynamics provide the conditions needed for the evolution of interfacial instability and roll cell formation,<sup>16, 107</sup> which were predicted and observed experimentally. As a consequence of stratified convective flow, certain regions of the interface are compressed, while some other regions are stretched. When the local compression reaches a critical value, folds are likely to appear at the interface, which would grow and pinch off to form emulsion droplets (Appendix A, Figure 6).

In the backdrop of these scenarios, it is, perhaps, safe to state that agitation-less spontaneous emulsification is not what its name purports to convey, and there remains a finite possibility that nano-sized emulsion would potentially form even at zero Reynolds number ( $Re$ ) as surmised from Figure 1.9. In order to explore these issues, we envisaged an experiment where a layer of oil would be deposited as gently as possible over an aqueous phase (Appendix A, Figure 7), with the surfactants pre-dissolved in water. The purpose of the experiment was to collect small aliquots of the aqueous phase close to the interface for examination with CHDF, as well as UV-Vis spectroscopy to interrogate if and when the nano-sized emulsions are formed. Dodecane and diesel served as contrasting oily phases because of the vast differences in their mutual solubilities with

water. During the course of the study with polymeric additives, we were gratified with the observation that PTBS has a peak (270 nm) that is distinct from that of diesel (220 nm) in the UV-Vis spectrum, which thus served as a useful marker with which to determine if it is encapsulated in the oil or not. This turned out to be a very useful way to discern, albeit indirectly, if the emulsion droplets are formed by a relatively quiescent or a violent process, as discussed below. PDMS, on the other hand, does not have any such unique signature in the UV-Vis spectroscopy; thus, the emulsification process with dodecane could not be analyzed in the same way as with diesel.

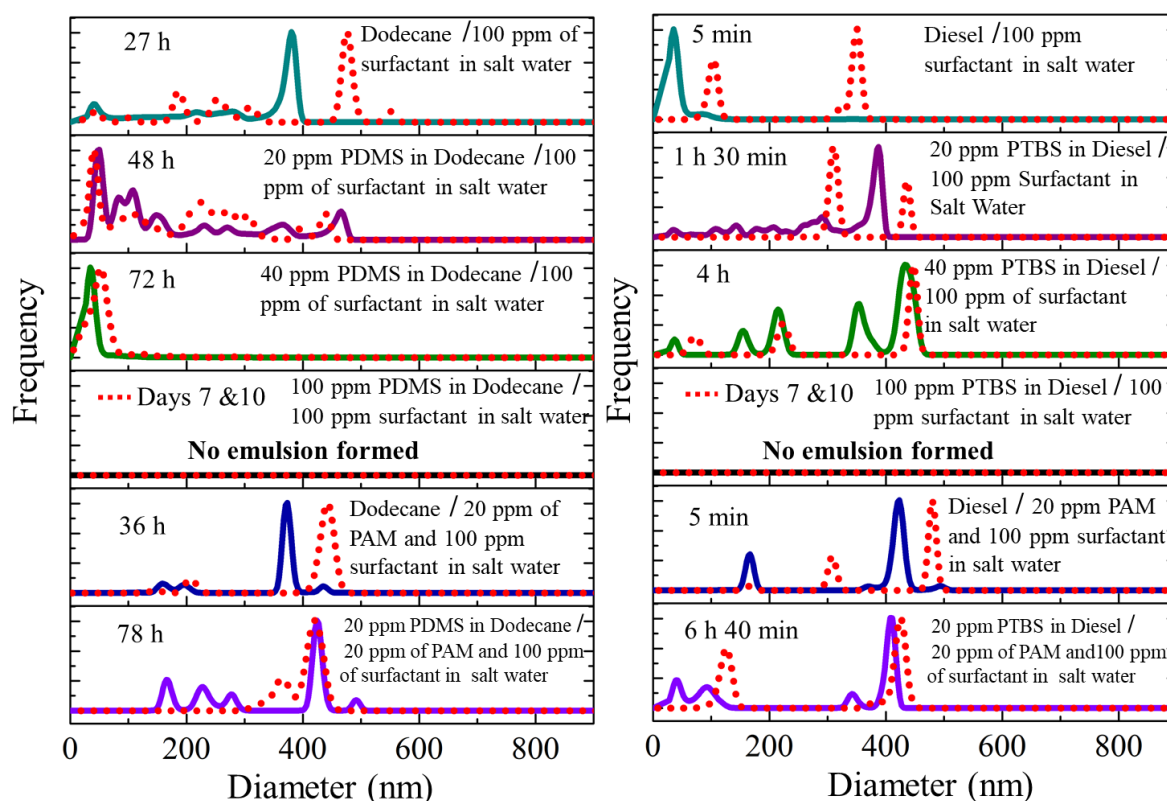


**Figure 1.18.** In the unstirred experiments, nano-sized droplets are always formed. However, the onset of its formation depends on what is present in oil or water. Furthermore, spontaneous emulsification can be thwarted with polymeric additives.

The results of these studies (Figure 1.18) reveal that nano-sized emulsions are always formed; with the time for the first appearance of emulsion varying greatly between dodecane and diesel. While, the emulsion formed rather quickly (within five minutes) with diesel, the corresponding time was

27 h with dodecane. This vast difference of the incubation time may be attributed to the large differences of the solubility of water in these two oils (0.0001 mg/L in dodecane and 100 mg/L in diesel). With a small amount (20 ppm) of PDMS added to dodecane, the time taken for the detection of first emulsification increases to 48 h, following which nano-sized emulsions with a broad distribution of size suddenly appear. With a further increase of PDMS (40 ppm), the dead time increases to 72 h and finally at a 100 ppm of PDMS in dodecane, emulsification is completely arrested with no sign of emulsification even after ten days.

The emulsification dynamics with diesel provides an intriguing contrast to that with dodecane. To begin with, emulsion droplets form with a small and tight size distribution rather rapidly, i.e. within minutes. With a trace amount (20 to 40 ppm) of PTBS added to diesel, the time to emulsification increases significantly and systematically, eventually it is totally suppressed at a concentration of 100 ppm PTBS in diesel. Just as the case with PDMS in dodecane, no sign of emulsification is detected even after ten days. Apart from the increase of the dead time, another noteworthy feature of these experiments is that the number density of the nano-sized emulsion decreases systematically with the increase of the concentration of the hydrophobic polymers in both the oils (Table 1.2).

**Table 1.2.** Number Density of Droplets Produced in Unstirred Experiments

|                                                                       | Time for<br>emulsion<br>formation | Number of<br>Droplets/Microliter |                                                                     | Time for<br>emulsion<br>formation | Number of<br>Droplets/Microliter |
|-----------------------------------------------------------------------|-----------------------------------|----------------------------------|---------------------------------------------------------------------|-----------------------------------|----------------------------------|
| Dodecane / 100<br>ppm Surfactant in<br>salt solution                  | 27h                               | 25                               | Diesel / 100<br>ppm Surfactant<br>in salt solution                  | 5 min                             | 30                               |
| 20 ppm PDMS in<br>Dodecane/ 100<br>ppm Surfactant in<br>salt solution | 48h                               | 15                               | 20 ppm PTBS<br>in Diesel/ 100<br>ppm Surfactant<br>in salt solution | 1h 30 min                         | 22                               |

|                                                                                |      |    |                                                                              |           |    |
|--------------------------------------------------------------------------------|------|----|------------------------------------------------------------------------------|-----------|----|
| 40 ppm PDMS in Dodecane/ 100 ppm Surfactant in salt solution                   | 72h  | 12 | 40 ppm PTBS in Diesel/ 100 ppm Surfactant in salt solution                   | 4 h       | 16 |
| 100 ppm PDMS in Dodecane/ 100 ppm Surfactant in salt solution                  | ---- | 0  | 100 ppm PTBS in Diesel/ 100 ppm Surfactant in salt solution                  | -----     | 0  |
| Dodecane / 20 ppm of PAM and 100 ppm Surfactant in salt solution               | 36h  | 6  | Diesel / 20 ppm of PAM and 100 ppm Surfactant in salt solution               | 5 min     | 14 |
| 20 ppm PDMS in Dodecane/ 20 ppm of PAM and 100 ppm Surfactant in salt solution | 78h  | 5  | 20 ppm PTBS in Diesel/ 20 ppm of PAM and 100 ppm Surfactant in salt solution | 6h 40 min | 11 |

**Table 1.3.** Incorporation of PTBS in Diesel in the emulsification Experiments

| Concentration of PTBS in oil (ppm) | Water phase (additive, ppm)     | Ratio of Areas corresponding to peaks at $\lambda_{270}$ and $\lambda_{220}$ | $A_{270} / A_{220}$ |
|------------------------------------|---------------------------------|------------------------------------------------------------------------------|---------------------|
| 20                                 | None<br>(Turbulence – 114 W)    | 0.49                                                                         | 0.22                |
| 20                                 | PAM, 20<br>(Turbulence – 114 W) | 0.46                                                                         | 0.18                |
| 20                                 | None                            | 0.44                                                                         | 0.16                |
| 40                                 | None                            | 0.41                                                                         | 0.14                |
| 20                                 | PAM, 20                         | 0.31                                                                         | 0.11                |

The high molecular weight PTBS does not dissolve in water, which was confirmed in UV-Vis spectroscopy that showed no sign of either oil or PTBS when surfactant free aqueous phase was used. From this consideration, we can discard the scenario that the oil molecules diffuse passively

in the aqueous phase (with surfactant), where they self-associate and form nano-sized emulsion droplets. The fact that the oil droplets always entrap the polymer (PTBS) molecules suggests that the emulsification results from transient or persistent shake up events, causing them to eject out of the interface while PTBS remains dissolved in it. PTBS, nevertheless, increases the incubation time for emulsification, which is illustrated with another experiment shown in Figure 1.19 (see also Table 1.2). Here, a quartz cuvette was partially filled with a small amount (3 mL) of salinized water containing 100 ppm of surfactant, following which 1 mL of diesel oil was deposited over it. With the optical path maintained at 0.4 cm below the oil-water interface, the cuvette was secured inside a UV-Vis spectrophotometer following which time dependent data acquisition was initiated. With diesel alone, emulsification occurs without any measurable dead time. However, when a small amount of PTBS is present in oil, no oil or PTBS is detected for about 2 h, following which the emulsification is announced by the sudden rise of the concentration of oil and PTBS in the aqueous phase. The ratio of PTBS to Oil remained the same throughout the 800 min of data acquisition.

Experiments carried out with the addition of 20 ppm PAM in the aqueous phase show that the time to emulsification is not enhanced markedly (Table 1.3) for either diesel or dodecane. Nevertheless, the number density of droplets is reduced significantly when compared with the control. When the combined effects of hydrophobic and hydrophilic polymers are pursued, both the incubation time for emulsification as well the number density of droplets are affected. We are thus evinced to consider that a dynamic instability underscores the process underlying the so-called spontaneous emulsification (see below).

### **1.2.8. Consolidation and Reiterating the Main Points**

At this stage, it would be prudent to consolidate and re-capitulate the main findings of this research, based on which we propose certain new possibilities to consider. To begin with, we found that the use of *drop resonance* provides a quick and effective way to obtain dynamic interfacial tension of an interface. The spherical harmonics of a drop can be excited via internal pressure fluctuation, which has the advantage over vibrating the entire drop in a liquid pool, although the latter method can also be adapted under favorable conditions. The method of pressure fluctuation is easily adaptable to cases where a liquid drop is immersed in another liquid. In some cases, we noticed that emulsification could also be induced during drop excitation, which prompts us to consider that exciting a drop with the typical (pre-programmed) noise of turbulence could be an intriguing extension of the studies described in this work.

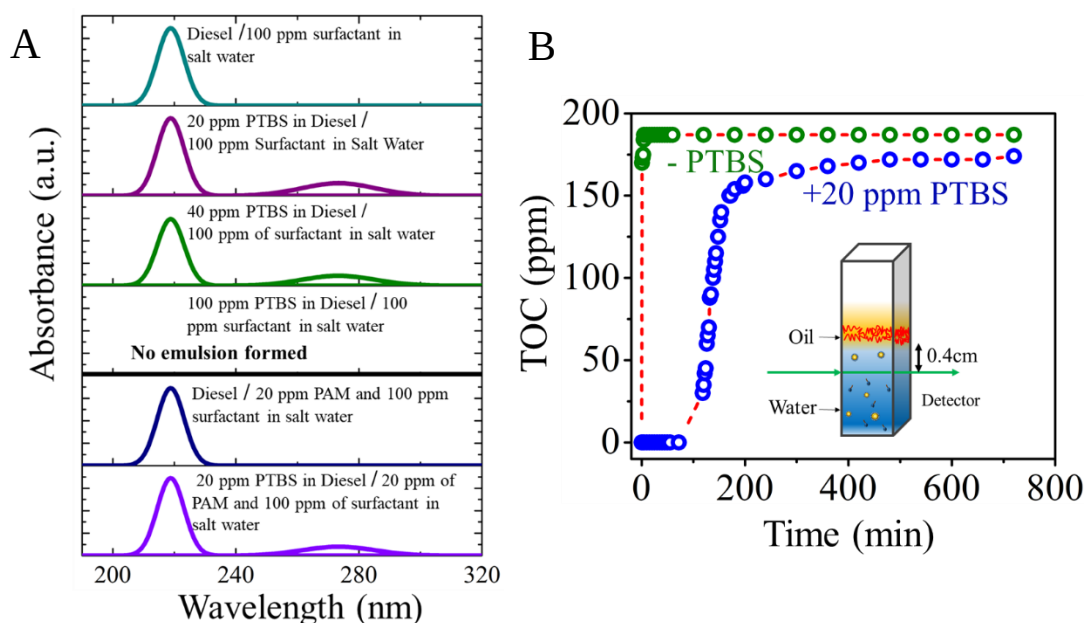


**Figure 1.19.** (A) The de-convoluted UV-Vis spectra of the emulsion collected under various conditions corresponding the experiments reported in Figure 1.18C. (B) Kinetics of emulsion formation obtained from UV-Vis spectrum obtained using the set up shown in the inset.

*Surface pressure constructs* provide additional information of the interface, even though the current measurements are limited to air-water interface. A method allowing such measurements at

the liquid-liquid interface is expected to provide even more detailed information about the physical properties of the surface separating two liquid phases, which would be profoundly relevant to understanding the mechanism of emulsification.

In the current work, the combinations of the above methods provided useful insights into the emulsification of oil in water in the presence of not only surfactants, but also when certain long chain polymers are added to either oil or water. Surface pressure-area constructs provided additional insights into the stability of a surface and how it can be enhanced.

Dynamic pressure fluctuations measured during turbulence ascertain that they are useful reporters to the roles of various parameters designed to modify the property of turbulence. For example, we learned how the infusion of air violently increases the dynamic pressure fluctuations, thereby promoting the formation of transparent emulsions containing nanometer size droplets. Addition of polyacrylamide, on the other hand, quenches the large hydrodynamic fluctuations, thereby limiting the formation of small emulsion droplets. We also learned that a hydrophilic polymer increases aging, presumably, by bringing the droplets close to each other via depletion-induced force, whereas a hydrophobic polymer thwarts aging by reducing the chemical potential of the oil molecules inside a droplet.

The production of the *nanometer size emulsion droplets* is beyond the range of prediction based on dynamic pressure fluctuations. The energy needed to produce a 10 nm size nano-droplet costs about couple of hundreds of  $k_B T$  amount of energy contributed by the interfacial and bending energies alone. Where do such large energies come from? Recently Josserand, Pomeau and Rica<sup>108</sup> provided a new insight in the physics of turbulence starting with a self-focusing non-linear Schrodinger equation, and proposed that the finite time singularities develop randomly in space and time near which the hydrodynamic dissipation occurs. We may consider the possibility of

phase transition of water being a sink of energy near such high intensity events, thereby inducing the formation of multiple nano-bubbles via cavitation. The subsequent collapse of these nanobubbles could potentially provide the type of energy needed for the creation of nano-size emulsion droplets. These high intensity singular events are likely the rare events that have been missed by our sensors due to the limitation of spatial and temporal resolutions. Secondly, the interface may degenerate due to shear-induced compression of the adsorbed monolayer or that originating from the shrinkage of a droplet during Ostwald ripening. Experiments performed with a PTBS marker present in the oil show that it is spontaneously entrapped in the emulsion when the oil phase gently comes in contact with the aqueous phase containing the surfactant.

Another noteworthy observation is that the droplets produced under agitation free condition were detected at a distance of about 1-2 cm below the oil water interface within minute, in some cases. Had the droplets reached that distance, entirely by passive diffusion, the required time would be astronomical ( $\sim 10^{10}$  s). The fact that the actual time was so much shorter than the diffusion time indicates that the droplets acquired significantly amount of kinetic energy as soon as they were formed and/or that the aqueous phase below the interface fluctuates more vigorously than would be the case with thermal noise alone. In view of these observations, some of the plausible mechanisms underlying the spontaneous emulsification are outlined below.

One pathway for emulsification, which resembles a *chemical ratchet* (Figure 1.20) or *active transport*, starts with a fluctuating monolayer of surfactant separating the oil and aqueous phases. If the interface fluctuates even passively, the adsorbed molecules would be rarified on some parts and relatively unperturbed on other parts of the interface. While this would cause a Marangoni flow attempting to bring the surface to equilibrium, adsorption of the surfactant from the bulk could also partially fill up the space created by rarefaction. This process would continue as long

as the chemical potentials are not equilibrated, or until the adsorbed monolayer is critically compressed, following which a folding transition would trigger the formation of nano-sized droplets. The ensuing pinch off instabilities would provide some kinetic energy to the droplets for it to travel faster than would be allowed by diffusion alone. The fact that the events related to co-operative folding transition can give rise to long-range disturbance to a monolayer has been beautifully demonstrated in the past.<sup>62,109</sup> Using fluorescence microscopy, the authors observed jerky events in a critically compressed monolayer, which were accompanied with sharp velocity spikes. These are similar to crackling noises seen in other discrete events, such as domain flip in magnetism, co-operative plastic deformation and earthquake to mention a few, where energy is liberated as bursts.

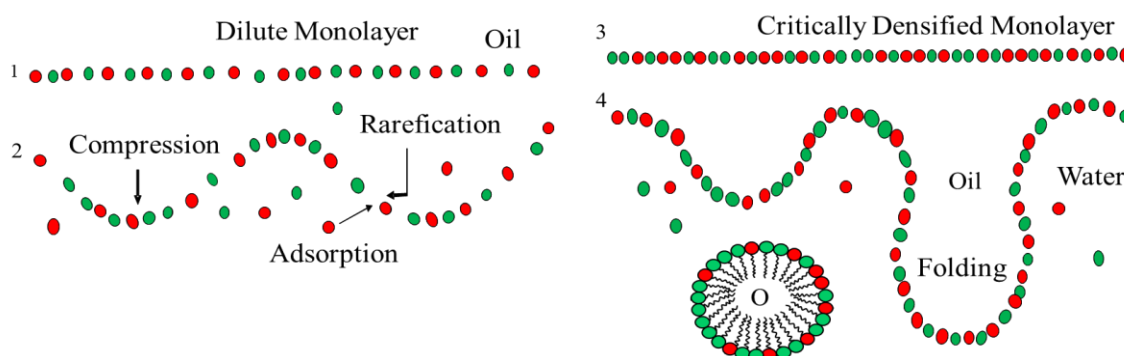


**Figure 1.20.** Emulsification via Surfactant Ratcheting to Interface

Another plausible mechanism underlying the formation of nano-sized emulsion (Figure 1.21) is related to phase *inversion*<sup>110,111</sup>, where we envisage that water molecules invade the oil phase, via molecular diffusion as well as at a supra molecular level, in which clusters of few water molecules in the size range are shot  $\sqrt{k_B T / \gamma} \sim 1 \text{ nm}$  out of the aqueous phase. Meanwhile, certain amount of surfactant diffuses from the aqueous to the oil phase as well. With the progression of time, a thin region of the oil side of the interface is enriched with water to such an extent that water solvated

micelles, lamellar or other structures, including water in oil nano-emulsions are formed. This hypothesis is supported by earlier publications that elucidated the formation of inverted emulsion of water in diesel.<sup>8,112</sup> As there exists virtually no energy barrier, the inverted (water-in-oil) emulsions are susceptible to grow spontaneously by fusing with each other as well as with the interfacial monolayer following which a curvature reversal (an instability) develops at the interface. During this process, as the local concentration of surfactant is enriched at the fusion sites, the ensuing Marangoni bursts could further agitate the interface. The possibility that Marangoni effect can cause shock waves is relatively a less studied phenomenon; however, a few reports convincingly support such a possibility.<sup>113, 114</sup>

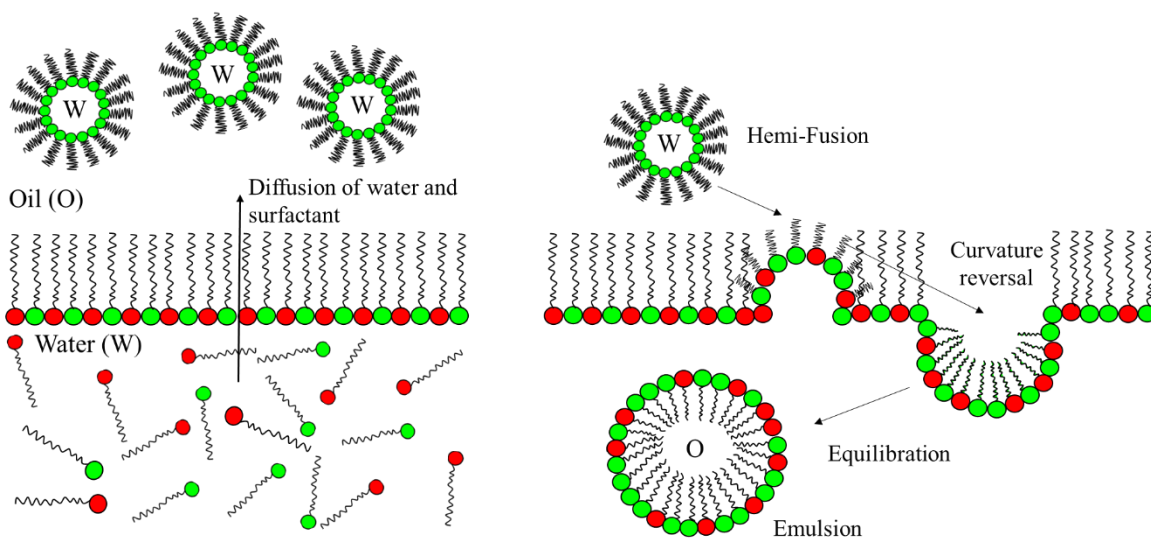


**Figure 1.21.** A schematic of emulsification via phase inversion.

It is noteworthy that the amount of PTBS incorporated in the nano-sized diesel droplets in the unstirred experiments is slightly lower (Table 1.2) than that observed in turbulence induced emulsification. This would be expected if the size of the emulsion approaches the radius of gyration of the polymer<sup>115</sup> (10-16 nm), as an entropic penalty has to be paid in trapping and confining a

polymer in a confined space. However, when the agitation of the interface is stronger as would be the case with high concentration (500 ppm) of surfactant in spontaneous emulsification or with turbulence; this limitation seems to be alleviated to some extent as we observe similar amount of PTBS incorporated in oil in both the cases.

The mechanisms described above are relatively passive compared to another possibility where more *violent agitation* of the interface may develop. Here, we are motivated by a proposition by Yves Pomeau (personal communication) as well as by Prosperetti and Plesset.<sup>116</sup> The later authors, in particular, were interested to model the instability of an evaporating liquid surface and invoked the equations of shock waves in doing so. The authors proposed that vortices could be produced near the surface due to the refraction of streamlines as in the Landau Darreus instability<sup>117-119</sup> incurred in the roughening of a flame. If the oil-water interface is, indeed, in a persistent or intermittent state of turbulence, and if the vortices resulting from the refracted streamlines play a role in destabilizing the interface, would a water-soluble polymer, which quenches hydrodynamic vortices, inhibit the nano-droplet production? Experimental observation that PAM inhibits spontaneous emulsification as it does in turbulence induced emulsification intrigues us.

### **1.2.9. Summary: Phase I**

The main conclusions of this work are as follows:

1. Dynamic pressure fluctuations in turbulent water are excellent reporters to how various factors affect emulsification, which is further augmented with careful interrogation of the interfacial and the bulk properties of the continuous phases.
2. Emulsions are formed, non-trivially, at an oil-water interface even in the absence of externally applied agitation. Models are proposed to capture the possible roles of interfacial instability in such processes.

3. Spontaneous emulsifications are affected in the same way as the turbulent induced emulsification with polymeric additives, particularly with a hydrophilic polymer, which is known to quench the hydrodynamic fluctuation in the latter. Supposedly, its origin is hydrodynamic, in that the polymer deters spontaneous emulsification by quenching the local fluctuation near the interface originating from interfacial instability.

4. These studies have been able to identify the relevant interfacial and hydrodynamic parameters, careful controls of which should be valuable in thwarting emulsification in various practical settings.

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## Phase II

# Spontaneous Emulsification: Elucidation of the Local Processes<sup>1</sup>

**Abstract.** Micro and/or Nano sized emulsions are formed when an organic liquid gently comes in contact with water in the presence of a surfactant, where no external agitation is required. Many years of research made it clear that the driving force for spontaneous emulsification arises from the differences of the chemical potentials of various components in the organic and aqueous phases, which triggers diffusion coupled hydrodynamic fluctuation. While extraordinary theoretical developments have taken place that attempted to describe these processes within the scopes of equilibrium and non-equilibrium thermodynamics, the local processes underlying spontaneous emulsification, however, still remain elusive. In this research, we investigate the local processes that involve the transfer of surfactant as well as water from one phase to another (i.e. water to oil), which results in the formation of water-in-oil emulsion in the organic phase and, subsequently. These emulsions invert into the oil-in-water emulsion, rather abruptly, as they cross the phase boundary. Studies based on UV spectroscopy and molecular dynamics indicate that these processes may involve explosive events and subsequent assembly of the fragments to other organized structures which are reminiscent of the cusp catastrophe proposed earlier by Dickinson. These processes lead to either a strong or a weak fluctuation of the component concentrations below the interface that also becomes evident in the fast (athermal) diffusion of the emulsion droplets from the interfacial region farther into the bulk water. These events can be arrested suitably with polymeric additives.

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## 2. Introduction

Microscopic or submicroscopic emulsions<sup>1</sup> are dispersions of droplets of one liquid into another that can be formed via agitation or even without it. Spontaneous emulsification, in which no agitation is required, was first discovered by Gad, followed by a series of papers by Quincke, Brucke, and others, which were documented by McBain and Woo<sup>1</sup>. While our understanding of agitation-induced emulsification has advanced considerably since the original publication of Hinze<sup>2</sup>, the processes that lead to emulsification without agitation<sup>1, 3-21</sup> continue to inspire new imaginations even after many decades of research in this field. The fundamental question that the researchers had to grapple with is how is it possible to create new surface areas associated with emulsification, which, of course, would be trivial to understand had the oil-water interfacial tension been negative<sup>7,8</sup>. While this scenario cannot be ruled out in a few specific cases, spontaneous emulsification, nonetheless, occurs predominantly with positive interfacial tension<sup>7</sup>. A conventional wisdom in this field is that the increase of the interfacial free energy due to the formation of multiple droplets is somewhat compensated by an increase in the entropy of dispersion. In other words, emulsions can form<sup>7</sup> if the net change of free energy is negative. Spontaneous emulsification is generally accompanied by various spectacular dynamic effects such as the kicking and oscillation of pendant drops, twitching and sudden bursts of an interface, and rapid penetration of droplets in a liquid against gravity. These phenomena are now well-known and well-documented in a plethora of publications<sup>3,4,14,15</sup>.

It has been realized over time that the hydrodynamic instabilities can develop at the interface that could originate from Marangoni instability due to local variation of interfacial tension at the interface. This may occur via spontaneous fluctuation of concentration, which, according to McBain et al.<sup>1,3</sup>, was first conceived by Quincke. The chemical potential gradients across the

interface lead to mass transfer and a concomitant hydrodynamic instability<sup>3</sup>, whereas an in-plane gradient of concentration can lead to Marangoni force-induced hydrodynamic flow. Due to a resurgent interest in this field of research, new insightful papers have continued to be published even recently<sup>17, 22-28</sup>, whereas detailed accounts of the earlier research have been reviewed<sup>16,18</sup>. As this particular article is not meant to be a review, here we summarize only the salient features of the related literature.

One important breakthrough that has occurred in understanding spontaneous emulsification is understanding the role of the so-called Interfacial Turbulence, which is the consequence of mass transfer coupled with solutary Marangoni flow near and at the interface. McBain et al.<sup>1,3</sup> presented some of the earliest observations. With experiments performed with drops of xylene placed on an aqueous surfactant solution, the authors observed that the droplets either explode violently or numerous small droplets are emitted from the larger droplet. The authors proposed an important concept in that the spontaneous emulsification results due to the self-generated eddies, which tear off large droplets of the oil. This picture is similar to that presented later by Hinze<sup>2</sup>, but in situations where the eddies are generated by agitation-induced turbulence.

McBain et al.<sup>3</sup> also proposed that the driving force for spontaneous emulsification in a system with positive interfacial tension arises from the energy of adsorption, as well as the solubilization of hydrocarbon in the aqueous detergent solution. A rigorous theoretical treatment of interfacial turbulence was provided later by Sterning and Scriven<sup>15</sup>, who performed a stability analysis of an interface across which mass transfer occurs. The base state of the problem defines the balance of the viscous and the Marangoni stresses. The bifurcation analysis can then be performed about the base state by allowing a fluctuation of surfactant concentration at the interface. At the scaling level, the interfacial flux can be described in terms of such well-known dimensionless parameters as the

Marangoni and Schmidt numbers. Golovin<sup>29</sup> stated two special scenarios. The first one is chaotic, in which disturbances are local and where the fluctuations die out fast following such sporadic activities as pulsation, bursts, and twinkling of the interface. Another scenario results with a slower dissipation of energy, in which periodic roll cell like flow patterns are formed below and above the interface<sup>14</sup>. Sherwood and Wei<sup>4</sup> as well as Gooch Pattader et al.<sup>30,31</sup> have provided a further exposition of the roles of such interfacial instabilities in various mass transfer processes, which have immense implications in liquid-liquid extraction technologies.

While interfacial convection results from Marangoni induced hydrodynamic instability, one may ask if such convection in itself, is responsible for the emulsification of one liquid phase into another. In order to explore this point Davies and Rideal<sup>32</sup>, and later Miller et al.<sup>10</sup>, suppressed the role of interfacial convection by tempering the Marangoni instability either by adding salt or excess surfactants in a system where an oil and a co-solvent were gently brought into contact with water. However, even in such conditions, emulsions were formed. This led Davies and Rideal<sup>32</sup> to suggest a mechanism called “diffusion and stranding”, in which a co-solvent diffuses in the aqueous phase carrying oil along with it. Subsequently, as the co-solvent diffuses away, oil molecules get stranded as droplets in the aqueous phase stabilized by adsorbed surfactant.

Following a line of argument proposed earlier by Kirkaldy<sup>33</sup> in the context of crystallization in a three-component system, Miller et al.<sup>10-12</sup> suggested that the concentration of a diffusively transferred species across an interface first reaches a supersaturation, from where stable phases are formed via the spinodal process. This idea of the formation of an organized structure from a supersaturated solution was proposed originally by Ostwald<sup>34</sup> in the context of crystallization. See also the work of Ostrovsky and Good<sup>9</sup>, and the references cited therein<sup>35</sup>, for further exposition of this idea in emulsion formation.

In order to exemplify the scope of chemical instability and from there, the phase transformation, Friberg<sup>36</sup> mapped the evolution of the concentration of the species on a ternary phase diagram, which allowed visualization of which of the paths lead to single- or two-phase regions. Recently, Neibloom et al.<sup>28</sup> extended similar ideas to spontaneous emulsification involving chemical reactions and elucidated the roles of diffusion and stranding underlying such processes.

The analysis of Sternling and Scriven<sup>15</sup> was restricted to the instability of planar interfaces, while, in reality, the interface can deform<sup>37,38</sup>. The concomitant refraction of hydrodynamic streamlines can create local vortices and hydrodynamic instability that may ensue even in the absence of a surface tension gradient. The deformation of the interface poses difficulties in tracking the evolution of a system as various paths are plausible. Kirkaldy<sup>33</sup> proposed that this problem can be resolved using the principle of non-equilibrium thermodynamics, in which the preferable paths are those that minimize the rate of entropy production.

There, of course, remains the possibility that all the events discussed above may participate concurrently in smaller or greater degrees in an emulsification process. Furthermore, if an oil containing a surfactant is brought into contact with an aqueous phase, water may diffuse in the oil, triggering an aggregation of a surfactant and then its precipitation out of the solution, either as crystal or amorphous aggregate. When these precipitates come into contact with the oil-water interface, it would deliver surfactants to the interface rendering it to be locally supersaturated. During the relaxation of the interface from the local supersaturated heterogeneity, it could generate an interfacial shock wave, local fluctuation of interfacial area, and folding/budding transition<sup>39,40</sup>. These could also trigger pulsation, twinkling, and bursts, which are ubiquitously observed interfacial events.

The brief discussion as presented above, highlights the richness and complexity underlying spontaneous emulsification, the understanding of which requires adequate blends of interfacial science, transport phenomena, and phase evolution kinetics within the domain of non-equilibrium thermodynamics. It may be naïve to presume that a general understanding of spontaneous emulsification is imminently forthcoming, although certain semi-empirical approaches, such as those based on the calculation of HLB<sup>1</sup> (hydrophobic lipophilic balance) and/or the HLD<sup>41</sup> (hydrophobic lipophilic difference) numbers for a combination of surfactant, oil, water provide useful insights into such mechanisms. Additionally, the sudden transformation of an oil/water to water/oil emulsions or vice versa, which are recognized to be parts of the overall emulsification hierarchy can be captured using the idea of cusp catastrophe<sup>42-44</sup>. However, this method, understandably, does not provide the much-needed mechanistic insights into the local processes as it does not claim to be anything more than a phenomenological model. We are motivated by the hypothesis that understanding the local processes, including those involving singular transformations of one phase to another, is important to develop a comprehensive understanding of the emulsification processes.

### **Background, Motivation, and Objective**

During the last five years, we have been conducting research, the purpose of which is to elucidate how emulsions are formed in the ship bilges that occur, sometimes, under vigorous agitation, and, other times without it. This is a vexing problem for the armed forces, as all the naval ships collectively produce a massive amount of oil-contaminated water that is difficult and/or expensive to purify before the purified water can be discharged back into the ocean<sup>45</sup>.

The complexity of bilgewater, which is wastewater containing oils, fuels, salts, lubricants, deck, and bilge cleaners, is very rich. An important question here is: how are the oil-in-water emulsions

formed in bilgewater, where the concentration of the surfactant is typically close to, but slightly lower than, the critical micellar concentration. This particular fact that micelles and, therefore, emulsions can form at a concentration below c.m.c is, in itself, not as striking as it might have appeared before the publication of a seminal work by Besseling and M. A. Cohen Stuart<sup>46</sup>. Using self-consistent field theory these authors demonstrated that the above-mentioned structures can form via nucleation. It is only that their formation becomes unchallenged at c.m.c when the energy barriers disappear, which is a general knowledge in emulsion and polymer sciences. The daunting challenge with the bilgewater stems from its highly complex composition. Nevertheless, it is possible to identify the minimum set of parameters with which the complexity of the problem can be preserved in a sufficient level with which to develop a rational understanding of the emulsification process in bilge water (see reference 26 and the references cited therein)

In our previous publication, we primarily focused on emulsification under agitated conditions that lead to hydrodynamic turbulence<sup>26</sup>. Here, we pay attention to what happens without any external agitation. The system that we use here is the same as that published previously: specifically, it involves an equi-weight mixture of an ionic (dodecanoic acid) and a non-ionic (Brij 35, Polyoxyethylene (23) Lauryl Ether) surfactant, dissolved in the 0.6 M aqueous salt solution over which various purified organic liquids were gently deposited. We would like to emphasize that an important distinction between the system we study here and those reported previously by Davies and Rideal<sup>32</sup> as well as Miller et al.<sup>10-12</sup> is that there is no co-solvent in our system. [Note: In what follows, we use the term oil for the organic phase intermittently for convenience although the term “organic phase” is more general and used most often]

What would be immensely useful in interrogating the dynamic and the self-organizing behaviors of the surfactants is to exploit a property of the surfactant itself that would be *reporting* the states

that they evolve through. In this regard, we mention here a recent elegant investigation<sup>48</sup>, where the authors used a solvatochromic surfactant, the fluorescent intensity of which depends on the polarity of the surrounding environment. This particular characteristic allowed a dynamic visualization of the surfactant dynamics at and near the oil-water interfaces.

In a similar vein as these previous studies, here we used ultraviolet (UV) spectroscopy that allowed us to discern whether the surfactants are in free or in the aggregated state in both the organic and aqueous phases. This was possible as the UV-absorbing carboxylic acid groups exhibit Bathochromic (red) and Hypsochromic (blue) shifts depending upon whether they form aggregates via H-bonding interaction with each other and/or with the solvent itself<sup>49,50</sup>. Information on such interactions in both the organic and aqueous phases has been vital in our understanding of the formation of various local processes. For example, if the relevant chromophore of a surfactant exhibits a red shift in a non-polar environment, we may say that this is possibly due to intermolecular H-bonds, thus inferring the presence of dimeric, trimeric, or polymeric states<sup>49,50</sup> that they are in. Higher order shifts would also be possible in a non-polar solvent if the latter contains a small amount of water thus promoting the formation of such a self-assembled structure as an inverted water-in-oil emulsion. When the surfactant is present in the aqueous phase, other types of chromic states could also be observed due to the polybasic character of the carboxylic acid<sup>51,52</sup>, which could be interrogated via pH-dependent Bathochromic titration (see below). While the UV spectroscopy allowed us to interrogate various types of self-assembled structures that are formed, these studies, when it is carried out in parallel with a dissipative particle dynamics<sup>53</sup> (DPD) and/or combined with a molecular dynamics (MD) simulation, we gained even a deeper insight into these structures and their stability.

The basic experiment consisted of an organic phase (alkane, aromatics, and diesel) that is deposited on the surface of an aqueous phase. Salt (sodium chloride, 0.6 M) was dissolved in water to produce a salinity comparable to that of seawater, following which an anionic surfactant (dodecanoic acid), a nonionic surfactant (Brij-35) or their mixture was dissolved in it at a total concentration of 100 ppm. These compositions are closely parallel to those recommended for the simulation of bilge water.<sup>27</sup>

What we learned, at one level, is that the surfactants as well as molecular water diffuse into the organic phase from the aqueous phase below it. The surfactants then self-assemble in the organic phase to form an inverted (water-in-oil) emulsion that then fuses with the interface thus forming an oil-in-water emulsion. These experimental results coupled with those obtained from the DPD-based Molecular Dynamics using the Large-scale Atomic/Molecular Massively Parallel Simulation (LAMMPS) software, provided a more complete picture into the emulsification processes. Another insight gained from these studies is that the micelles and vesicles that are formed in the aqueous phase fuse intermittently with the interface explosively, following which various fragments are produced. These fragments then re-combine and lead to the formation of inverted water-in-oil emulsion in the organic phase. Subsequently, the inverted emulsions reach the interface from the organic phase and disintegrate again explosively following which the fragments cluster together and form oil-water emulsions.

**2.1. Roadmap.** The Results and Discussion section presents the summary of all the experiments performed in this research, with an adequate introduction and analysis. Elaborate descriptions of the experimental methods are provided in the Appendix (A). After consolidating the main points of this research, several references are cited. As the literature is vast, we had no choice, but to omit, regretfully, many important references.

## 2.2. Results and Discussion

### 2.2.1. Bathochromic and Hypsochromic Shifts: The Polybasic Character of Carboxylic Acid

There exists a plethora of literature<sup>49-51, 54-56</sup> that elucidates the various ways alkyl carboxylic acids interact with each other and with water (Figure 2.1). For example, they can form an H-bonded cyclic dimer, not only in water but also in a non-polar liquid<sup>55</sup>.

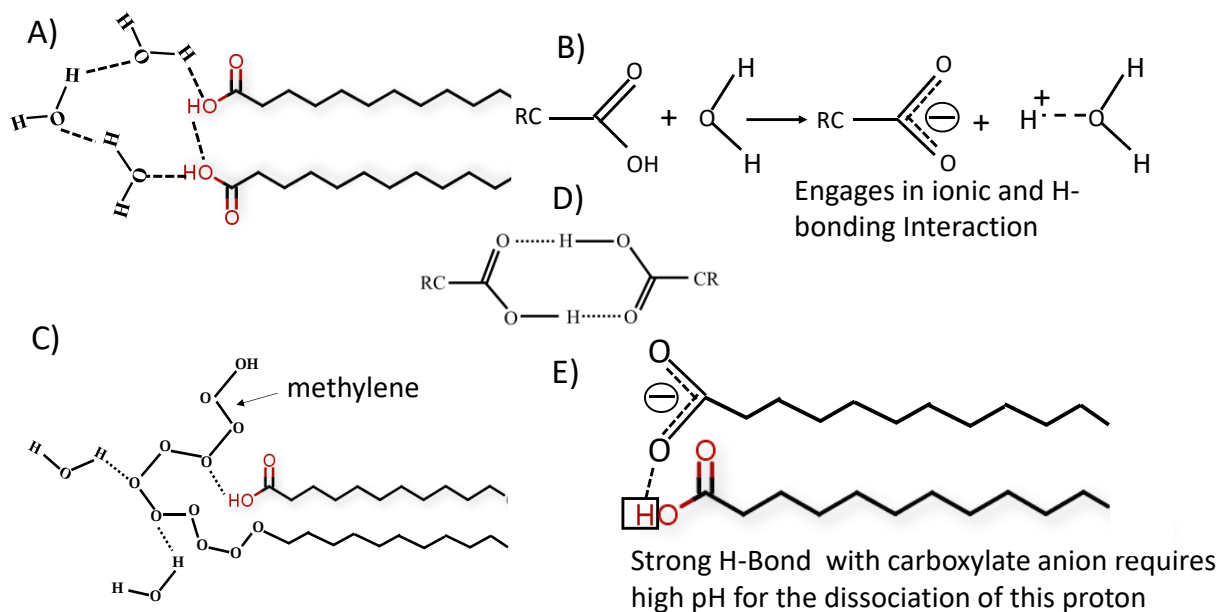


**Figure 2.1.** Various types of H-bonding interactions exhibited by carboxylic acid. A) Two carboxylic acids can interact with each other directly via H-bonding interaction or B) through H-bonding interaction with water<sup>49</sup>. C) Carboxylic acid interacts with the ether group of a non-ionic surfactant via H-bonds. D) Two carboxylic acid groups forming dimer E) A deprotonated carboxylic acid acquires a net negative charge, which can interact with a neighboring protonated group via H-bonding interaction.

While two fatty acids can self-associate via hydrophobic attraction<sup>54,56</sup> of the alkyl groups in water, the association is strengthened due to additional H-bonding interaction with each other, either directly or indirectly via H-bonding interaction with water. The carboxylic acid groups can also deprotonate thus forming carboxylate ions, which can also form various types of H-bonds with water

or with another proton-donating group. The ether group of a non-ionic surfactant can also engage in an H-bonding interaction with the protons of water or the carboxylic acid.

Ruderman et al.<sup>49</sup> published an important paper, where they demonstrated via UV absorption spectroscopy and molecular dynamics simulation that acetic acids form dimer, trimer, and higher order aggregates by forming H-bonds with each other and/or with water. The signature of the extended H-bond formation was evident in UV spectroscopy that exhibited progressive Bathochromic (red) shift with the concurrent increase of the aggregate size that occurs when the concentration of the acetic acid is increased. This knowledge has been very crucial in interpreting the Bathochromic or Hypsochromic behaviors of surfactants, notably when a carboxylic acid is a functional group of the surfactant.

**2.2.2. Surfactants in Aqueous Phase.** Similar to those reported by Ruderman et al.<sup>49</sup>, we too observed that the UV absorption peak of the carboxylic acid exhibits a progressive red shift (Figure 2.2 A) as the concentration of dodecanoic acid is increased in an aqueous phase from 2 ppm to 100 ppm. When these studies are carried out by changing the pH of the aqueous solution, the primary absorption peak (210 nm) undergoes a pronounced red shift starting from about a pH of 6 (Figure 2 B). After a more basic pH (i.e. in the range of 9 to 12) is achieved, no further shift occurs. Presumably, these red shifts occur due to the H-bonding interaction between the unprotonated and deprotonated carboxylic acids in an extended network as suggested by Katchalsky et al.<sup>52</sup>

The fact that the density of the carboxylic group plays a role in the Bathochromic titration is evident in that the shifts are much smaller in magnitude when the concentration of the surfactant is decreased to about 20 ppm (Figure 2). From the midpoint of such a titration, the pKa of the carboxylic acid is found to be about 7.5, which is larger than that (5.2) expected of this organic

acid in its native state. Similar behavior, i.e., the shift of the pKa to greater than 5.2 (Figure 2 C), has been reported in the past<sup>51</sup> with the so called “contact angle titration experiments” in which water drops of various pH were deposited on a carboxylic acid functional surface of polyethylene.

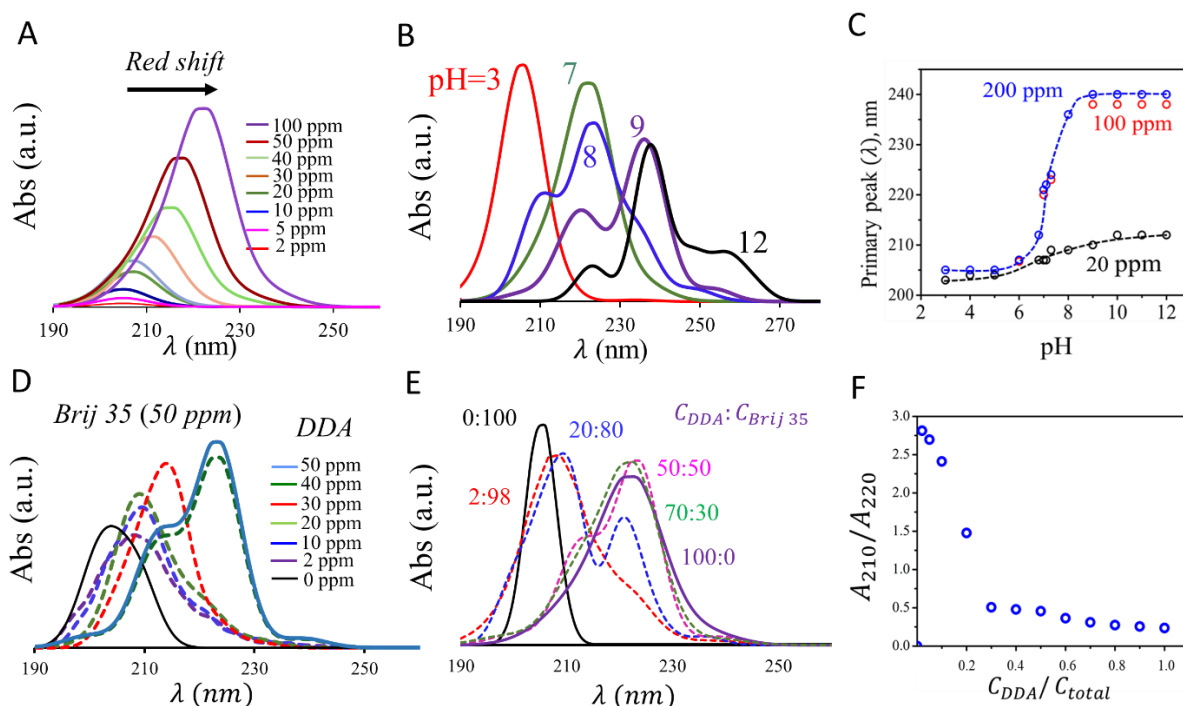


**Figure 2.2** A) UV absorption spectrum of dodecanoic acid (DDA) exhibits progressive Bathochromic (red) shift as the concentration of the surfactant is increased. B) UV absorption spectra of dodecanoic acid exhibiting a Bathochromic shift as the pH of the aqueous phase increases. C) A titration plot is obtained by plotting the primary absorption peak as a function of pH. D) UV absorption spectra of a mixture of dodecanoic acid and Brij-35 (Polyoxyethylene (23) Lauryl Ether), where the concentration of a non-ionic surfactant (Brij 35) is kept at a constant value (50 ppm), whereas the concentration of DDA is increased from 0 to 50 ppm. E) The ratio of Brij 35 to DDA is altered by keeping the total concentration to 100 ppm. F) The ratio of peak heights at  $\lambda = 210$  nm and  $\lambda = 220$  nm decrease till the concentration of DDA reaches 30 ppm, beyond which this ratio changes only slowly.

After performing the experiments without salt and with 0.1 M salt in water, the authors of that study<sup>51</sup> found no discernable dependency of the pKa on salt concentration.

Although we did not perform the Bathochromic titration experiments by varying salt concentration, we cite two previous observations<sup>56</sup> that support that the basic deprotonation behavior of carboxylic acid remains preserved even at high salt concentration. One of those observations pertains to the interaction of oil droplets (containing dodecanoic acid) with an amine functional substrate, as studied using contact angle measurements. These studies performed in 0.6M salt solution as a function of pH showed that the oil droplet barely adhered to the aminated substrate at a pH that is less than 6 or more than 10, whereas the adhesion was most tenacious at a pH near pH=8, where the de-protonated dodecanoic acid could interact with the protonated amine. In another related experiment, it was found that the efficiency of the extraction of DDA containing Oil-in-water emulsion with amine-functionalized particles was maximum at a pH close to 8. We emphasize that those previous studies are consistent with the current Bathochromic titration results in that the carboxylic acid groups do deprotonate in 0.6 M salt solution, and it does so at a pH in the vicinity of 7.

It is known from the previous studies<sup>49,52</sup> that the polybasic acids ionize at a pH higher than that of its native pKa, as the deprotonation of an acid group becomes progressively inhibited by some of the ionized groups via electrostatic stabilization<sup>51</sup>. We note the carboxylic acid at a very low pH (i.e., pH=3), exhibits a hypsochromic shift relative to that at pH 7 as the probability of the formation of electrostatic stabilization is reduced substantially at  $\text{pH} \ll \text{pKa}$ . The main claim that we would like to make is that the Bathochromic shift of the carboxylic acid chromophore at a  $\text{pH} \sim 7$  and its polybasic character suggest that the dodecanoic acids are in close proximity to each other thus forming H-bonds, as would be expected if the surfactant exists in a self-assembled structure e.g. a micelle or a vesicle.

**2.2.3. Cooperative interaction between DDA and Brij 35.** In order to further interrogate the physical chemistry of the extended H-Bond formation, we investigated what happens when a nonionic surfactant is mixed with an anionic surfactant. The data summarized in Figure 2.2 (D and E) show that the dodecanoic acid exhibits a red shift in water when mixed with Brij 35 even when the latter is present at a rather low concentration (2 ppm), which is evident in two related but separate experiments. In the experiment, Brij-35 pre-existed in the aqueous phase at a concentration of 50 ppm, DDA was then added starting with a concentration of 2 ppm and ending at about 50 ppm. While DDA by itself does not display an absorption peak  $> 205$  nm at a concentration of 2 ppm, it shows absorption peaks at higher wavelengths in response to the increase in the concentration of the anionic surfactant (Brij-35).

In the second experiment, the concentration of both the surfactants in the aqueous phase were varied from 0:100 to 100:0 ratio. In Figure 2.2 (F), we plot the ratio of the intensities of the peaks corresponding to 210 nm and 220 nm as a function of the concentration of DDA in such a mixture. Here, a precipitous drop in this ratio occurs as the concentration of DDA is increased from 2 ppm to about 30 ppm, beyond which the ratio changes only slowly. These results are consistent with the scenario presented above that DDA engages in H-bonding interaction with Brij-35, and that a critical percolation threshold exists in such type of cooperative H-bond formation. More results related to these observations can be found in the supplementary materials section (Figures S3 and S4).

**2.2.4. Surfactants in the organic phase.** We now explore what happens when the surfactants are dispersed in an organic phase. The UV-spectroscopic studies were conducted with pure DDA, Brij-35, and their mixture in dodecane. Figure 2.3 shows that the peak corresponding to 100 ppm of DDA, which is centered around 210 nm, is rather broad. This is consistent with the

existing literature<sup>55</sup> that carboxylic acid self-associates even in an apolar solvent. One would expect that the probability of dimerization would be rather low if DDA is present at a low concentration. This result is indeed borne out, as Figure 2.3 shows that at a 0.1 ppm concentration of DDA, the UV peak of the carboxylic acid becomes narrower than it exhibits a hypsochromic shift relative to that at a 100 ppm concentration. We expected that a similar hypsochromic shift should occur in the aqueous phase as well, provided that its concentration is rather low and if the study is conducted at a low

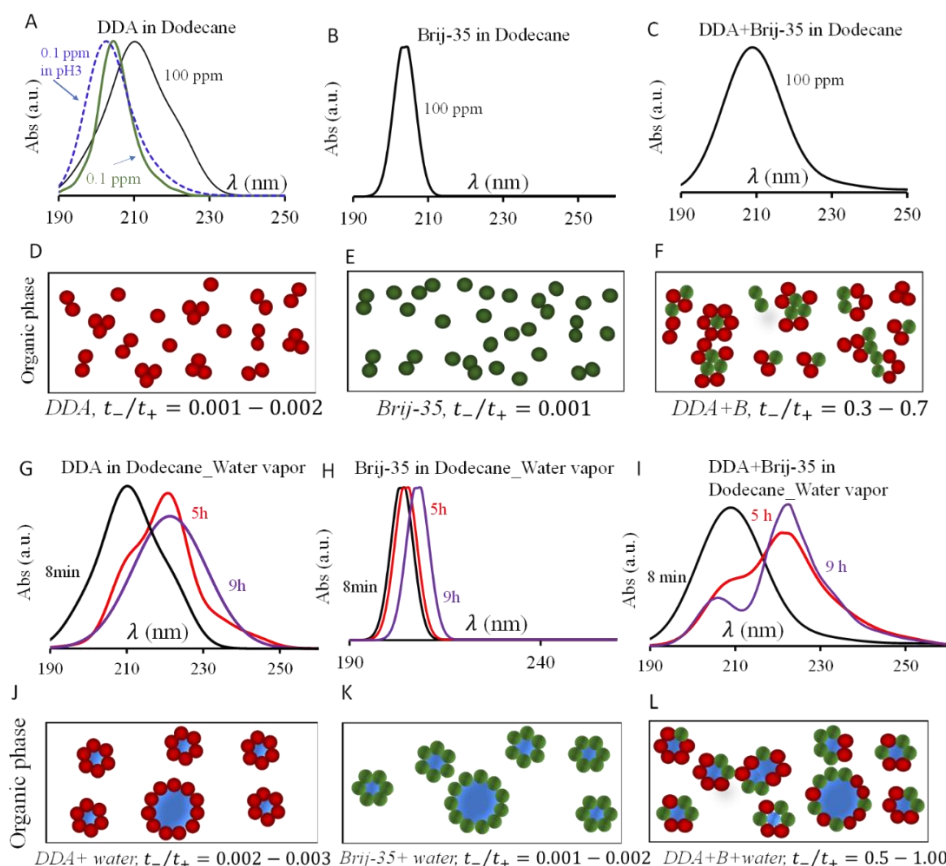


**Figure 2.3.** UV spectra of (A) Dodecanoic acid, (B) Brij-35, and (C) their mixture (50:50) in dodecane in the absence of water. In Figure A, the spectrum obtained for 100 ppm of dodecanoic acid is compared with 0.1 ppm dodecanoic acid in dodecane and that in the aqueous phase at pH=3. DPD-MD simulations (D-F) show that dodecanoic acid molecules aggregate at least up to a trimer on its own, while Brij-35 formed dimers (E) under similar conditions. However, together with Brij-35, a larger cluster (F) are formed. Panels (G-I); water vapor is infused into the samples. DPD-MD simulations show that inverted emulsion can form with each of the surfactants Panels (J-L), and

the stability of any of the aggregates can be discerned from the ratios of  $t_-$  and  $t_+$  (see text). Color coding are as follows, Red: DDA, Green: Brij-35, and Blue: water.

pH (i.e.  $\sim 3$ ), where both the H-bonding with the protonated and de-protonated carboxylic acid would be diminished, which is, indeed, borne out in the experimental observation. Figure 2.3A shows that the UV peak of DDA dispersed in the aqueous phase at pH 3 is rather close to that of DDA in dodecane when its concentration is as low as 0.1 ppm. The mixture of DDA and Brij-35 (50 ppm:50 ppm) in dodecane shows an absorption peak at 210 nm, which is similar to that of 100 ppm DDA in dodecane (compare Figures 3A and 3C). The peak at 205 nm for the Brij-35 (Figure 2.3 (B)) virtually disappears in the mixture as it merges with that of the dodecanoic acid.

Let us contrast these observations with what we learned from the hydrodynamically coupled dissipative particle dynamics (DPD) coupled with molecular dynamics (MD) simulations. Application of computational methods to understand the kinetics of formation oil in water and water in oil emulsions<sup>57-72</sup> has a long history, including the recent advances in non-equilibrium dissipative particle dynamics coupled molecular dynamics (DPD-MD) simulations<sup>73-80</sup>. One of the methods involves the use of a two-phase system in which the oil phase was modeled as a DPD fluid and the water phase modeled as a DPD-MD fluid<sup>81-88</sup>. In our current work, we treated both the oil and the aqueous phases as DPD-MD fluids by considering the hydrodynamic interactions to understand the phenomenology of spontaneous emulsification. The thermodynamics and kinetics of the formation of various ordered structures were investigated in both the aqueous and organic phases in order to capture the non-equilibrium transitions at different stages, which are discussed below.

In order to find out the clustering abilities of the surfactants, the DPD-MD simulations were carried out. with either 100 ppm of DDA, 100 ppm of Brij-35, or a 50 ppm:50 ppm mixture of the two surfactants in dodecane. In a different set, these simulations were repeated in the presence of a small amount (100 ppm) of molecular water. Further details are provided in the method section, The results of these simulations, as summarized in Figure 2.3 (D - F), show that DDA can form weak dimers or trimers in dodecane. While Brij-35 forms a few dimers in dodecane, larger complexes are formed when DDA and Brij-35 are present together, in which the DDA clusters around Brij-35. These DPD-MD simulations also allow an estimate of the time ( $t_+$ ) of the formation of an aggregate and the time ( $t_-$ ) of its dissolution. The ratio ( $t_-/t_+$ ) is thus a measure of the stability of the aggregates, which is very low for both pure DDA (0.002) and pure Brij-35 (0.001) but is rather high (0.3 to 0.7) for the mixture of the anionic and nonionic surfactants. Overall, we see the picture developed from the UV spectroscopy contrasts positively with that obtained from the DPD-MD simulations in that an aggregated structure formed from a mixture of the ionic and non-ionic surfactants is more stable than those of the pure surfactants.

**2.2.5. Role of Moisture.** After gaining the needed insights into the interactions of the surfactants in pure dodecane, we next turn our attention to the role of the vapor of water infusing into the oil phase and the ensuing stability of the aggregates thus formed. To achieve this objective experimentally, water vapor saturated air was made to bubble through dodecane with surfactants pre-dissolved in it. As time progresses, it is observed that the primary peaks of the surfactants shift towards the higher wavelengths (Figure 2.3 (G - I)). The peak for DDA corresponding to 210 nm decreases, whilst that at 220 nm increases. These bathochromic shifts mark the role of water in the formation of H-bonded structures, which would be possible if the surfactants are in close proximity to each other, as would be the case if they form oil-in-water emulsions. DPD-MD

simulations Figure 2.3 (J - L) clearly shows the possibility of the formation of water-in-oil emulsions with pure and mixed surfactants. However, these inverted emulsions exhibit different degrees of stabilities, as indicated by the ratio  $t_-/t_+$ . Here, too, as is the case with dry dodecane, the mixture of the anionic and nonionic surfactants is more stable than those formed with the pure surfactants.

Based on the observations made so far, we can safely state that if the organic phase becomes enriched with surfactant, inverted (i.e., water-in-oil) emulsions can form provided that the organic phase contains water as well. This is an important issue, as the particular system that we are interested to resolve is that of an aqueous phase with surfactant contacting an organic phase without the surfactant. One expects that inverted emulsions would form in the organic phase provided both the surfactant and water diffuse into it from the underneath aqueous phase. This issue was addressed previously by Davies, J. T.; Wiggill<sup>89</sup>.

This issue is also related to a recent interesting study by Yang and Abbott<sup>90</sup>, who reported the growth of water droplets on a hydrophobic surface immersed in water, where water vapor had to pass through a layer of oil following which it could undergo nucleation and growth on the hydrophobic substrate. Hence, there already exists evidence that water can dissolve in, and diffuse through, oil. If such is the case, the results summarized in Figure 2.3 suggest that an inverted emulsion would form in that phase in the presence of surfactant. The enrichment of an organic phase by a surfactant due to diffusion from the aqueous phase is directly detectable in UV spectroscopy (see below). The issue regarding water diffusion is addressed next.

**2.2.6. Evidence of Water in Organic Phase.** One straightforward way to resolve this issue is to measure the amount of water in the organic phase using a standard Karl Fischer test after equilibrating a given amount of this phase with an aqueous salt solution. The results summarized

in Table S2 (Supplementary Materials) show that all organic solvents that are devoid of water to begin with collect a certain amount of water after equilibration. The actual emulsification process is, however, more complex, as when the inverted emulsions are formed, the amount of water would be depleted from the organic phase. However, this loss would be compensated by the continuing transfer of water from the aqueous to the organic phase. To make a realistic assessment of the dynamic evolution of water in the organic phase, we designed an experiment by modifying a strategy that we reported in the past<sup>91</sup>.

Previously, we reported an experiment in which a drop of a concentrated aqueous solution of a mixture of sugar (i.e., glucose and sucrose) resembling that of plant-based nectar was exposed to a humid atmosphere<sup>91</sup>. As such a nectar drop is very hygroscopic, it grows by absorbing moisture from the environment. Here, we performed a similar experiment, in which a nectar drop was immersed in the organic phase by keeping it slightly above the interface of the organic liquid and salt water.

The results summarized in Figure 2.4 shows that the small nectar drop grows at a rate, which, as a first approximation, is nearly independent of the nature of the organic liquid. As the osmolarity of water in the nectar drop continues to decrease due to the dilution of sugar, its growth kinetics slows down and is eventually halted. If we start with the nectar drop with an initial osmolarity of 7.5 moles/L its volume has to increase by a factor of six so that its osmolarity in the diluted state becomes the same as that of salt solution (1.2 moles/L). This is in the ball part of what is observed experimentally (Figure 2.4).

The chemical potential of water in the nectar drop is determined not only by the concentration of sugar present in the drop but also by the Laplace pressure resulting from its curvature and its interfacial tension. In the beginning, the difference in osmolarity is the main driving force.

However, at a later stage, when the difference in the osmolarity becomes small, the Laplace pressure would control the growth process. As the interfacial tension of the nectar drop is lowered due to the adsorption of the surfactant at the interface of the nectar drop and oil phase, the equilibrium size of the nectar drop with surfactant is expected to be higher than that without it.

The above consideration helps us to understand the fact that at equilibrium, the volume of the droplet with surfactant is higher than that without it. The higher growth rate of the drop with surfactant is likely due to the fact that when water-in-emulsions continue to form it readily supplies water to the organic phase when it is depleted. All these lead to a situation known as “facilitated transport”. We postpone a detailed analysis of this interesting phenomenon to the future.

We also note what happens when certain polymers are dissolved either in the organic or in the aqueous phase. These results reported in Figure 2.4 show that the growth of the droplet is arrested, suggesting that polymers thwart the solubility and/or the diffusion of water from the aqueous to the organic phase. This result is corroborated by the Karl Fisher test (Table S2, Supplementary Materials) which exhibits undetectable amount of water in the organic phase in the presence of such additives.

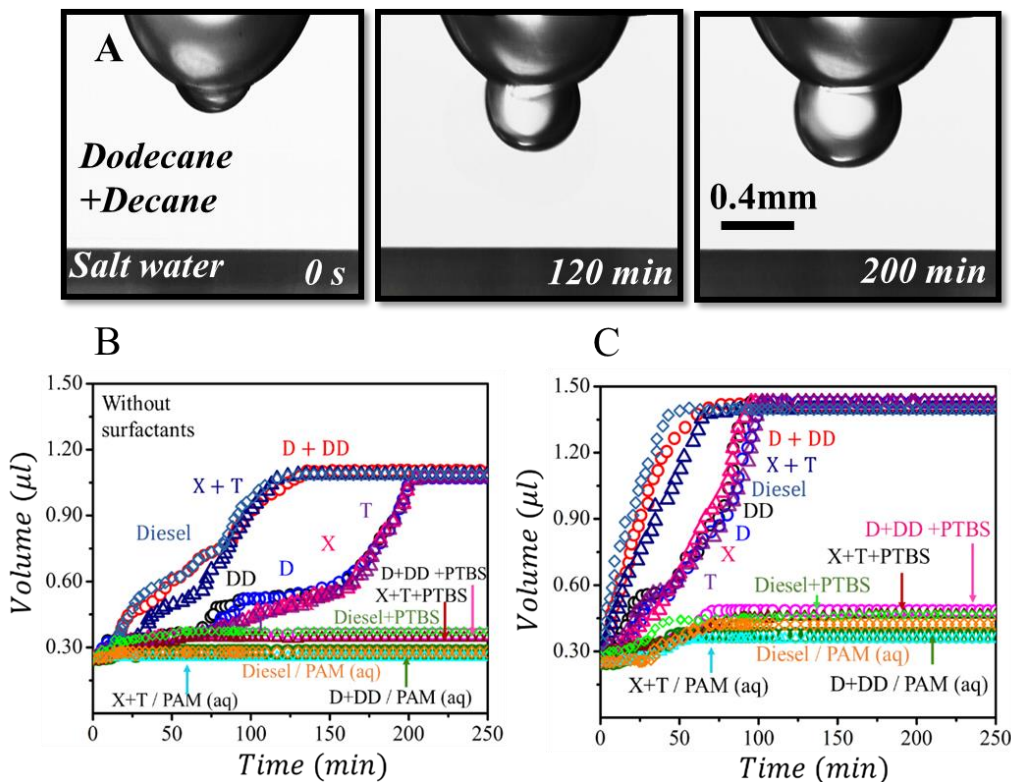


**Figure 2.4** (A) A nectar drop (on a glass support) is immersed in an organic phase and placed about 0.7 mm above the interface of the organic phase and 0.6 M salt solution. As water molecules escape from the aqueous phase to the organic phase, the nectar drop absorbs them and grows. (B) Growth of nectar drops with and without the presence of surfactant are shown in Alkanes (such as Decane, Dodecane, and their mixtures), Aromatics (such as xylenes, Toluene, and their mixtures), and Diesel. (C) Same as B, in this case with surfactants dissolved in the aqueous phase. Here, X=xylene, T=toluene, DD=dodecane, D=decane, PTBS= poly-4-tert-butyl styrene, PAM = polyacrylamide (20 ppm), and PTBS 18 ppm in the organic phase.

A short summary of what we learned so far is:

1. Dodecanoic acid interacts cooperatively with Polyoxyethylene (23) Lauryl Ether. This interaction is stronger in the presence of a small amount of water.
2. Remarkably, when these surfactants are pre-dissolved in dodecane and water vapor is infused in that phase, water-in-oil emulsions can form.
3. If surfactants are present in an oil, a small amount of water is needed to form water in oil emulsions. While they can form with either the anionic or non-ionic surfactants, they are not as stable as those formed when both surfactants are present together.

At this convenient juncture, we wish to point out that a DPD-MD simulation indicates that oil-in-water emulsion can form in the aqueous phase in the presence of a small amount of oil in the aqueous phase. However, the stability of the emulsions formed with the mixed surfactant is far greater than those formed with the pure surfactants. While this trend is similar to what we observed with the water-in-oil emulsions, this type of emulsification requiring the diffusion of oil from the organic to the aqueous phase would be a slow process as the solubility of oil in water is very low.

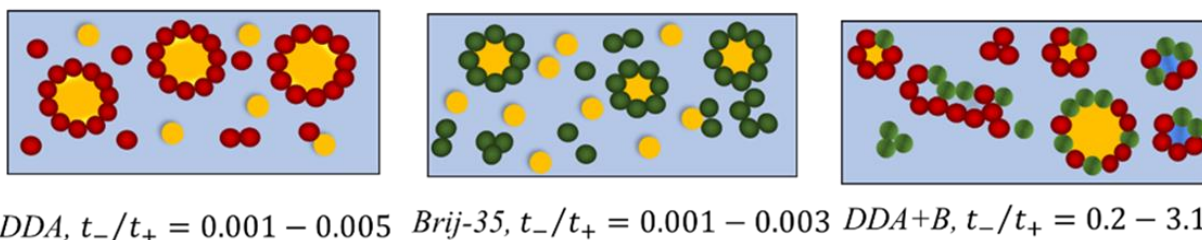


**Figure 2.5.** The results of the DPD-MD simulations carried out with 100 ppm of surfactant in an aqueous salt solution in the presence of 1000 ppm of dodecane. Stabilities of the different aggregates can be discerned from the ratios of  $t_-$  and  $t_+$  (see text). The color coding is as follows, Red: DDA, Green: Brij-35, Blue: water, Yellow: Oil)

Some of the fast kinetics of emulsification that we report next indicates a different route to emulsification that involves a catastrophic instability of the interface following which the inverted emulsions formed in the organic phase cross the interface and transform into oil-in-water emulsions.

**2.2.7. Experiments on spontaneous emulsification and analysis.** In order to proceed further, an experiment was performed, in which a thin layer of an organic liquid (2.2 ml) was deposited above a 2.2 ml of 0.6 M salt solution containing a surfactant inside a quartz cuvette (Figure 2.6). The height of the quartz cuvette was so adjusted inside the spectrometer sample holder that the UV beam passed either above the interface of the salt solution and the organic liquid, slightly below (1 mm), and even farther below (4 mm) the interface. When the UV beam

passed through the cuvette above the interface, it interrogated the sequences of events occurring in the organic phase, i.e. the fate of the surfactants as it diffuses from the aqueous to the organic phase. The UV beam passing through the aqueous phase, similarly, interrogated the sequences of events occurring in the aqueous phase. One disadvantage of the current experimental procedure stems from the limitation that the organic and aqueous phases could be studied simultaneously. These experiments had to be performed separately in order to collect information on the events occurring in the three regions, being aware of the possibility that there could be some discrepancies in the time courses of the events that we are interested to explore. Nevertheless, with adequate care, these experiments could be performed that provided a meaningful picture of the phenomena with sufficient details and acceptable reproducibility. Although these experiments were performed with various types of organic liquids, here we present the results obtained with a few selected liquids. Additional results are summarized in Figure 2.7.

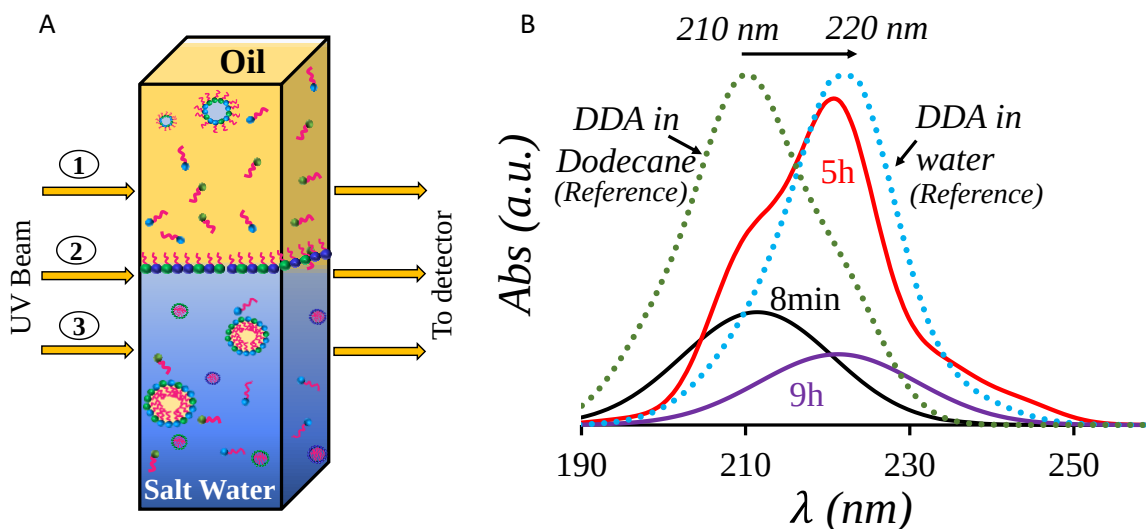


**Figure 2.6.** (A) Interrogation of an oil phase (dodecane) about 4 mm (as indicated by UV beam in A1) above the interface shows the enrichment of this phase with dodecanoic acid with time. (B) The primary absorption peak is observed at about 210 nm, which is lower than that (210 nm) in water. As time progresses, this peak diminishes with the concomitant increase of a peak close to

220 nm, which is observed when the surfactant is in water. For a long time, the primary absorption occurs at 220 nm, which, however, decreases with time. See also **Figure 2.7**, below.

**2.2.8. Evidence of Inverted Emulsion in Organic Phase.** The results summarized in Figure 2.6 (B) illustrate the evolution of the concentration of DDA in an organic phase (dodecane). Initially, the primary absorption peak is observed at 210 nm, which is lower than that (220 nm) of the surfactants dissolved in an aqueous phase. This indicates that DDA, which engages in extended H-bonding in the aqueous phase breaks free when it first enters the organic phase, as evidenced by the observation that the primary absorption peak is found to be the same as that of the surfactant in the organic phase in the absence of water. With the progression of time, a peak appears at about 220 nm corresponding to the hydrated state of the surfactant, while the 210 nm peak continues to grow and persists for a certain amount of time. At a longer time, the peak at 210 nm virtually disappears; while the new peak centered around 220 nm spans a broad region (220 nm to about 250 nm), which is similar to what is observed with DDA when it is dispersed in the aqueous phase. This indicates the formation of an extended bonding network in the organic phase. During the formation of this network, both the protonated and the de-protonated carboxylic acid must be participating if we assume that the pH of the water, with which the surfactants nucleate, is close to 7.0 (contrast this value to the pKa of DDA, which is about 7.5). Ultimately, the concentration of the surfactant decreases in the organic phase, presumably due to the fusion of the inverted emulsion with the interface and its subsequent re-entry into the aqueous phase in the form of an oil-in-water emulsion.

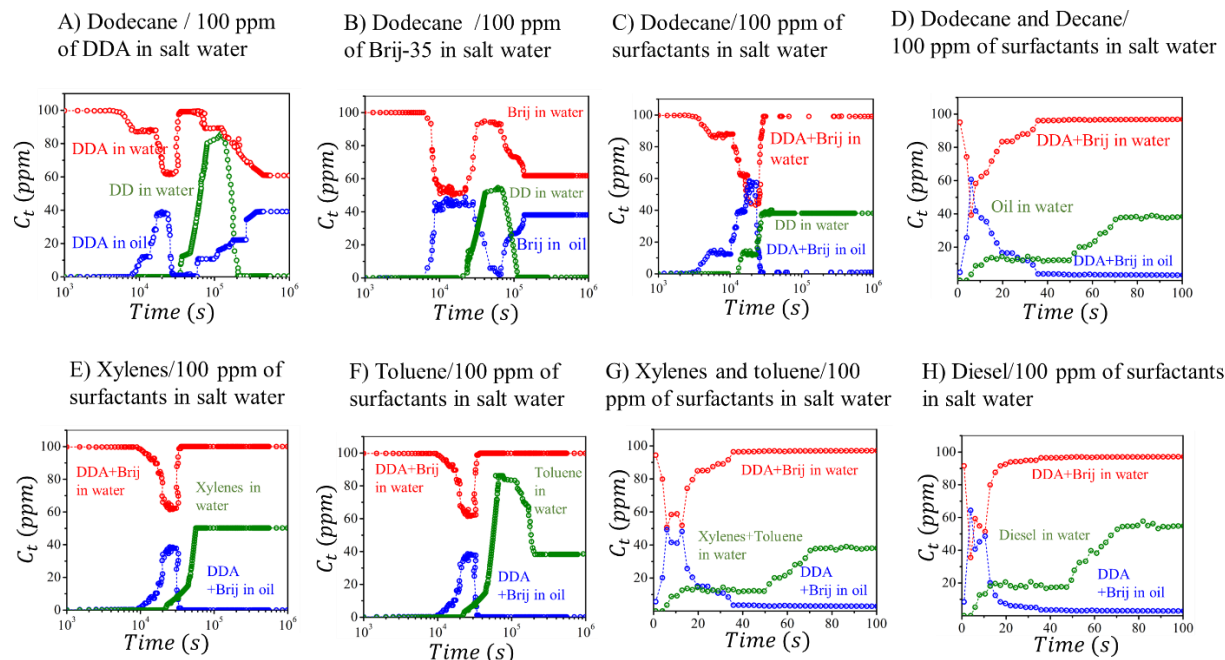


**Figure 2.7.** Evolution of the concentration of various surfactants and their mixtures in organic and aqueous phases as a function of time. Note the fast dynamics of surfactant transports in mixed solvents (D and G) as well as in Diesel (H), which is composed of various organic solvents.

The overall spectroscopic signature of the surfactant is similar to that shown in Figure 2.3. Nevertheless, while the total surfactant remains constant in the experiment described in Figure 2.3, the dynamics of the surfactant in the current experiment results from the combination of the transport across the phases, the transformation from an unhydrated to hydrated state, and its subsequent re-entry into the aqueous phase. These kinetic results are plotted over a long period of time in Figure 2.7, where with the anionic and non-ionic surfactants and their mixtures were dissolved in dodecane, toluene, xylene, and in the solutions of decane and dodecane as well as toluene and xylene. In these plots, we also include the evolution of the concentration of essential components in the aqueous phase. As far as the aromatics are concerned, they are UV active; while the alkanes are not. In order to detect the presence of alkane in the aqueous phase, we added a small amount (10 ppm) of Triphenylmethane (TPM) in it as a spectral reporter. As

Triphenylmethane dissolves in the organic phase but is totally insoluble in the aqueous phase, its presence in the aqueous phase via UV spectroscopy signifies the presence of the alkane if it presents itself as a droplet. From a calibration curve of the concentration of this marker in alkane vs UV intensity, the amount of alkane in the aqueous phase could be estimated from the spectral intensity obtained from a given experiment.

With dodecane above water, we note that the concentration of DDA ( $C_{DDA}^{oil}$ ) initially increases with time as the surfactant diffuses from the salt solution to dodecane. While  $C_{DDA}^{oil}$  increases, the concentration of DDA ( $C_{DDA}^{Aq}$ ) decreases in the aqueous phase (Figure 2.7). Upon reaching the optimal values in the organic and aqueous phases,  $C_{DDA}^{oil}$  decreases with a concomitant increase of  $C_{DDA}^{Aq}$ . This observation coupled with the concomitant increase of concentration of oil in the aqueous phase ( $C_{oil}^{Aq}$ ) indicate that oil-in-water emulsions are formed in the aqueous phase during this time. At the longer time, these emulsions appear to break down as evident from the decrease of  $C_{oil}^{Aq}$  while DDA is pseudo-equilibrated in the two phases, when  $C_{DDA}^{oil}$  becomes comparable to  $C_{DDA}^{Aq}$ . While the results reported in Figure 2.7 correspond to a window of five days, the concentrations continued to evolve and fluctuate beyond beyond that (Appendix B). Analysis of the long term result is, however, complicated as the kinetics at the late stage is influenced by Ostwald ripening and fusion induced aging of the emulsion droplets. Furthermore, the large droplets lose the freedom of Brownian motion and tend to accumulate at the interface. We thus stayed away from interpreting these long time results. Another reason for us to avoid performing these long term measurements systematically is technical, as the spectrophotometer itself begins to malfunction due to excessive heating of the electronics when it is operated for a very long time.

Experiments carried out with Brij 35 exhibited a behavior similar to DDA, where the evolution of the concentration of the surfactant displays a mirror symmetry in the organic and aqueous phases.

While the behavior of the mixed surfactants is similar to that of DDA or brij-35 (Panel 1C and 2C) in the beginning, the long term behavior is found to be quite different in that the oil remains in the aqueous phase, quite likely in the form of oil-in-water emulsions. Very similar behavior was also observed with toluene, xylene and other organic liquids (Figure 2.12). The main conclusion that we can reach from these observations is that neither the anionic nor the non-ionic surfactant forms stable oil-in-water emulsion, whereas stable emulsions are formed with the mixed surfactant, where the cooperativity between the anionic and nonionic surfactants, and the resulting extended H-bond formation appears to play the critical role. See also Figures 2 and 3, and the associated discussions where this issue was highlighted.

A remarkably surprising result is observed when these experiments are performed in a mixture of decane and dodecane or in a mixture of toluene and xylene, which showed a dramatic enhancement of the kinetics of the surfactant transport (Figure 2.7 (D and G)). Here, the evolutions of the concentration of both the oil and surfactant occur much faster than the pure solvents, in that they reach the pseudo-equilibrium states in less than a minute. Similar results are also found in Diesel (Figure 2.7 (H)), which, in essence, is a mixture of various organic solvents. Furthermore, when we reconstituted the composition of the diesel using various organic solvents, and performed these experiments, we observed surfactant dynamics that is similar to that of commercial diesel (Figure 2.7 (H)).

While we do not have a satisfactory explanation for the fast surfactant dynamics observed with the mixed solvents, we do note that the solubilities of the surfactants in the mixed solvents are greater than those in the pure solvents (Figure 2.8). While the increased solubility may play a role in the phenomenon described here, we suspect that its true origin is possibly hidden in the formation of local heterogeneity at the interface thus triggering local Marangoni instabilities. We are

encouraged to speculate such a possibility from certain drop spreading experiments, which are not reported here. When a droplet of a pure organic liquid was deposited on the surface of the salt solution containing a surfactant, it spreaded uniformly. However, when a mixture of organic liquids was deposited on the surface of the salt solution, it disintegrated spontaneously forming multiple thin lense shaped droplets, the edge of which continued to undergo instability and smaller droplets were formed. Postponing further studies on this very interesting topic to future. Now, we report what we learned from the MD-DPD simulations regarding the self assembling behavior of the pure and mixed surfactants in the organic and aqueous phases.

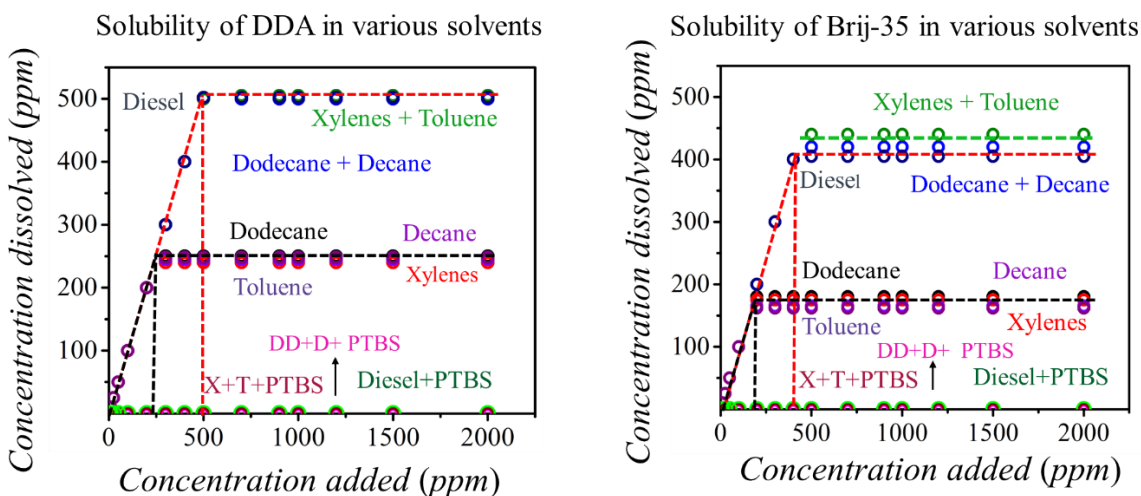


**Figure 2.8.** Solubility of Dodecanoic acid and Brij-35 in various solvent systems. In all cases, solubility is higher in mixed solvents than in pure solvents. When these experiments were carried out with PTBS, it was added in the organic solvent at a concentration of 18 ppm.

The results summarized in Figure 2.3 show that each of the anionic and the nonionic surfactants can form micelle, although their stabilities are rather low. On the other hand, when both the surfactants are present, more stable structures are formed in the form of micelles and vesicles, the anatomies of which can be visualized from the plots of the concentrations of water, hydrocarbon, carboxylic acid, and ethylene oxide across the diameter of the resultant structures (Figure 2.9 (C)).

As expected, the emulsion droplets formed in oil show the presence of water in the core region that is surrounded by a lamella composed of hydrocarbon, ethylene oxide, and carboxylic acid groups. On the other hand, the emulsion droplets formed in the aqueous phase show the presence of oil in the core region that is surrounded by a lamella composed of hydrocarbon, ethylene oxide, and carboxylic acid groups. Furthermore, for the oil-in-water emulsion, the hydrophilic carboxylic acid and ethylene oxide groups face away from the central hydrocarbon core towards the water, the reverse of which is observed with the water-in-oil emulsion. When the mixed surfactants are present in water, both micelles and vesicles appear to form.

The interfacial tensions of the various interfaces could also be estimated using these simulations, which are tabulated in Tables 2 and S4 (Supplementary Materials). These simulations were carried out using two different grain sizes ( $0.1 \text{ nm}^3$  and  $1 \text{ nm}^3$ ) to ensure that the estimated values are independent of the grain size, which is found to be the case. The area per molecule was estimated by counting the number of hydrocarbon chains, which are present in both the molecules. The data summarized in Table 2 show that the average interfacial area of the surfactants adsorbed at the flat oil-water interface is close to  $0.8 \text{ nm}^2$ , which is close to the value ( $0.9 \text{ nm}^2$ ) obtained from the standard Gibbs' adsorption equation<sup>7</sup>. While a tightly packed hydrocarbon chain occupies an area of about  $0.2 \text{ nm}^2$ , one would expect that the average area per molecule in an emulsion or in a vesicle would be higher than this value as they would be more disordered. On the other hand, the average area occupied by the ethylene glycol group of the non-ionic surfactant should be greater than ( $0.6 \text{ nm}^2$ ), as obtained<sup>26</sup> from the surface pressure-area isotherm. The average area per molecule, as estimated on the basis of the number of hydrocarbon chains) range from  $0.34 \text{ nm}^2$  to  $0.4 \text{ nm}^2$  for the emulsions and vesicles (Table 2 and S4). The fact that this range of values is larger than that  $0.2 \text{ nm}^2$  but less than  $0.6 \text{ nm}^2$  suggests that the ethylene glycol groups

spread above the carboxylic acid groups of the DDA molecules, i.e. the Polyoxyethylene (23) lauryl ether molecules accommodate some of the dodecanoic acid molecules under its umbrella in the self-assembled structures.

A close scrutiny of all the different cases summarized in Table 2 reveals, unsurprisingly, that the interfacial tension decreases with the average area per molecule. The interfacial tension of the oil-water interface containing 100 ppm of surfactant, as measured by the Du Nuoy ring method, is about 14 mN/m (Table S1), although a lower value (7.5 mN/m) was obtained with a drop vibration technique. These values can be compared and contrasted with what is obtained in the current simulation. The interfacial tensions of the two emulsions and the vesicles are significantly lower than that of the flat interface, suggesting that the surfactants have organized more tightly in such structures than that at the flat interface, which is a thermodynamic necessity in that the interfacial tension would tend to be as low as possible within the available entropic constraints. What this scenario prompts are the question: what happens when these, presumably, kinetically formed self-assembled units of lower interfacial tension come into contact with the oil-water interface having a higher interfacial tension? If they fuse, the surfactants of these structures would tend to spread at the interface causing a local Marangoni instability. The resulting perturbations could either decay quiescently or violently producing shock waves propagating along the interface. These could have important consequences in the evolution of the subsequent structures. This issue is related to the formation of oil-in-water emulsion at it might happen when an inverted emulsion crosses the interfacial barrier via a singular transformation of one phase into another, which is, otherwise known as phase inversion<sup>40</sup>.

**Table 2.** Interfacial tension and molecular area analyzed using MD-DPD simulation using a grain size of 1 nm<sup>3</sup>.

| Component             | Interfacial Tension, mN/m | Total Area A (nm <sup>2</sup> ) | $N_{DDA}$ | $N_{Brij}$ | $\frac{N_{DDA}}{N_{Brij}}$ | $\frac{A}{N_{DDA}+N_{Brij}}$ nm <sup>2</sup> |
|-----------------------|---------------------------|---------------------------------|-----------|------------|----------------------------|----------------------------------------------|
| Flat interface        | 8.2                       | 10,000                          | 5874      | 5425       | 1.12                       | 0.88                                         |
| Oil in Water Emulsion | 1.7                       | 493                             | 717       | 720        | 1.46                       | 0.34                                         |
| Water in Oil Emulsion | 2.1                       | 1319                            | 1901      | 1450       | 1.31                       | 0.39                                         |
| Vesicle               | 2.3                       | 1360                            | 2145      | 1530       | 1.21                       | 0.37                                         |

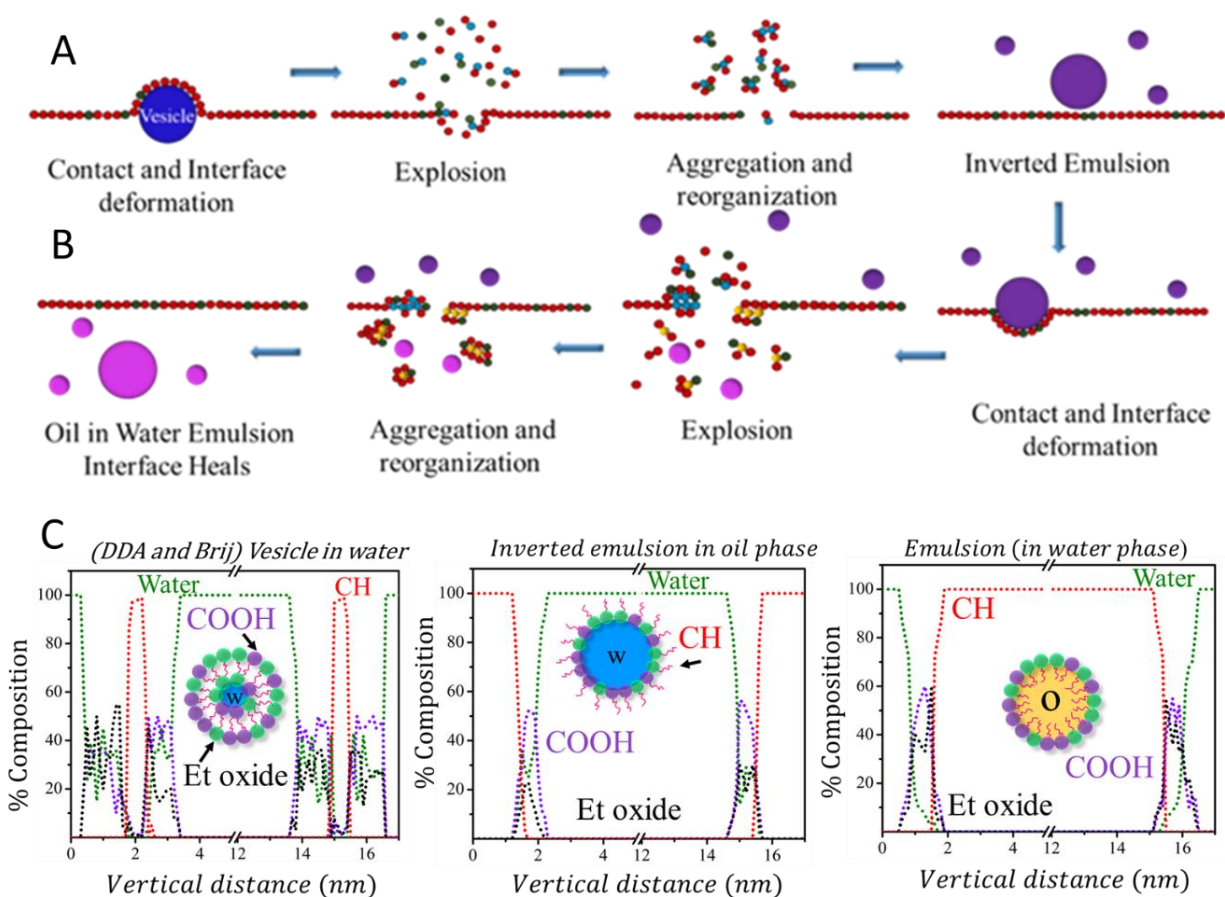


**Figure 2.9.** Schematics illustrating the formation of water-in-oil and oil-in-water emulsions. A) When the surfactants form vesicle in the aqueous phase, it eventually comes into contact with the interface and explodes. The fragments resulting from this explosion cluster together and form the

inverted (i.e. water-in-oil) emulsion. B) When such an inverted emulsion comes into contact with the interface, another explosion occurs, following which the fragments cluster together and transform into oil-in-water emulsions. C) Anatomies of different types of self-assembled structures that are formed either in oil (water-in-oil emulsions) or in water (vesicle and oil-in-water emulsions). The color codes are as follows, Navy blue: Vesicle, Red: DDA, Green: Brij-35, Blue: water, Yellow: Oil, Purple: inverted emulsion, Pink: Emulsion.

We now address this issue of phase inversion that could occur via the “so-called” cusp catastrophe<sup>41-43</sup>. This was accomplished via non-equilibrium DPD-MD simulations, in which an aqueous phase containing either DDA, Brij-35, or their mixture comes into contact with a layer of dodecane. The results summarized in Figure 2.9 (A) show that the vesicles that are formed in the aqueous phase first come into contact with the interface and deform it. Following this contact, the interphase region disintegrates rather explosively into various sub-structures, which subsequently cluster together and lead to an inverted emulsion structure in the organic phase. The inverted emulsions eventually come into contact with the interface and undergo another explosion. The resulting sub-structures then cluster together and form the oil-in-water emulsion, while the interface heals and separates the oil from the aqueous phases. This mechanism of formation of water-in-oil emulsion differs from the other, relatively quiescent scenario, which stipulates that the surfactants and water diffuse passively in the aqueous phase, where they self-associate and form nanosized emulsion droplets (e.g. Figure 2.3). However, the formation of the oil-in-water emulsion from this water-in-oil emulsion via phase inversion should be the same as that shown in Figure 2.5.

This kind of explosively formed emulsion in the aqueous phase was already hinted at in our effort to quantify the amount of oil in the aqueous phase, specifically with the experiments in which a small amount of water-insoluble marker (Triphenylmethane, TPM) was dissolved in the organic phase. As this marker is totally insoluble in the aqueous phase, its presence there strongly indicates

that it does not evolve in the aqueous phase via simple diffusion. The more logical scenario is that the oil is injected into the aqueous phase as a droplet via transient or persistent shake up events due to instabilities occurring at the interface. Such a picture was presented in our earlier publication<sup>26</sup>,

where we conjectured that the inverted (water-in-oil) emulsions first fuse with the interfacial monolayer following which a curvature reversal (an instability) develops at the interface, thus triggering the phase inversion. We also conjectured that *violent agitation* of the interface may develop due to local vortices formed due to Marangoni and/or Landau Darreus instabilities as suggested by Yves Pomeau (personal communication). Because of the difference in the interfacial tensions between the flat interface and the water-in-oil emulsion, we surmise that local heterogeneous Marangoni instability to underly the explosive phase inversions as depicted in Figure 2.9 (A and B), although the roles of other types of instabilities cannot be ruled out.

**2.2.9. Evidence of Inverted Emulsion in Organic Phase.** While we do not have a direct way to interrogate the above-mentioned explosive events at present, we presume that these events should occur intermittently over a long period of time, the signature of which should be present in the fluctuations of the number of emulsion droplets, and thus the concentration of the organic content inside them.

In order to elucidate the above point, UV spectrophotometric measurement was carried out 1 mm below the oil-water interface (Figure 2.10 (A)) at a rate of 1 acquisition/second. These data summarized in Figure 2.10 (B) show that the fluctuation of UV absorbance, which starts almost immediately in some cases as the data acquisition begins, whereas in some other cases, the fluctuation begins after a certain lag time. Note that such lag time was evident in the concentration

evolutions as shown in Figure 2.7. Furthermore, the intermittency occurs at fast pace in some cases whereas they are sparse in other cases.

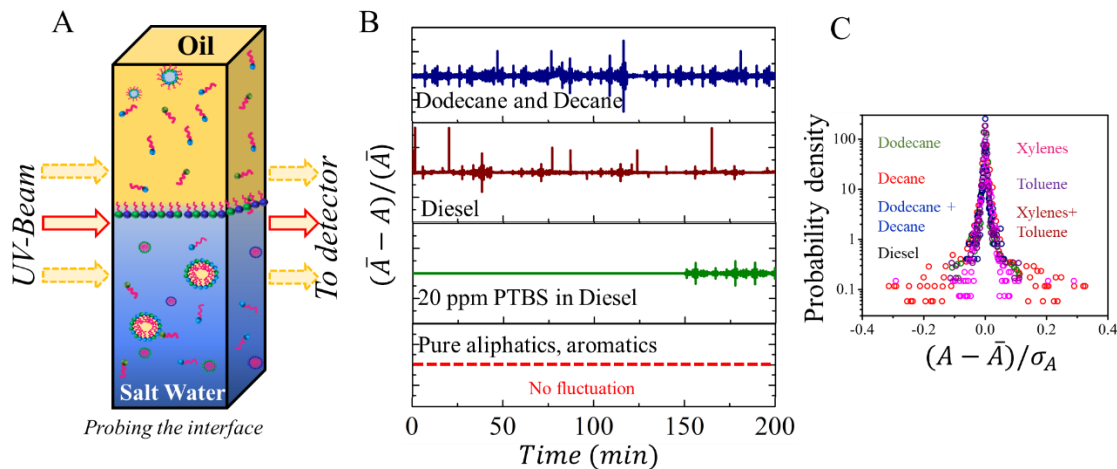


**Figure 2.10.** (A) The region just below the oil-water interface exhibit significant fluctuation of the concentration of the organic phase. (B) Different types of fluctuations are observed. In some cases, intermittency is rapid and in some other cases, the intermittency is delayed. (C) The probability distribution functions of these fluctuations exhibit non-Gaussian behavior.

For pure liquids, such as alkanes, no such fluctuation of concentration could be observed when the surfactant concentration was 100 ppm. However, with the exactly same system, significant fluctuations were observed when the concentration of surfactant increased to about 500 ppm. The power spectral densities of the time series of the concentration fluctuation generally exhibit bluish noise, with the probability distribution function of the fluctuation exhibiting a non-Gaussian behavior. We surmise that they are all related to the burst events resulting from the explosive formation of emulsions as observed in the DPD-MD simulations.

The emulsions produced below the interface should diffuse farther into the aqueous phase. If the concentration is probed at a fixed distance  $x$  from the interface, then it should evolve according to equation 1.

$$\frac{C_0 - C(t)}{C_0} = \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right) \quad (1)$$

where,  $C_0$  is the concentration at saturation,  $C(t)$  is the concentration at a given time  $t$ , and  $D$  is the diffusivity. Equation 1 can also be re-arranged as follows:

$$\operatorname{erf}^{-1}(\varphi) = \left(\frac{x}{\sqrt{4Dt}}\right) \quad (2)$$

Where,  $\varphi = \frac{C_0 - C(t)}{C^*}$ . Thus, a plot of  $\operatorname{erf}^{-1}\varphi$  vs  $1/\sqrt{t}$  should be a straight line from the slope of which, the diffusivity can be estimated. Since there is a lag time ( $t_0$ ) for the diffusion front to reach the region where the concentration is measured, it makes sense that the diffusivity be estimated from the slope the plot of  $\operatorname{erf}^{-1}\varphi$  vs  $\frac{1}{\sqrt{(t-t_0)}}$  in the long-time limit, i.e. when  $t \gg t_0$ .

In order to estimate the diffusivity in the short time limit, we use the time  $t_0$  that is elapsed before the first sign of organic liquid is detected in UV. Taking  $\varphi \approx 1$  at  $t = t_0$ , diffusivity can be estimated from equation (2) using  $x^2 = \pi D t_0$ . These diffusivities are normalized by dividing their values with the respective Stokes-Einstein diffusivities:  $D_e = k_B T / (6\pi\eta r)$ , where  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $\eta$  is the viscosity of the aqueous phase.  $r$  is the average radius of the droplet, which was estimated<sup>26</sup> using CHDF (capillary hydrodynamic flow chromatography). Since the fluctuation of concentration below the interface encodes the magnitude of the diffusivity of the emulsion droplets, we found it convenient to show the wide range of the value of  $D/D_e$ , by plotting it against mean square value of fluctuation  $\sigma_A^2$  of UV absorbance (which is a measure of  $\sigma_C^2$ ) as obtained from Figure 2.10 (B).

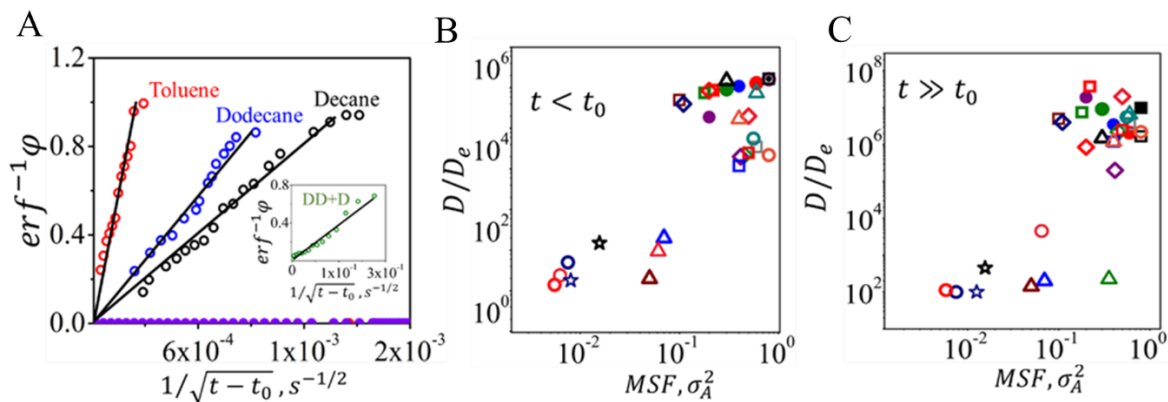


**Figure 2.11.** A)  $\text{erf}^{-1}(\varphi)$  is plotted against  $1/\sqrt{(t-t_0)}$  for a few representative cases, where  $t_0$  is the dead time following which the concentration begins to rise,  $\varphi = [(C_0 - C(t))/C_0]$ ,  $C_0$  being the saturated concentration, at long time. The slope of this curve gives the estimate of diffusivity at short (B) and long times (C). In B and C, The ratio of the estimated diffusivity and the Stokes-Einstein diffusivity  $D_e$  is plotted against the mean square fluctuation of UV absorbance (hence concentration).

Figures 11 (B and C) show that the effective diffusivities of emulsions produced in the aqueous phase exhibit a wide range of  $D/D_e$  values that, in general, increase with  $\sigma_A^2$ . Had the diffusion of droplets been governed entirely by usual thermal noise,  $D/D_e$  would be close to unity. There are only few cases, which present this type of value [Table S5a], for which  $\sigma_A^2$  values were undetectably small that they could not be potted along with the other data in Figure 2.11 . However, in most cases  $D$  is several orders of magnitude higher than  $D_e$ . The fact that  $D \gg D_e$  indicates that the droplets acquire certain amount of additional kinetic energy as soon as they were formed in the aqueous phase below the interface. We conjectured such a possibility previously; however, the current studies clearly suggest that such a fast diffusion could be controlled by the non-thermal fluctuations that result from the explosive events reported in Figure 2.9 (A and B).

### 2.3. Consolidation of the important points.

The research presented here is a modest contribution to the saga that has continued over a century to understand the mechanism of spontaneous emulsification. Interrogating the transfer of

surfactants and oil (or the organic liquid) using UV spectroscopy helped develop an intuitive picture of the relevant processes, whereas the non-equilibrium DPD-MD simulations provided a complementary insight needed to understand the local processes. Some of the main observations made in these studies are as follows.

1. When either an anionic or a non-ionic surfactant containing aqueous phase contacts an organic liquid, the surfactant and water can diffuse into the organic phase, where inverted (water-in-oil) emulsions are formed.
2. A parallel mechanism for this inverted emulsification is that the micelles or the vesicles present in the aqueous phase fuse with the interface explosively, following which the ensuing fragments self-assemble and form water-in-oil emulsions.
3. In both cases ( 1 and 2 above) , the inverted emulsions fuse with the interface rather explosively, but intermittently. The resultant fragments then turn into an oil-in-water emulsion.

This current picture is related to, yet it differs from, what we conjectured previously, in that the inverted (water-in-oil) emulsions was thought to fuse with the interface, following which a curvature reversal induced instability develops at the interface. In this work, the non-equilibrium MD-DPD simulations identify the intermediate state, which is the reminiscent of what was called cusp catastrophe by Dickinson<sup>42</sup>.

We feel that more future work is warranted that would couple a detailed analysis of the thermodynamic and kinetic processes in unravelling new and rich physics underlying such types singular transformation of one type of phase into another.

A remarkable observation is that the transport and self-association dynamics of the surfactants is faster in the mixed solvents than that in the pure solvents. Whenever such fast events occur, the

concentration fluctuation near the interface is amplified, concomitantly. A question here is whether the origin of this phenomenon is thermodynamic or kinetic? A partial answer of this question comes from the water infusion induced emulsification studies of the type presented in Figure 2.3. In these experiments, surfactant is already dissolved in the organic phase before passing water vapor through it. Thus, any emulsification, if it occurs, would here be de-coupled from any kinetic processes related to the transfer of water and surfactant from the aqueous to the organic phase. The results summarized in Figure 2.7 show that emulsification kinetics, as evidenced from the shift of the UV spectra, is always immensely faster in mixed solvents than in pure solvents, just is the case with both surfactant and water migrating into the organic phase from the aqueous phase below it. Diesel is essentially a mixture of various aliphatic and aromatic hydrocarbons, which thus falls in the same group as mixed solvents. Enhanced solubilities (Figure 2.8) of the surfactants in the mixed solvent, although the underneath cause of which remain unclear, suggest that part of the effect is thermodynamic in origin, we cannot rule out the possibility that water vapor may engender an instability at the vapor-liquid interface that being the cause of the fast kinetics observed here.

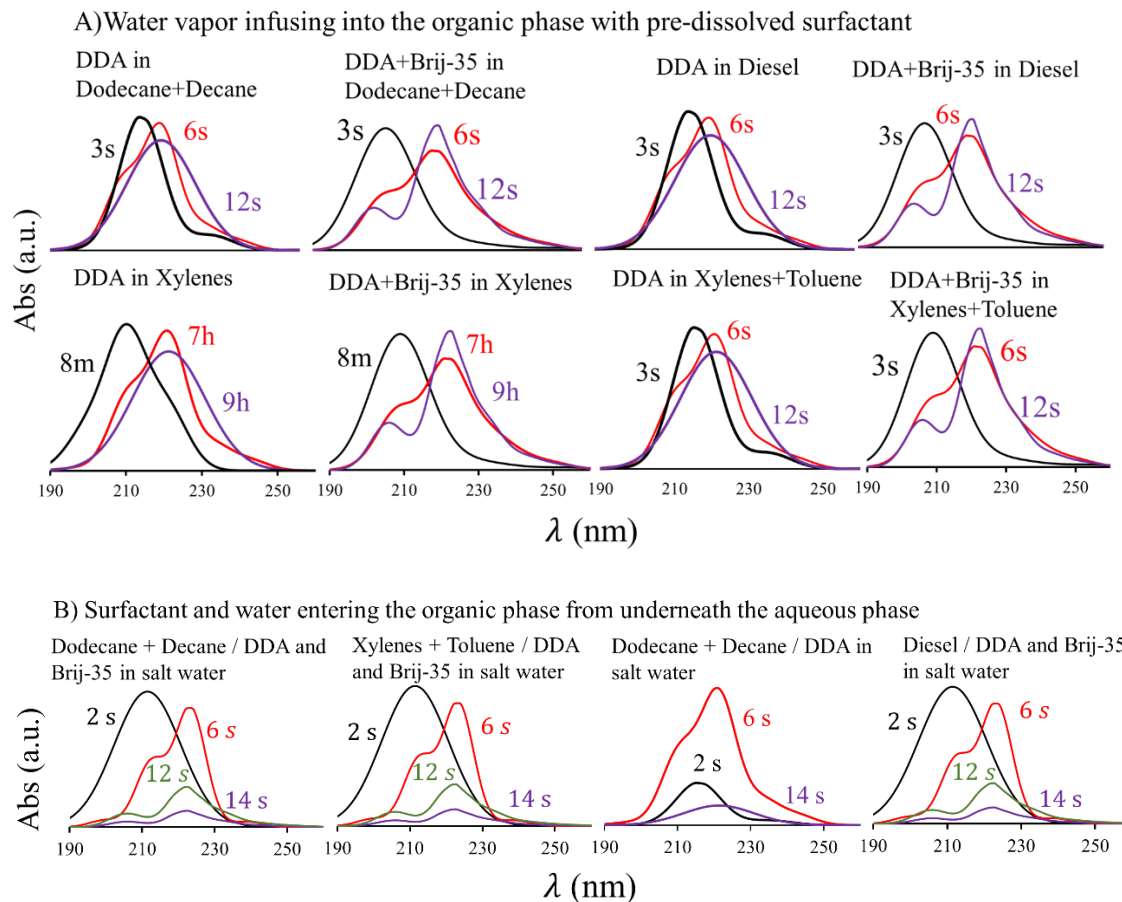


**Figure 2.12.** Bathochromic (red) evolutions of the UV spectra of Dodecanoic acid, Brij-35 and their mixture (50:50) in various organic solvents and their mixtures. See also Figures 3G and 6B. Two points can be noted here. All the Bathochromic shifts occur much faster in mixed aliphatic or organic solvents compared to any pure solvent.

Another remarkable observation is that the emulsification is inhibited when either a high molecular weight hydrophilic polymer is present in the aqueous phase or when a high molecular weight hydrophobic polymer is present in the organic phase. Some of the experimental results performed with PTBS are summarized below.

1. The water infusion experiments of the type presented in Figure 2.13 (A) show that the dodecanoic acid remains unhydrated when PTBS is pre-dissolved in the organic liquid. Note that similar results are also obtained in experiments, where surfactant and water have to migrate into

the organic phase from the aqueous phase. While the latter experiment is dependent on the solubility and the mass transfer kinetics of water from the aqueous to the organic phase, which are drastically arrested by PTBS (Figure 2.13 (B)), emulsification in the water infusion experiment is decoupled from the issue of surfactant transport.

2. No fluctuation of concentration of oil under the interface is evident in the types of experiments reported either (Figure 2.10 (B)). This is, however, possibly an effect ensuing from the causes related to suppressed diffusivity and solubility of DDA in the organic liquid in the presence of PTBS.

3. After a very long time, the surfactants are only mildly depleted from the aqueous phase with a concomitant increase of the surfactants in the organic phase and a slight increase of oil in the aqueous phase (Figure 2.13 (C and D)). All these concentrations are eventually re-equilibrated following which DDA and oil virtually disappear from the aqueous phase.

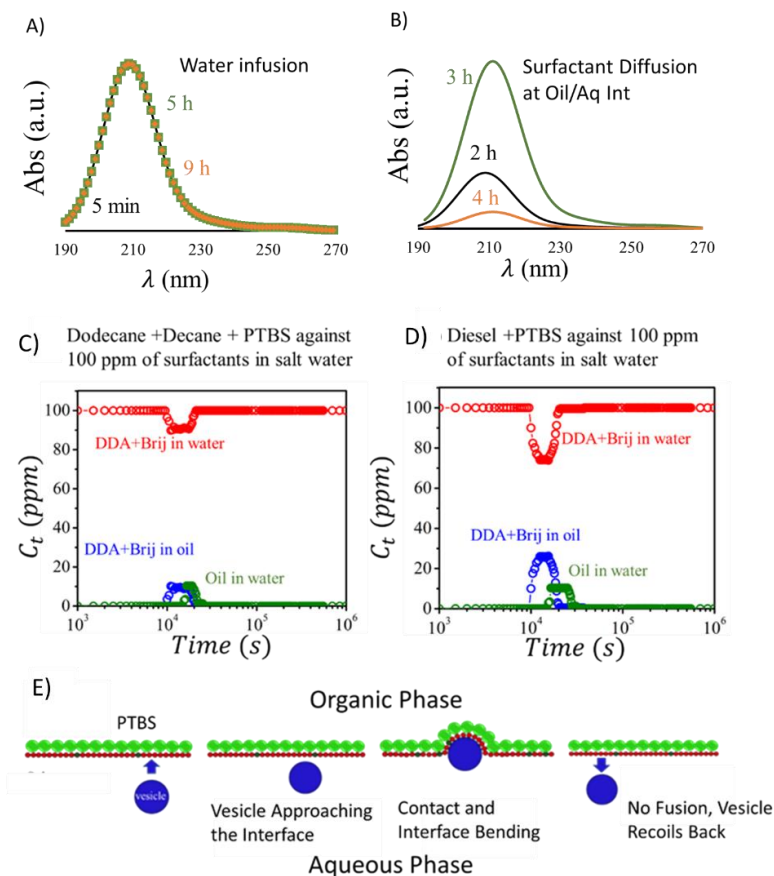


**Figure 2.13.** A and B: Evolution of the concentration of a mixture of DDA and Brij-35 in organic and aqueous phases as a function of time. C) Schematics illustrating that PTBS inhibits formation of the inverted emulsion. The color coding are as follows, Navy blue: Vesicle, Red: DDA, Green: Brij-35, Fluorescent green: PTBS) 18 ppm PTBS

4. Finally, an MD-DPD simulation carried out with a small amount of PTBS (18 ppm) pre-existing in oil show that the polymer adsorbs at the interface from the oil side. A vesicle formed in the aqueous phase deforms the interface somewhat, without undergoing fusion. The vesicle, in turn, is recoiled back into the aqueous phase.

## 2.4. Conclusions

Spontaneous emulsification occurs when the pre-formed water-in-oil emulsions cross the oil-water interface by undergoing phase inversion. The water-in-oil emulsions can form in one of two ways.

The first path to its formation is that the surfactant and water diffuse in the organic phase and self-assemble there. The second path to its formation is the fusion of the micelles and vesicles, which are formed in the aqueous phase, with the oil-water interface. This process leads to explosive fragmentation of the interface locally, before they self-assemble to form the water-in-oil emulsion. What is crucial is that both water and surfactant diffuse into the organic phase from the aqueous phase. If this diffusion and the fusion events occurring at the interface can be arrested, spontaneous emulsification can be thwarted.

## 2.5. Acknowledgements

Financial support from The Strategic Environmental Research and Development Program (Grant No. WP18-1074, managed by Robin Nissan and Braxton Lewis) is gratefully acknowledged. We also thank Professors El Aasser and Steve Regen for donating various equipment to our laboratory, which were crucial for the studies described here. Wes Patel, an undergraduate student, helped us with the nectar drop experiments.

## 2.6. Appendix

Text describing experimental details including the materials and the analytical test procedures along with eleven Figures and five tables are available free of charge via the internet.

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## **Appendix A: Phase I**

### **A. Experimental Methods**

#### **1. Materials**

Dodecane (reagent plus), Ethylene glycol (anhydrous), Dimethyl sulfoxide (anhydrous), Hexadecane (anhydrous) and Heptane (HPLC grade) was purchased from Sigma Aldrich, USA. Diesel oil (with sulfur < 50 ppm) was purchased commercially from a local Shell gas station, Dodecanoic acid (Analytical Standards, 99 % pure) and Brij 35 (Analytical Standards, 99 % pure) were all purchased from Sigma-Aldrich, USA. Polydimethyl siloxane (MW: 308,000 Da) was purchased from Gelest, USA. Poly(4-tert-butylstyrene) (MW:  $1.5 \times 10^6$  Da, 99% pure) was purchased from Polymer source Inc., Canada. Formamide (ACS grade) and sodium chloride salt (ACS grade) was purchased from Fisher Scientific, USA. The 0.4 mm glass capillary tubes and the Kimax - 51 (KIMAX) glass pipettes used in the construction of the accelerometer sensor were purchased from Fisher scientific, USA. In the dynamic interfacial tension measurement experiments, the rectangular cuvettes (acrylic rectangular refraction cells) were purchased from Fisher scientific, USA. The capillary PTFE tubing used in the above experiment were purchased from Sigma-Aldrich, USA. The activated alumina (AA400G 28x48) used in the column chromatography was purchased from Delta Adsorbents, USA. All the chemicals were used as received, with the exception for diesel, which was purified chromatographically using activated alumina. Diesel was stored in air tight glass containers inside a refrigerator unless it is used immediately after purification. Water used in these experiments was distilled and de-ionized (resistance: 18.0 M $\Omega$ ), with a turbidity of 0.1 NTU (Nephelometric turbidity units).

#### **2. Analytical and process instruments**

The droplet size distribution of the emulsion was analyzed with an acoustic particle sizer (Matec APS-100, MATEC Applied Sciences) and a capillary hydrodynamic fractionator (CHDF-2000, MATEC

Applied Sciences). The emulsion was filtered through a  $1.5\ \mu\text{m}$  Whatman glass microfiber filter (934-AH) for the CHDF analysis, these filter papers were purchased from Fisher scientific, USA. Spectroscopic studies were performed with the NanoDrop-oneC UV-Visible spectrophotometer, purchased from Thermo Fisher Scientific. The microscopic images were captured with the Nikon Diaphot inverted differential interference contrast microscope. The surface pressure-area isotherms of the monolayers spread on the surface of salinized water was carried out with a Langmuir Blodgett trough (NIMA, Type: 622), in which the data acquisition from the pressure sensor was executed with the help of microprocessor interface IU4. The interfacial tensions were measured using the Fisher Autotensiomat surface tension analyzer (Model - 215). In the dynamic interfacial measurement studies, the mechanical vibrator of model 1A SF-9324 (PASCO Scientific) purchased from Fisher scientific was used for generating the vibration of the liquid droplets inside a needle of internal diameter 0.7 mm. While the dynamics of the drop was visually perceived using a telescopic microscope, the resonance mode was more accurately identified using a PCB accelerometer sensor (Model – 352C68, sensitivity: 100 mV/g, weight:  $\sim 2\ \text{g}$  frequency range ( $\pm 5\%$ ): 0.5 to 10,000 Hz), which captured the dynamic fluctuations of the droplet surface at the interface with a help of a PCB 4-channel signal conditioner (Model – Y-482C05). This Fotonic sensor measured the fluctuation of the surface of the drop with high precision. The displacement measured by this Fotonic sensor was fed to a computer by NIDAQ analog to digital data acquisition unit (Model – USB 6003). An Agilent signal generator (Model – 33120A) induced the sinusoidal vibration to the mechanical vibrator.

The distilled water used in this study was prepared from the Durastill Automatic distiller (Model 3040U). The Peristaltic pumps (Masterflex L/S Easy-Load II and economy drive) used in the turbulence emulsification study were purchased from Cole-Parmer. The ultrasound-probe sonicator (Sonifier, S-450 (20 kHz)) was used in pulsed mode for the homogenization of the surfactant solutions and dispersion of

polymers into the oil. This unit was purchased from Fisher scientific, USA. The dynamic pressure fluctuation during the turbulence induced emulsification was captured with a PCB accelerometer sensor (Model – 352C68, sensitivity: 100 mV/g, weight: ~2 g frequency range ( $\pm 5\%$ ): 0.5 to 10,000 Hz), the voltage output of which was acquired for data processing with the help of PCB 4-channel signal conditioner (Model – Y-482C05). This, in turn, was interfaced to a computer with a NIDAQ analog to digital data acquisition unit (Model – USB 9162 with NI 9213 input unit). The agitators used for the emulsion formation was a Mainstays blender (6-speed, used in blend mode) purchased from a local vendor. The speed of the agitator was controlled with the switch mode bench power supply, which delivered power ranging from 40 W to 225 W, and the rotational speed of the agitator ranging from 5830 to 15452 rpm (measured using a non-contact laser Neiko 20713A digital tachometer, with a range of 2.5 to 99,999 rpm). The agitation Reynolds number for a given power input was estimated from the rotational speed of the agitator using the relation:  $Re = D^2 N \rho / \mu$ ,  $D$  is the diameter of the agitator blades (0.052 m),  $N$  is the revolutions per second, measured when the conduit was filled with water,  $\rho$  ( $1000 \text{ kg/m}^3$ ) is the density of the fluid and  $\mu$  is its dynamic viscosity ( $8.9 \times 10^{-4} \text{ Pa.s}$ ). The range of the agitation Reynolds number ( $Re$ ) was from 300,000 to 800,000.

With respect to the emulsification under turbulence, a given oil was injected continuously into the conduit with a help of Perfusor pump (Braun) (Perfusor VI, variable control volume: 0.6 – 600 mL/h). The turbidity of the emulsion was measured with a turbidity meter (Orion AQUAfast AQ3010) purchased from Thermo Fisher Scientific. A gentle agitation of the emulsion in the storage tank was carried with a RIGID mud mixer attached to customized mixer blades for efficient mixing (powered by the autotransformer, at a constant voltage of 20 V (800 rpm). The viscosity of oil was measured with a cannon U-tube capillary viscometer (H-472). The glass containers used for storing the emulsion samples were purchased from Fisher scientific, USA.

### 3. Turbulence induced emulsion formation

#### 3.1. Measurement of Interfacial tension using Du Nouy Ring

The interfacial tensions of the oil-water interfaces were measured using the standard Du Nouy ring (Fisher Autotensiomat surface tension analyzer). The Autotensiomat consists of the following components in its construction: the measuring probe, the force sensor and a vertically movable mechanical stage inside a closed chamber that could be manipulated with an automatic controller. The measuring probe was a platinum-iridium ring attached to the tungsten rod. The force sensor and the movable stage were electronically manipulated with a digital controller. The interfacial tension between the oil-water interface was measured using the above unit at constant temperature. The measuring probe (ring) was meticulously cleaned with distilled water followed by flame treatment. The pre-calibrated du Nouy ring was first immersed into the aqueous phase stored in an 80 mL glass beaker ( $\gamma_w = 72 \text{ mN/m}$ ). The ring was then gradually lifted from the liquid and the corresponding force transferred through the strain gauge transducer was measured using the digital controller. As the probe was lifted through the surface of the liquid, the surface tension was measured. For the measurement of surface tension of the oil-water interface, surfactant solution (equal mixture of dodecanoic acid and Brij 35) in salt water (0.6 M) was loaded into the sample cell (40 mL each) over which, 5 mL of the oil (Dodecane/Diesel) was gently added. Here the interfacial tension was measured as the probe gradually passed through the oil-water interface. After each measurement, the measuring probe was cleaned thoroughly by immersing it in a pool of distilled water and oxidizing using flame treatment. For the long term measurement, after the Du Nouy ring was already immersed in the aqueous phase and the oil was poured over water, the setup was kept undisturbed for 24 h, following which, the interfacial tension was measured following aforementioned protocol.

### 3.2. Measurement of Dynamic interfacial tension

The method of estimating interfacial tension of rapidly fluctuating interface was based on drop resonance as shown in Figure 3. Here, the sample holder is a rectangular acrylic cubical cell (A), whose base was affixed to a metal stage. For the measurements performed in air, liquid was injected into the cell through a needle attached to the inner wall of the acrylic cell using a Gilmont syringe (D) (Model: GS - 1200). This Gilmont syringe was connected to a 50 mL glass syringe (E), which acted as the sample reservoir. The Gilmont syringe can thus be filled with the liquid of interest from the larger syringe ensuring that no negative pressure develops in the system. This syringe set-up was connected to a pressure sensor (G) using a three way valve. All these units were interconnected with each other with the help of 1 mm ID PTFE capillary tubes. The terminal end of the capillary tube emerging from the Gilmont syringe needle was connected to the needle attached to the inner wall of the acrylic cell. In order to induce droplet fluctuation, liquid was pumped out gently using the Gilmont syringe while it was vibrated externally by inducing vibration to the flexible tube through which the liquid passed. This vibration was achieved by sandwiching a part of the tubing between a mechanical vibration unit (B) and a metallic block connected to a micrometer (C). Meticulous care was taken to assemble all the units of the apparatus to ensure that no backflow of liquid occurs when a drop was produced at the tip of the needle inside the acrylic cell. To identify the resonance mode of the liquid droplet, an accelerometer sensor attached to a tungsten (1.75 mm) probe, which was in-turn caged in a 2 mm glass capillary was placed right above the surface of the liquid drop, which captured the dynamic fluctuations of the drop. This could be done both in air and even when the drop is produced inside another liquid. As the droplet produced at the tip of the needle was inflated the intensity of the fluctuation increased was maximum at a critical volume, which was estimated from its static image using ImageJ software via Pendant drop plugin. The dynamic interfacial tension values thus obtained by this method has a constant standard deviation of  $\sim 0.01$  mN/m.

### 3.4. Surface Pressure Area Isotherms

A Langmuir-Blodgett trough was used to study the surface pressure area isotherms of the surfactants. The standard solution was prepared by adding 1 mg of the surfactant in 1 mL of chloroform. After filling the trough with salt solution (0.6 M), 70  $\mu\text{L}$  of the surfactant solution was deposited upon it drop by drop, while the sliding barriers (made of Derlin) were in completely open positions. A rectangular blotting paper (Area – 1.2  $\text{cm}^2$ ) serving as a Wilhelmy plate was suspended from an electro-balance that was brought into contact with the surface of water using a micromanipulator. The surface pressure was measured by the force exerted on the Wilhelmy plate, which was always immersed partly into the sub-phase of water during the compression of the monolayer. As the monolayer was compressed at a speed of 250  $\text{cm}^2/\text{min}$ , the force exerted on the Wilhelmy plate was continuously recorded. The measured force was converted into surface pressure automatically and the  $\pi - A$  isotherm was constructed using the software provided by the manufacturer. In some studies, a clean circular aluminum disk of 5 cm diameter was attached to the mechanical stirrer and gently brought into contact with the surface of water. The disc was rotated at a rate of 20 rpm, which created a gentle disturbance on the surface.

Before and after each experiment, the Langmuir- Blodgett trough was cleaned several time with distilled water ( $\gamma_w = 72 \text{ mN/m}$  and  $\text{pH} = 7$ ), and subsequently filled with the salinized water. Removal of the surfactant from the surface of water was accomplished by aspirating the surface following a standard procedure with the help of a vacuum pump. The standard precautions were taken to prevent back flow of the vacuum oil vapor using cold a trap. These steps were repeated several times, until the surface pressure returned to a zero value.

### 3.5. Design of the reactor

The turbulent induced emulsification was carried out inside an airtight cylindrical conduit, which was made of polymethyl methacrylate (PMMA). This was affixed horizontally, above the optical table with

the help of several metal stands. The PMMA conduit (Length – 48 cm, Diameter – 8 cm, Thickness – 0.8 cm, Volume – 2.45 L), was perforated at its two ends that served as the inlet and the outlet ports for the water and the emulsion. Water was supplied to the conduit through the inlet from an over-head tank with a capacity of 30 L powered by the hydrostatic pressure head (0.8 m). A mud mixer fitted with a Teflon stirrer (Length – 45 cm) was inserted inside this tank and gently rotated to induce gentle mixing of the liquid. The water exited the conduit with the help of a peristaltic pump at a rate of 300 mL/min. Near the entrance of the liquid, turbulence was generated inside the conduit by means of a four-winged turbine blade (Diameter – 5.2 cm and thickness - 0.6 cm) which also enabled the axial flow of water. The rotational speed of the agitator was regulated with the help of variable DC power supply. The conduit was fitted with another similar agitator near the outlet, which was used to remove the trapped air bubbles in the dead zones of mixing at the start-up of the experiment. During turbulence emulsification, this agitator near the exit was rotated only minimally to avoid deposition of the emulsion on the wall of the conduit. Several perforations in the conduit allowed the insertions of the accelerometers, and oil injection port. Two tall vertical columns connected near the entrance and exit of the tank reported the difference of pressure at these two locations. This also allowed monitoring that the average pressure of the water flowing conduit was always positive, which prevented the undesired infusion of air from the atmosphere into the conduit.

### **3.6. Sensor for Dynamic pressure fluctuation**

Accelerometers were used to measure the dynamic pressure fluctuations inside the conduit. In order to avoid the external agitations and the wall effects, the accelerometer unit was magnetically levitated. The dynamic pressure sensor was made by attaching a tungsten rod (Diameter – 1.5cm and Length – 3.5cm) to a PCB 352C68 accelerometer with a hot melt adhesive. A circular ring magnet placed in between the rod and the accelerometer unit allowed magnetic levitation of the sensor. The electrical noise of the

accelerometer due to the putative mechanical distortion of the circuit cable was avoided by connecting a small segment ( $\sim 5$  cm) of Chromium-Nickel-Manganese alloy wire (Diameter – 0.1 mm) to the positive and negative terminals of the accelerometer units which, in-turn, was soldered to the accelerometer cable wire. The dynamic force sensed by the calibrated accelerometer was passed through a signal conditioner (PCB 482C05), which gave the output signal in terms of voltage. The output from the signal conditioner was recorded in a data logging device (NIDAQ data acquisition unit), which was connected to a computer for data storage and analysis. The port for the accelerometer was made by creating a circular opening on the upper surface of the conduit (Figure 7) through which, a 1.7 cm long glass capillary, jacketed by a clear vinyl tubing was inserted. The lower edge of this glass capillary, which resides inside the conduit was fitted with a 0.45 mm metal capillary tube, made of titanium, which increased the stability of the tip in strong turbulence. In order to sense the pressure fluctuations in a small region in the fluid, the capillary diameter needed to be reduced further. Hence, a glass capillary of 0.4 mm ID was inserted inside the metal capillary tube and was securely sealed with a hot-melt adhesive. In order to levitate the accelerometer over the port, the base of the septum stopper (1.7 cm diameter) was inserted into the circular opening, through which the glass capillary arrangement was fixed inside the conduit. Two circular ring magnets were attached to the top of the septum stopper. The similar polarity of the ring magnets fixed to the septum stopper and that of the magnet attached to base of the accelerometer probe created repulsion, thereby levitating the accelerometer above the conduit. When emulsification began, the liquid filled up the glass capillary, which also acted as a lubricant for tungsten rod to move freely inside the capillary. The fluctuations occurring at the tip of the accelerometer probe was sensed by the dynamic motion of the accelerometer probe along the length of the capillary. The pressure fluctuations occurring inside the conduit were measured by the accelerometer probe, at various power inputs, controlled by a switch mode power supply unit.

### 3.7. Turbulence induced emulsification

To begin with, a concentrated surfactant solution (1000 ppm of Dodecanoic acid and 1000 ppm of Brij - 35 in 0.6 M sodium chloride solution) with a help of ultrasound-probe sonicator, which ensured fast dissolution of the powdered surfactants in distilled water ( $\gamma_w = 72 \text{ mN/m}$ ). This concentrated solution of surfactant solution was added to a 0.6 M salt water in the over-head tank to make a dilute solution of 100 ppm surfactant (Dodecanoic acid – 50 ppm and Brij 35 – 50 ppm) in salt water. This solution was allowed to flow into the conduit by means of the hydrostatic pressure head created by the elevation of the holding tank from the conduit. As the liquid flows into the conduit, the hydrostatic pressure head above the level of the conduit was monitored in order to ensure that a net positive pressure is always maintained in the conduit. The liquid was removed from the conduit using a positive displacement pump (figure 7) at a flow rate of 300 mL/min. Initially, the aqueous solution was recirculated from the holding tank to the conduit and then back to the tank, while turning on both the impellers. This procedure ensured that that all the trapped air is removed from the system. This procedure was continued until the water in the conduit was completely transparent. After ensuring that all the trapped air had been removed, the speed of the impeller at the exit end was turned to a minimum speed where the rotating blade could be visualized to the naked eye. At the same time, the speed of the impeller at the entrance of the conduit was set to a control value. When the steady state was achieved as indicated by the fluctuations of the accelerometer, oil was injected into the conduit at a constant flowrate of 30 ml/h. With some pre-adjustments of the flow rates, it was ensured that the concentrations of the surfactant to oil was maintained at the ratio of 100 to 1000 ppm. For most of the experiments, the emulsified liquid was collected from the conduit following a single pass. For a few experiments, the emulsion was circulated through the holding tank in the closed circuit mode for about 30 minutes before collecting it for analysis. In some experiments with single pass, air bubbles were injected inside the conduit at a rate of  $\sim 5.2 \text{ mL/min}$

through the air inlet port (Figure 7). The single pass emulsification experiments were conducted in some cases at a turbulence power input of 114W with certain polymers added either to water or to the oil. The additive to water was polyacrylamide (PAM, Mol.wt. 1,000,000 Da) and that to oil was Polydimethylsiloxane (PDMS, Mol.wt. 308,000 Da) or Poly(4-tert-butylstyrene) (PTBS, Mol. wt. 1,500,000 Da) at a desired concentration to dodecane and diesel respectively. In all the above cases of emulsification, the preliminary analysis performed was to measure the pH of the emulsion. Which was found to be ~7 irrespective of various system conditions studied. Following emulsification, acoustic particle sizer (APS), capillary hydrodynamic fractionator (CHDF) and microscopy analyzed the samples. The time series of the dynamic pressure fluctuation was converted to a probability density function for each case of various studies reported here. The method of predicting the droplet size distribution using such a pdf is discussed in the text. The number density of droplets as reported in figure 12 was estimated from the Hinze and Kolmogorov scale using the relation:  $N(d_0) = (C/L^3) \times d_i^3$ , where C is the concentration of oil ( 1000 ppm) in water,  $L^3$  is the active volume of emulsion formation (L being the diameter of the impeller),  $d_i$  is the length obtained from Hinze scale ( $d_H$ ) and Kolmogorov scale ( $d_K$ ).

#### **4. Analysis of droplet size distribution**

##### **4.1. Microscopic analysis**

The droplet size distribution of the emulsion was visually observed with the help of the glass microchannel, as shown in Figure 9. Here, couple of glass micro-slides were attached to each other with a help of a double sided tape at the edge, making a small spacing between them. After filling the microchannel with a small amount of emulsion, all of the open sides were sealed in order to prevent evaporation of water. The micrographs of the emulsion sample were taken with a help of Nikon Diaphot microscope by focusing at different depths inside the channel. Several such images were analyzed by automatic image processing technique using ImageJ software. By this method multiple images were

analyzed simultaneously and the droplet size distribution of the samples were obtained in the microscopic range.

#### **4.2. Acoustic attenuation spectroscopy**

After the initiation of the APS instrument, 150 mL of the emulsion passed through a Whatman filter paper was charged into its sample cell. The pore size of the filter paper is large enough that no emulsion was trapped. However, this filtration removed the undesired air bubbles that occasionally interfered with the APS measurements. The emulsion was continuously and gently stirred inside the sample cell with a help of a mechanical agitator as per the protocol of this procedure that ensures homogeneity of the emulsion sample. The temperature of this cell was kept at 26 °C during the analysis.

#### **4.3. Capillary hydrodynamic fractionation**

The submicroscopic emulsion droplets were analyzed using the method of capillary hydrodynamic fractionation after the emulsion was passed through a glass microfiber filter with a pore size of 1.5  $\mu\text{m}$ . Fifty microliter of the filtered sample were injected through the sample port to an eluent stream followed by the equal amount of marker solution<sup>65</sup>. A standard retention time of 10 min was used for analyzing all the samples reported in this study.

#### **4.4. Measurement of Viscosity**

A standard method, ASTM D445-88, was used to measure the viscosity of the oils used in this study. First, the kinematic viscosity was determined by measuring the time for a known volume of liquid flowing under gravity through a calibrated glass capillary viscometer (Cannon U-tube capillary viscometer (H-472)). The kinematic viscosity was estimated by multiplying the efflux time with the calibration factor as provided by the supplier. The efflux time measurements were performed at constant ambient temperature, by submerging the capillary viscometer inside a pool of water, which was maintained at constant temperature (25°C). The kinematic viscosity ( $\nu$ ) values were converted to dynamic viscosity ( $\mu$ ) by multiplying it with density ( $\mu = \nu\rho$ ). The dynamic viscosity of the dodecane

and diesel were obtained as 1.34 mPa-s and 1.84 mPa-s respectively. On the addition of 20 ppm of PDMS and PTBS to dodecane and diesel, the resulting dynamic viscosities were obtained as 1.35 mPa-s and 1.88 mPa-s respectively. All the measurements were repeated three times to ensure the reproducibility of the measured values. The resulting standard deviation was  $\pm 0.001$  for the cases with dodecane and  $\pm 0.002$  for the cases with diesel. From the above dynamic viscosity measurement results, it can be concluded that there is no significant change in the viscosities with the addition of hydrophobic polymers to the oil.

#### **4.5. Spontaneous emulsification**

The spontaneous emulsification experiment is depicted in Figure 22. A 250 mL conical flask was fixed over the vibration isolation table by means of a metallic stand following which a 100 mL of the salt solution (with/without surfactant) was loaded into the conical flask. This setup was sealed with a Y – shaped glass stopper with two open ports (1.5 cm diameter), which were closed with rubber septum stoppers (1.7 cm diameter). A needle was inserted into one of the septum and a 0.2 mm (I.D.), whereas a Teflon capillary tube was inserted into the other septum stopper. The needle inserted into the first stopper acts as a vent to the atmosphere. One open end of the Teflon tubing was inserted 2 cm below the surface of water. This terminal end of this tube was connected to a polyvinyl stopper and a needle assembly, through which the liquid sample from inside the conical flask was siphoned out drop by drop and collected at a rate of  $\sim 1$  mL/min. After making sure that the Teflon tube was fully filled with the aqueous phase, and the disturbance of the surface subsided, 30 mL of oil (with/without additive) was gently poured over it. Before collecting the emulsion, some amount of the salinized water that pre-filled the tube was discarded, following which, the samples were collected at pre-set intervals.

## B. Supplementary Figures

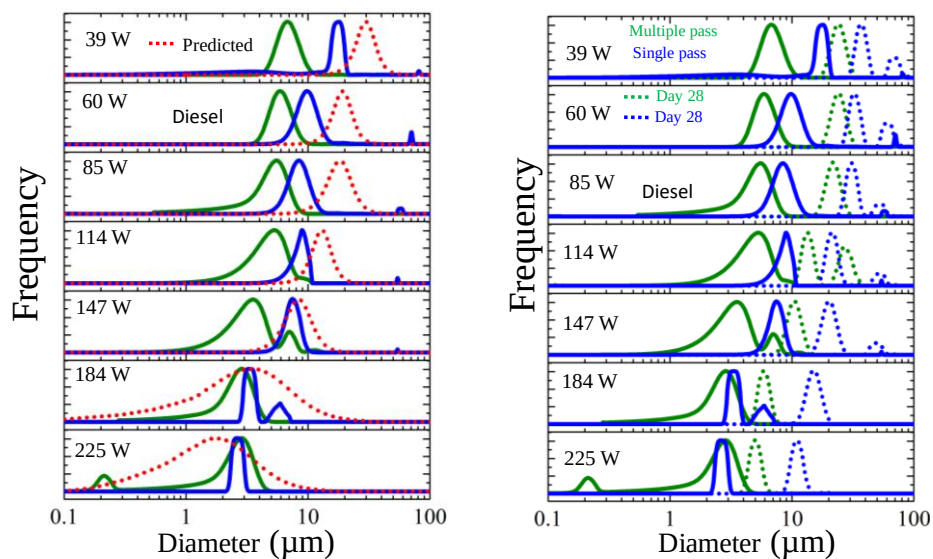


**Figure S1** (Left) Comparison of the droplet size distribution obtained from APS and those predicted from the hydrodynamic fluctuation spectra obtained at different input powers. These experiments are for diesel emulsified in salinized water in the presence of a 50:50 (W: W) mixture of dodecanoic acid and Brij-35 at the concentration of 100 PPM. The blue colored spectra correspond to single pass whereas the green colored spectra correspond to multi pass experiments. (Right) Ripening of the droplet size distribution over a period of 28 days. Solid lines correspond to the spectra obtained soon after preparation, whereas the dotted spectra correspond to 28 days. The colors of the dotted curves are kept the same as that of first day to signify which corresponds to what.

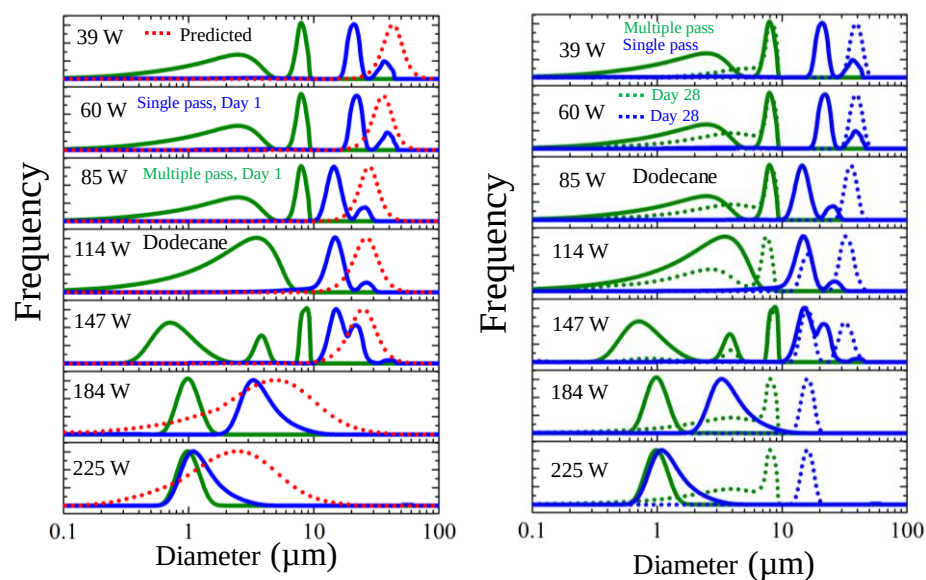


**Figure S2** Same as Figure S2. These results are for Dodecane instead of Diesel.

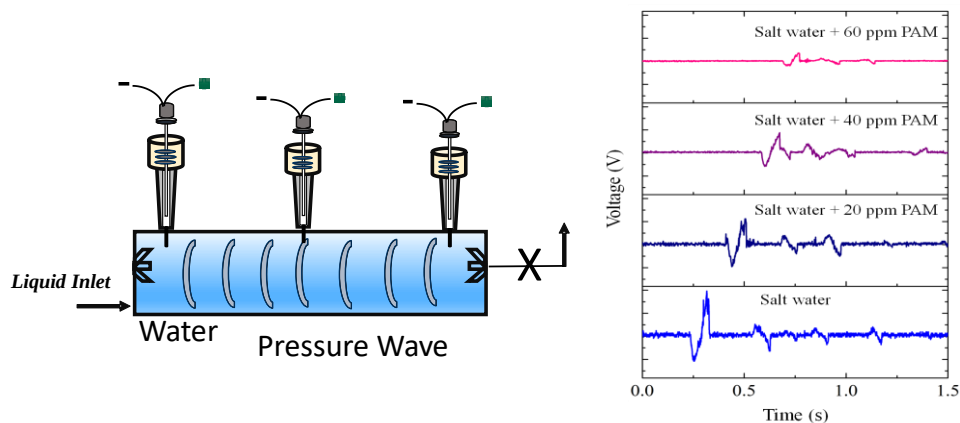


**Figure S3** Left figure is the schematic of the setup to study the propagation of hammer pressure wave. Dynamic pressure sensors, as described in the text, are used to detect pressure waves. The data obtained from the sensor placed at a distance of 70cm from the exit point summarized in the right hand figure show that the pressure wave is quenched as the concentration of polyacrylamide increases in the aqueous phase.

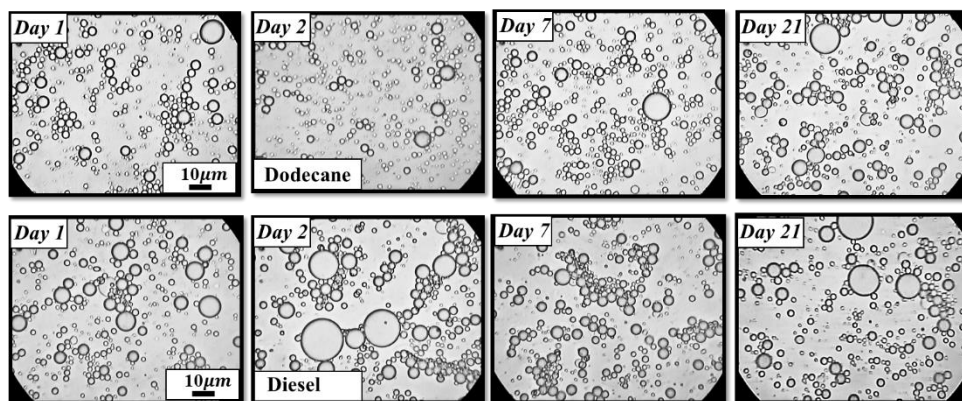


**Figure S4** DIC microscopic images of emulsions formed with the Dodecane and Diesel in salinized water-surfactant system at a nominal power input of 114 W observed over three weeks. In these experiments, 20 ppm of polyacrylamide was added in the aqueous phase prior to emulsification. Dodecane and Diesel contained 20 ppm of polydimethylsiloxane (MW=308000) poly(4-tert-butylstyrene) (MW= 1.5MM), respectively.

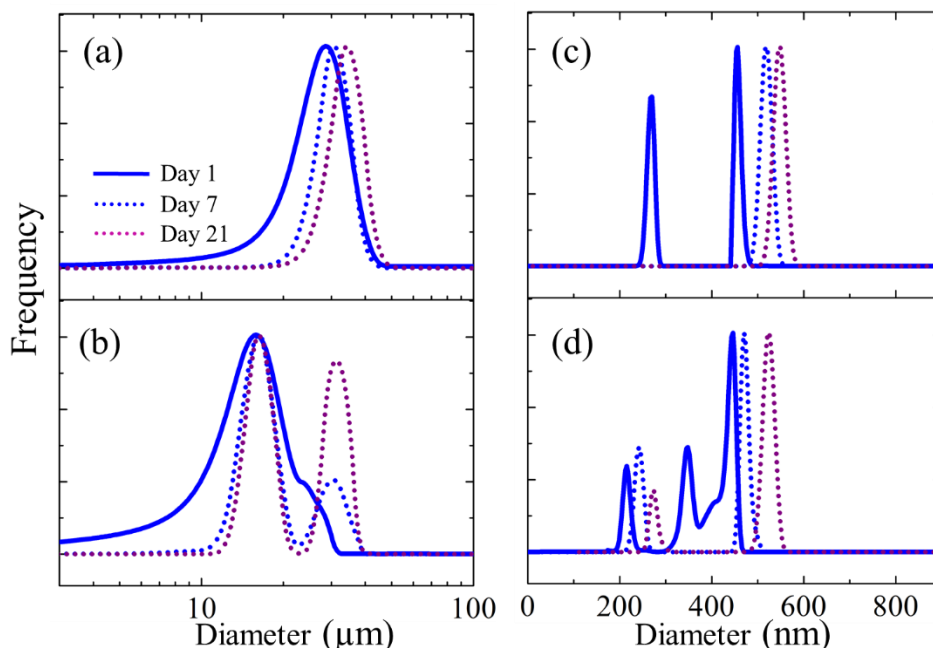


**Figure S5** Droplet size distributions of the oil-water emulsions as described in figure S5 as obtained from acoustic impedance spectroscopy[(a) and (b)] and capillary hydrodynamic fractionation [(c) and (d)]. The blue curves (—) are obtained soon after the emulsions were formed. The dotted curves (····), (····) are obtained after 7 and 28 days respectively.

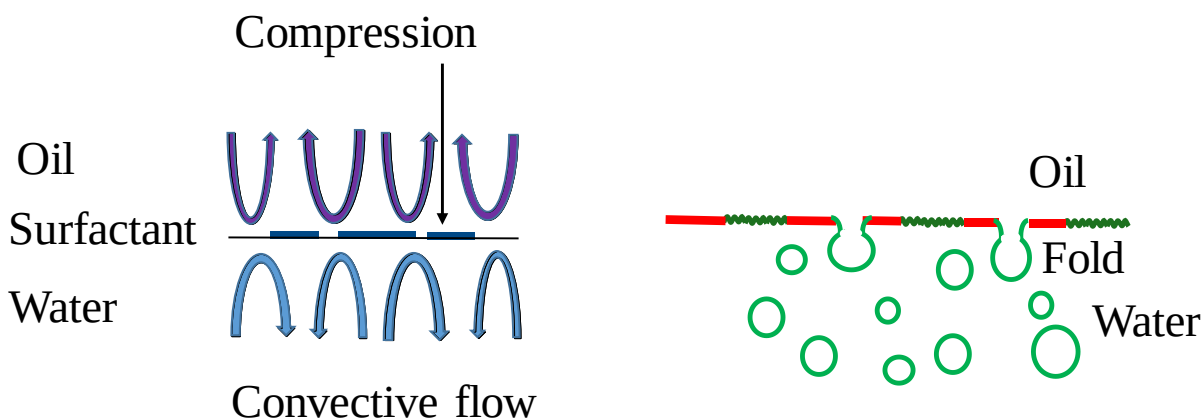


**Figure S6.** A schematic illustrating that roll cell type convective flow near the interface would tend to compress some regions on the surface, and stretch other regions. While Marangoni effect would try to bring the entire surface to a uniform value, if the adsorption dynamics is fast enough, the stretched regions may also be filled up by the diffusion of the surfactant from the bulk phase. Folding instability may occur in the compressed regions of the interface, which are the possible precursors to the formation of nan-sized droplets.

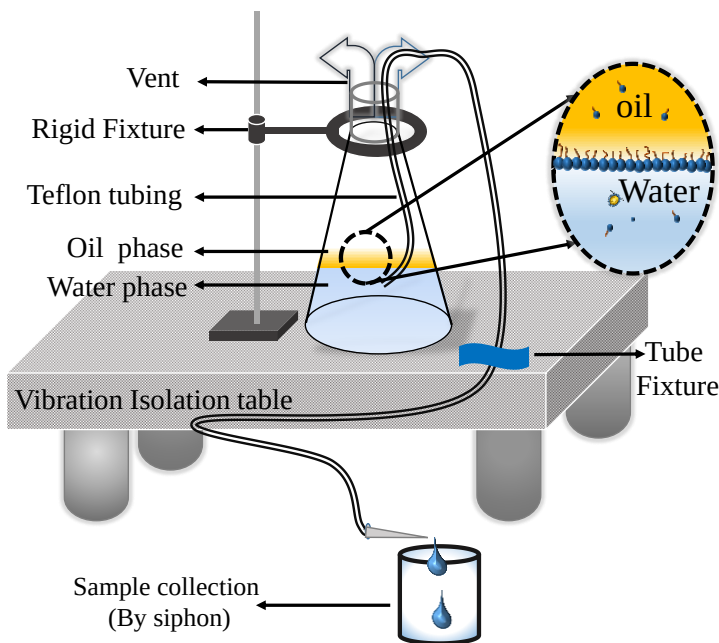


**Figure S7.** Schematic representation of the set up used to study the formation of emulsions in agitation less condition. The important point of this experiment is to collect the aqueous phase below the interface very slowly (i.e. siphoning) in order to avoid spurious agitation.

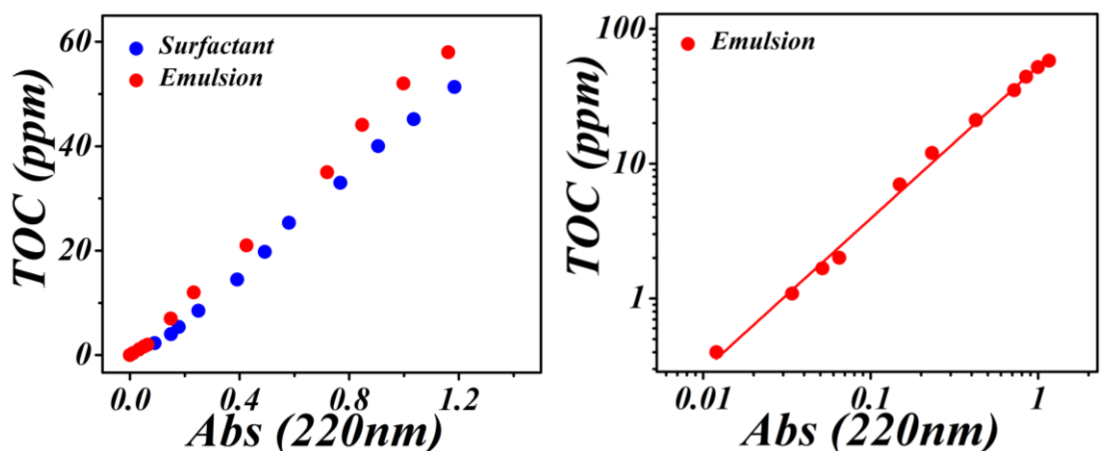


**Figure S8.** TOC calibration of emulsion measured as a function of UV-Vis absorbance. (a) Shows the calibration plot of TOC Vs the UV-Vis absorbance at 220 nm analyzed for various concentrations of the emulsion and surfactants. (b) Shows the log-log plot of 1 (a) emulsion, indicating the straight line that represents the power law relationship between the TOC and the absorbance value. See also the supporting information of reference 1 in the text.

## **Appendix B: Phase II**

### **Experimental Methods**

**Materials** Dodecane (reagent plus), Heptane, Toluene, Benzene, Styrene, Xylenes (HPLC grade), Dodecanoic acid (Analytical Standards, 99% pure) and Brij 35 (Analytical Standards, 99% pure) were purchased from Sigma Aldrich, USA. Decane (HPLC grade) and Octane (HPLC grade) were purchased from Fisher scientific, USA. Diesel oil (with sulfur < 50 ppm) was purchased from a local Shell gas station, which was purified as discussed below. Poly (4-tertbutylstyrene) (MW:  $1.5 \times 10^6$  Da, 99% pure) was purchased from Polymer source Inc., Canada. Each of the solvents was purified by passing it through a column of activated alumina three times. The activated alumina (AA400G 28x48) used in the column chromatography was purchased from Delta Adsorbents, USA. All the purified samples were stored in airtight glass containers inside a dust free cabinet, unless it is used immediately after purification. D-Glucose (Anhydrous, analytical Standards, 99% pure) was purchased from Thermo Fisher, USA and D-Fructose (Anhydrous, analytical Standards, 99% pure) was purchased from Alfa Aesar, USA. Water used in these experiments was distilled and de-ionized (resistance: 18.0 M $\Omega$ ), which had a turbidity of 0.1 NTU (Nephelometric turbidity units).

**Analytical and process instruments** The Spectroscopic studies were performed with the NanoDrop-oneC UV-Visible spectrophotometer, purchased from Thermo Fisher Scientific. The droplet size distribution of the emulsion was carried out with a capillary hydrodynamic fractionator (CHDF-2000, MATEC Applied Sciences), after filtering it through a 1.5  $\mu m$  Whatman glass microfiber filter (934- AH, Fisher scientific, USA) before the CHDF analysis (Note: Filtration step is added to avoid any cross contamination in the system; the droplet size distribution did not depend

on it). The interfacial tensions (IFT) were measured using the Fisher Autotensiomat surface tension analyzer (Model – 215). IFT measured for various organic phases against salt solution with and without surfactants are reported in figure S3. The water was distilled using a Durastill Automatic distiller (Model 3040U), following which it was deionized using Barnstead E-Pure deionizer from Thermo Fisher, USA. . The ultrasound-probe sonicator (Sonifier, S-450 (20 kHz)) was used in pulsed mode for the homogenization of the surfactant solutions and dispersion of polymers into the oil. This unit was purchased from Fisher scientific, USA. The viscosity of oil was measured with a cannon U-tube capillary viscometer (H-472). The glass vials and flasks were used for storing the emulsion samples were purchased from Fisher scientific, USA. Vials used as received. Flasks were cleaned with a standard piranha solution followed by rinsing with copious amount of distilled water.

**Spectroscopic studies.** The UV spectroscopic studies were carried out with two types of quartz cuvettes, one of which was a flow cell type cuvette with a side arm, which was used for the water vapor infusion studies (Figure S1). In order to study the role of hydration of the bathochromic shift of a surfactant, it was dissolved in an organic solvent inside a conical flask. Water vapor saturated air (produced by a FTIR dry gas generator from American Laboratory, Thermo Fisher, USA) was bubbled through the organic liquid in the conical flask at a rate of 62 bubbles/min (bubble diameter – 2-3 mm) while the liquid was stirred continuously with a magnetic stirrer (100 rpm). This liquid was passed (~2 ml/min) through the quartz cuvette [FireflySci's macro spectrophotometer flow through cell (3 mL capacity) with detachable inlet/outlet quartz tubes, Fisher scientific, USA] using a tygon tube that connected the cuvette and the liquid in the conical flask with the help of a Peristaltic pump (Masterflex L/S Easy-Load II and economy drive, Cole-Parmer)

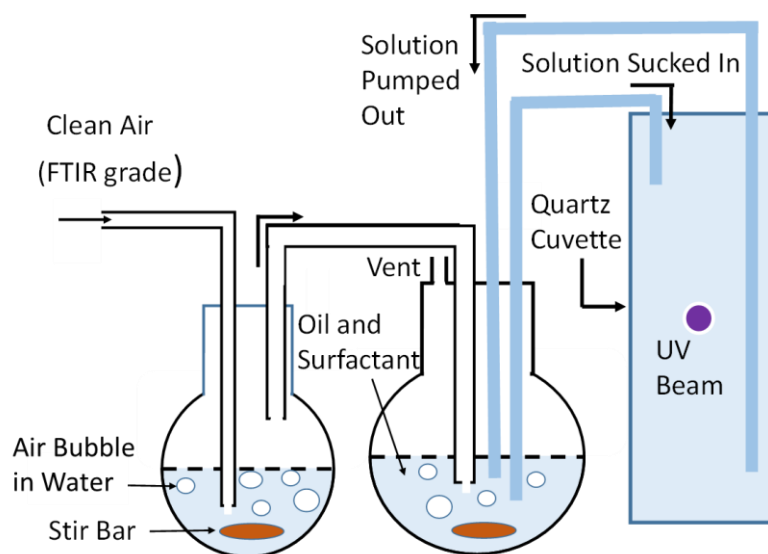


**Figure 1.** Schematic describing how the surfactant dissolved in an organic solvent is hydrated by passing water vapor through it.

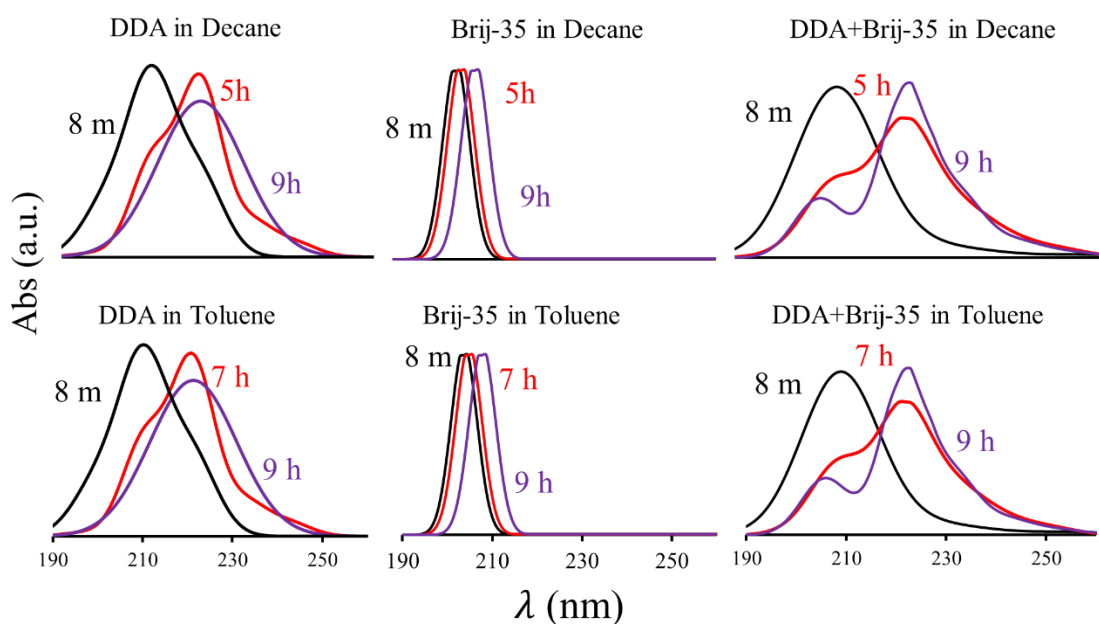


**Figure 2.** Bathochromic (red) evolutions of the UV spectra of Dodecanoic acid, Brij-35 and their mixture (50:50) in various organic solvents and their mixtures as Water vapor infusing into the organic phase with pre-dissolved solvent.

The other quartz cuvette (LAB4US UV Quartz Cuvettes, 10 mm path length from fisher scientific, USA) was used to study the evolution of the concentration of the surfactant as it diffused from the aqueous to the organic phase as well as the evolution of the concentration of oil and surfactant in

the aqueous phase. An organic liquid (2.2 ml) was gently deposited above 2.2 ml of 0.6 M salt solution inside the cuvette (Figure 5). The height of the quartz cuvette was so adjusted inside the spectrometer sample holder such that the UV beam passed either above the interface of the two liquids, as shown in the self-explanatory schematic (Figure 9). The UV beam passing through the organic phase monitored the concentration of surfactant as it diffused from the aqueous to the organic phase.

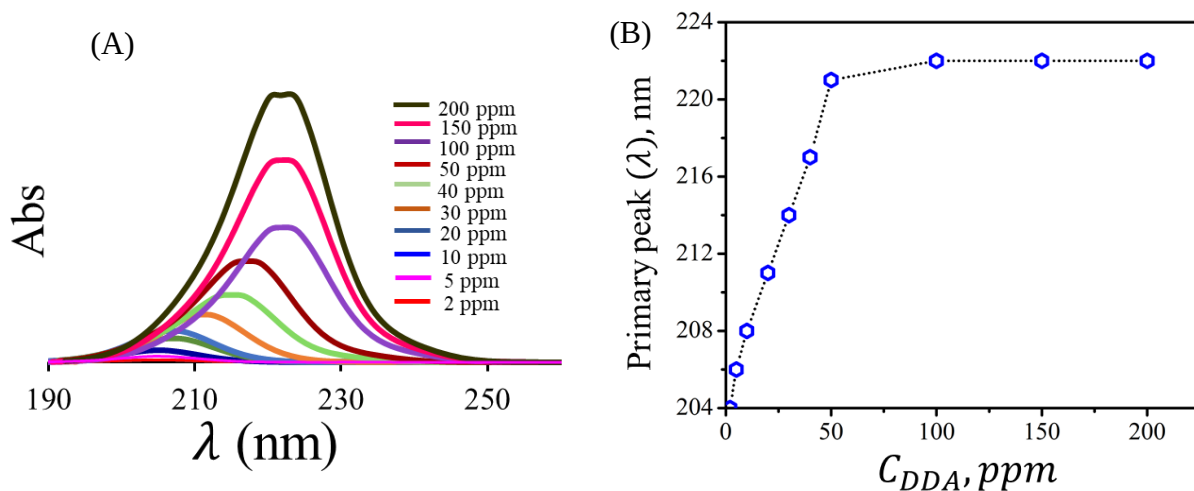


**Figure 3.** (A) UV absorption spectra of dodecanoic acid in 0.6 M salt water as a function of increasing concentration at pH 7. For very low concentration of DDA, the peak maximum appears at 205 nm, which shifts to higher wavelength as the concentration of DDA increases. (B) Shows the plot of primary peak position as a function of increasing concentration of DDA in the aqueous phase at pH 7, which shows a critical concentration ( $\sim 30$  ppm) beyond which the spectrum remains unchanged.

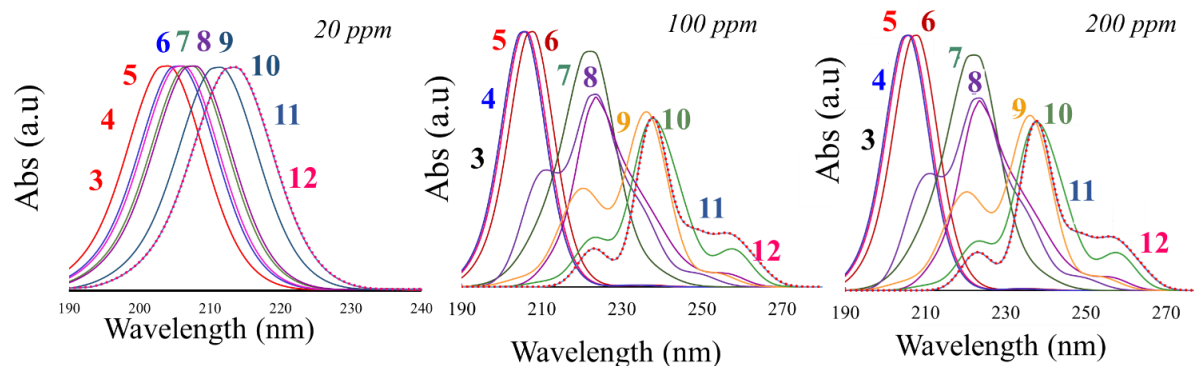


**Figure 4.** UV absorption spectra of dodecanoic acid in 0.6 M salt water as a function of pH for three concentrations of DDA. As the pH becomes more basic, the primary absorption peak exhibits a red shift.

The beam passing through the aqueous phase monitored the concentrations of the surfactant the organic liquid that was emulsified. In order to measure the fluctuation of the concentration of surface below the interface, the height was re-adjusted with the help of Teflon spacers in the holding cell. The cuvette was initially loaded with surfactant solution containing a surfactant of pre-selected concentration, following which, an organic liquid was added carefully over the aqueous phase so as to avoid undesired agitation. This loaded cuvette placed inside the sample holder of the spectrophotometer was then closed with a Teflon cap and spacers as needed. The kinetic measurements were initiated using a customized kinetic program that could record and store the spectroscopic data at 1 sec interval.

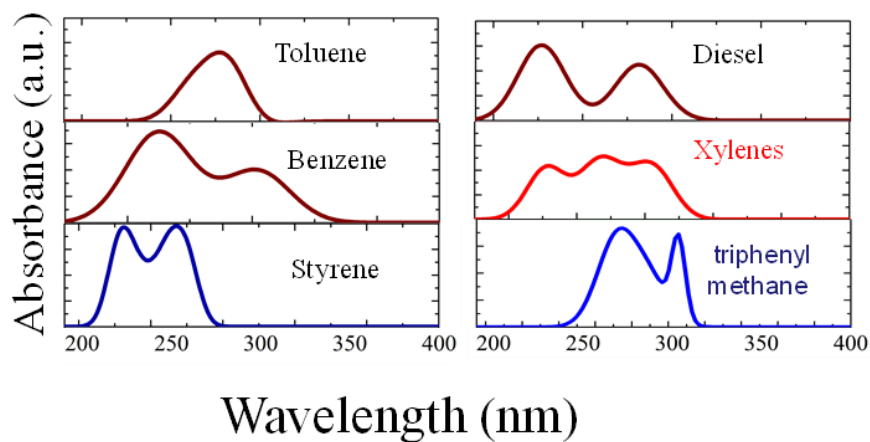


**Figure 5.** UV spectra of the organic liquids used in this experiment. Triphenylmethane is an additive in alkanes, as the latter, itself, is not UV active.

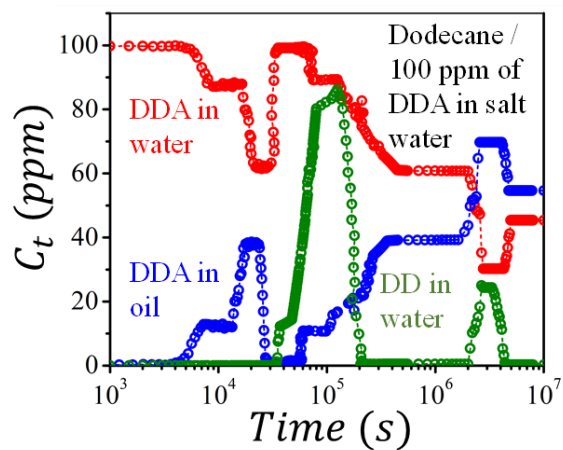


**Figure 6.** Evolution of the concentration of surfactant in dodecane and salt water as a function of time. This Figure represents the data presented in Figure 6, but for longer time.

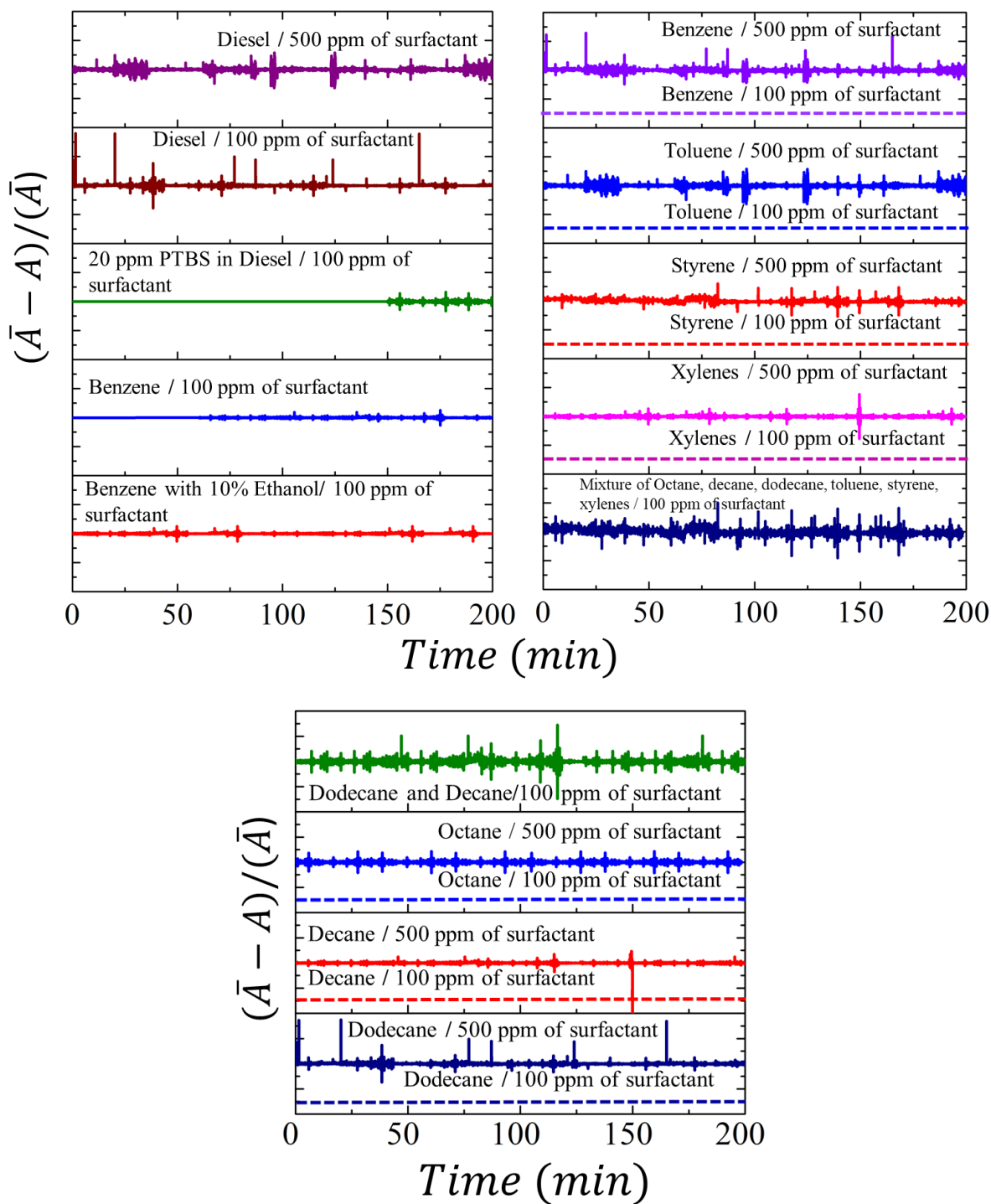


**Figure 7.** Fluctuation of the concentration of the organic phase below the oil-water interface. These results are similar to those reported in figure 9, but for more different cases.

**Measurement of Interfacial tension using Du Nouy Ring** The interfacial tensions of the oil-water interfaces were measured (23 °C) using the standard Du Nouy ring (Fisher Autotensiomat surface tension analyzer) following standard methods, which we described in reference<sup>26</sup>.

**Table 1.** Interfacial Tensions of various liquids against 0.6 M salt aqueous solution with and without the addition of surfactants measured by Du-Nouy ring method.

| Organic solvent  | Interfacial tension<br>Without surfactant<br>(mN/m) | Interfacial tension<br>With DDA<br>(mN/m) | Interfacial tension<br>With Brij-35<br>(mN/m) | Interfacial tension<br>With DDA+Brij-35<br>(mN/m) |
|------------------|-----------------------------------------------------|-------------------------------------------|-----------------------------------------------|---------------------------------------------------|
| Dodecane         | 52.0±0.12                                           | 10.3±0.02                                 | 15.0±0.30                                     | 14.2±0.10                                         |
| Decane           | 51.6±0.10                                           | 13.1±0.01                                 | 15.8±0.08                                     | 14.1±0.04                                         |
| Dodecane+Decane  | 51.8±0.01                                           | 13.0±0.02                                 | 14.8±0.30                                     | 14.0±0.01                                         |
| Octane           | 50.8±0.08                                           | 11.5±0.02                                 | 14.5±0.25                                     | 13.8±0.10                                         |
| Cyclohexane      | 51.0±0.11                                           | 10.8±0.05                                 | 15.1±0.04                                     | 14.0±0.10                                         |
| Benzene          | 35.0±0.10                                           | 9.2±0.01                                  | 10.2±0.08                                     | 9.8±0.03                                          |
| Toluene          | 36.0±0.20                                           | 9.5±0.08                                  | 11.2 ± 0.05                                   | 10.0±0.22                                         |
| Styrene          | 37.0±0.10                                           | 8.9 ± 0.09                                | 11.4 ± 0.07                                   | 10.2±0.23                                         |
| Xylenes          | 36.4±0.10                                           | 8.5±0.11                                  | 11.2 ± 0.10                                   | 10.1±0.21                                         |
| Xylenes+Toluene  | 36.5±0.32                                           | 10.0±0.04                                 | 10.4±0.01                                     | 10.1±0.15                                         |
| Diesel           | 48.0±0.20                                           | 10.0±0.06                                 | 12.6±0.24                                     | 11.8±0.12                                         |
| Simulated Diesel | 50.2±0.02                                           | 9.8±0.05                                  | 12.2±0.07                                     | 11.2±0.06                                         |

**Measurement of Viscosity** A standard method, ASTM D445-88, was used to measure the viscosity of the oils used in this study. The dynamic viscosity of the dodecane, decane, octane, xylenes, styrene, toluene, benzene, and diesel were as follows: 1.34, 1.33, 1.46, 1.44, 1.42, 1.42, 1.41 and 1.84 mPa-s respectively. On the addition of 18 ppm of PTBS to various organic solvents, the resulting dynamic viscosities were obtained as 1.35, 1.33, 1.42 and 1.88 mPa-s respectively. From these dynamic viscosity values, it is concluded that there is no significant change in the viscosities of the liquids with the addition of hydrophobic polymers to the oil.

**Study of Spontaneous Emulsification.** The spontaneous emulsification experiment is depicted in **Figure S8**, a 250 mL conical flask was fixed over the vibration isolation table by means of a metallic stand following which a 100 mL of the salt solution (with/without surfactant) was loaded into the

conical flask. This setup was sealed with a Y – shaped glass stopper with two open ports (1.5 cm diameter), which were closed with rubber septum stoppers (1.7 cm diameter). A needle was inserted into one of the septa and a 0.2 mm (I.D.), whereas a Teflon capillary tube was inserted into the other septum stopper. The needle inserted into the first stopper acts as a vent to the atmosphere. One open end of the Teflon tubing was inserted 2 cm below the surface of water. This terminal end of this tube was connected to a polyvinyl stopper and a needle assembly, through which the liquid sample from inside the conical flask was siphoned out drop by drop and collected at a rate of  $\sim 1$  mL/min. After making sure that the Teflon tube was fully filled with the aqueous phase, and the disturbance of the surface subsided, 30 mL of oil (with/without additive) was gently poured over it. Before collecting the emulsion, some amount of the salinized water that pre-filled the tube was discarded, following which, the samples were collected at pre-set intervals.

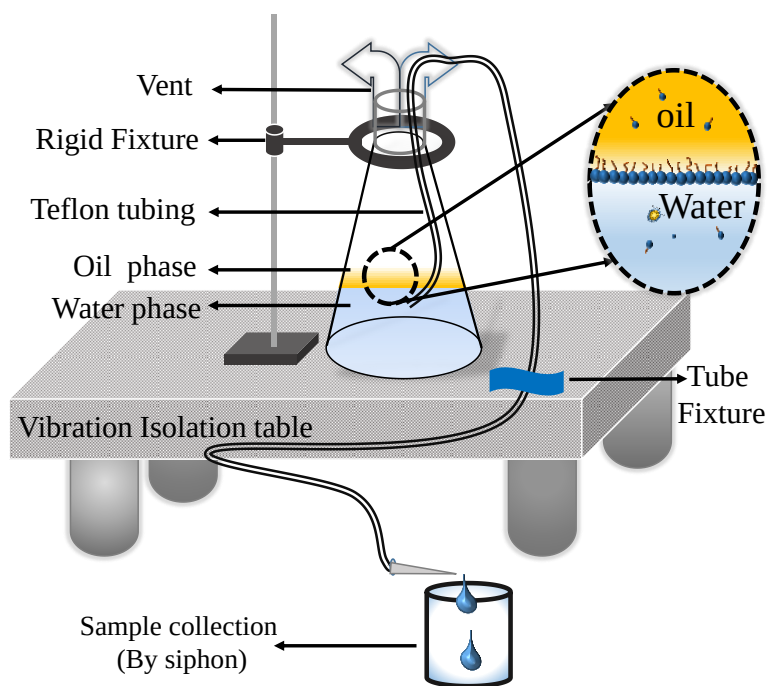
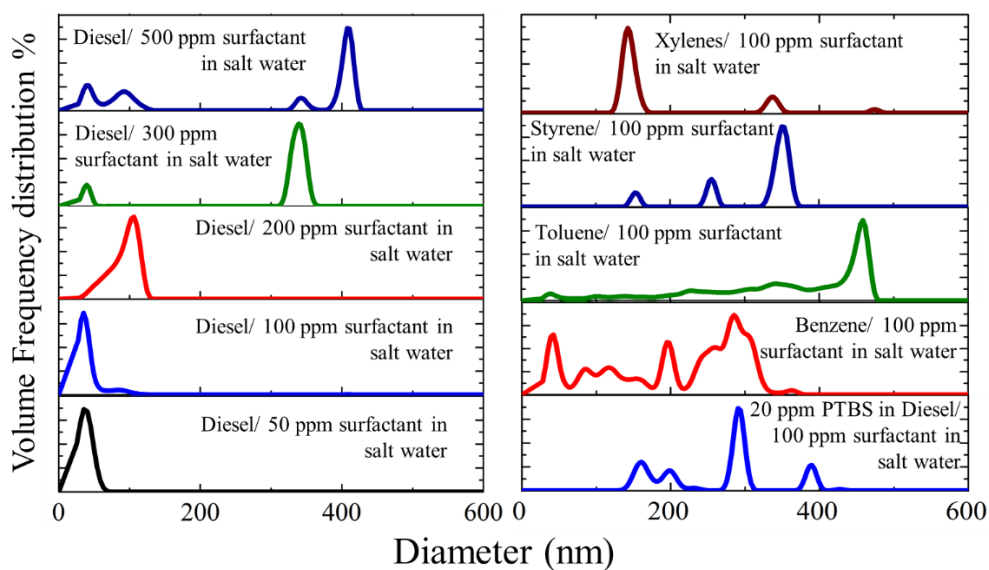


**Figure 8.** A conical flask containing the salinized water and the organic liquid was placed on a vibration isolation table to minimize the effects of ground vibration. The aqueous phase below the organic liquid was collected by a slow siphonic process in which the aqueous phase was collected

drop by drop at a rate of about 1 mL/min. Examination of this liquid using CHDF showed the presence of sub-microscopic emulsion droplets of various sizes, but all were less than 600 nm. An optical microscopic image showed the presence of such nano-droplets; however, its size could not be determined by this method as it was less than the optical resolution. After collecting the aqueous phase in a glass vial and examining it in CHDF in subsequent days showed that the droplet size distribution shifted to higher values either via Ostwald ripening and/or fusion.

**Capillary hydrodynamic fractionation** The submicroscopic emulsion droplets were analyzed using the method of capillary hydrodynamic fractionation after the emulsion was passed through a glass microfiber filter with a pore size of 1.5  $\mu\text{m}$ . 50  $\mu\text{L}$  of the filtered sample were injected through the sample port to an eluent stream followed by the equal amount of marker solution. A standard retention time of 10 min was used for analyzing all the samples reported in this study.



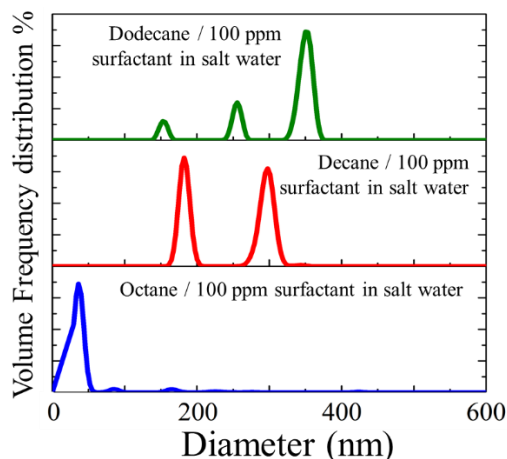


**Figure 9.** CHDF spectra of the spontaneously formed emulsion droplets in the aqueous phase (0.6 M salt solution).

**Solubility of Surfactants in different solvents.** Known quantities of the surfactants were dissolved in the solvents individually in increasing concentration, until further dissolution is thwarted. This surfactant saturated oil was sealed and shaken vigorously in an orbital shaker for 5 min and then stored in the dry air purged environment for 15h. This solvent mixture was then filtered through a 1-micron pore size, Whatman filter and then analyzed in UV-Vis spectroscopy. The calibration plot for the concentration of the surfactant as a function of absorbance value in the respective solvent are described in our previous publication<sup>45</sup>. The point of intersection of the slopes of the region where there is change in the absorbance to the saturated region gives the direct measure of the equilibrium solubility of the surfactant mixture in the corresponding solvent.

**Evidence of Water in Organic Phase.** The concentration of water in the organic solvent which is in contact with the aqueous phase was estimated by Karl Fisher water content analysis. The following protocol were used for analyzing various organic solvents: Each organic solvent (such as Decane, Dodecane, Diesel, Xylenes and Toluene) were individually purified by passing it thrice through activated alumina columns. These purified solvents were initially analyzed for estimating the

concentration of water in it by Karl Fisher analyzer (Mettler Toledo, automatic titrator, Robertlit Laboratories, USA). At this stage, the studies on equilibrium water content in each of the organic solvent which are in contact with aqueous phase were systematically conducted (as experimental system listed in Table S1) after storing it for 24 h in isolation chambers to prevent cross contamination. In-order to estimate the water concentration in the organic phase after equilibration with the aqueous solution, a thoroughly cleaned conical flask (50 mL) was initially filled with 20 mL of aqueous phase (0.6 M salt water) in the presence (50 ppm of DDA and 50 ppm of Brij-35) and absence of surfactants (with and without addition of 20 ppm of PAM), following which, 20 mL of purified organic solvent (With and Without 18 ppm of PTBS pre-dissolved in it) was gently deposited over the aqueous phase using a Teflon tube (Dia = 1.5 mm). This setup was carefully made on a vibration isolation table. At this stage, the Teflon tube which is immersed in the organic phase whose other end is suspended freely in the atmosphere (with closed valve) was carefully siphoned to collect the organic solvent at the end of 24 h. All the above collected samples were tested using a standard Karl Fisher (KF) moisture/water content analysis technique (results tabulated in Table S1).

**Table 2.** Karl-Fischer analysis of various organic liquids equilibrated against 0.6 M salt water solution in the presence and absence of surfactants pre-dissolved in the aqueous phase. In all cases surfactant is a mixture of a 50ppm amount of a non-ionic surfactant (Brij 35) and Dodecanoic acid.

| System                                               | Concentration of water (ppm) |
|------------------------------------------------------|------------------------------|
| Dodecane                                             | $< 0.01 \pm 0.001$           |
| Decane                                               | $< 0.01 \pm 0.002$           |
| Dodecane+Decane                                      | $< 0.01 \pm 0.001$           |
| Dodecane/ salt water                                 | $23 \pm 0.12$                |
| Dodecane/Surfactant in salt water                    | $28 \pm 0.22$                |
| Decane/ salt water                                   | $20 \pm 0.52$                |
| Decane/ Surfactant in salt water                     | $28 \pm 0.35$                |
| Dodecane + Decane / Salt water                       | $72 \pm 0.15$                |
| Doecane+Decane/ Surfactant in salt water             | $89 \pm 0.85$                |
| Doecane+Decane+18 ppm PTBS/salt water                | $< 0.01 \pm 0.001$           |
| Doecane+Decane+18 ppm PTBS/ Surfactant in salt water | $< 0.01 \pm 0.001$           |

|                                                        |                    |
|--------------------------------------------------------|--------------------|
| Dodecane+Decane/20 ppm PAM in salt water               | $< 0.01 \pm 0.003$ |
| Dodecane+Decane/20 ppm PAM in Surfactant in salt water | $< 0.01 \pm 0.001$ |
| Diesel                                                 | $< 0.01 \pm 0.002$ |
| Diesel+20 ppm PTBS                                     | $< 0.01 \pm 0.001$ |
| Diesel/salt water                                      | $102 \pm 2.56$     |
| Diesel/ Surfactant in salt water                       | $193 \pm 3.15$     |
| Diesel+20 ppm PTBS/salt water                          | $12 \pm 0.1$       |
| Diesel+20 ppm PTBS/ Surfactant in salt water           | $18 \pm 0.12$      |
| Diesel/20 ppm PAM in salt water                        | $25 \pm 0.07$      |
| Diesel/20 ppm PAM in Surfactant in salt water          | $30 \pm 0.22$      |
| Xylenes                                                | $< 0.01 \pm 0.001$ |
| Toluene                                                | $< 0.01 \pm 0.001$ |
| Xylenes+Toluene                                        | $< 0.01 \pm 0.002$ |
| xylenes+toluene+20ppm PTBS                             | $< 0.01 \pm 0.001$ |
| Xylenes/salt water                                     | $32 \pm 0.21$      |
| Xylenes/ Surfactant in salt water                      | $48 \pm 0.32$      |
| Toluene/salt water                                     | $15 \pm 0.24$      |
| Toluene/surf in salt water                             | $23 \pm 0.18$      |
| Xylenes+Toluene/salt water                             | $38 \pm 0.15$      |
| Xylenes+Toluene/ Surfactant in salt water              | $50 \pm 0.11$      |
| Xylenes+Toluene+20 ppm PTBS / salt water               | $< 0.01 \pm 0.001$ |
| Xylenes+Toluene+20 ppm PTBS / Surfactant in salt water | $< 0.01 \pm 0.001$ |
| Xylenes+Toluene/20 ppm PAM in salt water               | $< 0.01 \pm 0.001$ |
| Xylenes+Toluene/20 ppm PAM in Surfactant in salt water | $< 0.01 \pm 0.001$ |

**Migration of water into the oil phase studied using nectar drop** We examined the kinetics of the growth and the decay of the size of a nectar drop by placing a small (0.52  $\mu$ L) droplet on the tip of a glass bead that was formed by melting a fine glass capillary tube and silanizing it with perfluorooctyl trichlorosilane. The small droplet of the sugar solution was deposited in the glass bead by bringing it in contact with a thin film (15  $\mu$ m thickness) of sugar solution coated on a glass slide, followed by quick removal. This glass bead with the syrup drop was then dried in hot air and placed inside a plexiglass chamber saturated with water vapor, the growth of which was observed under a microscope. The concentrated sugar solution was prepared by replicating as closely as possible the chemical composition of Agave nectar by adding 54 % (w/w) of D-Fructose (Fisher

Science Education) and 18 % (w/w) of D-Glucose (Fisher Chemicals) in 28 % (w/w) of deionized (DI, Thermo Scientific Barnstead E-pure unit) water. The viscosity of this solution at room temperature (21 °C), as measured using an Ostwald viscometer, was found to be 13 mPa-s. The mixture was heated to 65 °C with constant stirring until a homogeneous solution was obtained. This drop hanging from the support was placed facing vertically down at a distance of ~1.2 mm from the interfacial region in the oil phase. At constant temperature and pressure, we can observe that the droplet size of the sugar drop grew larger in size based on the system of consideration.

**Molecular dynamics simulation.** Molecular dynamics simulations were performed using Large Atomic Molecular Massively Parallel Simulator (LAMMPS, ion source version 16Mar2018). Since this is an open-access software, we do not see the need to repeat the related details that are already available publicly<sup>81-88</sup>. Nevertheless, we found it necessary to provide a few details that are relevant to this work, where dodecane was used as the organic phase, with dodecanoic acid (100 ppm), Brij-35 (100 ppm), and their mixture (50 ppm:50 ppm) as surfactants, and 0.6 M sodium chloride in water as the aqueous phase. The Optimized Potentials for Liquid Simulations, All Atom (OPLS-AA) forcefield parameters were used. As for the non-bonded and bonded potential parameters of the various organic components, OPLS-AA forcefields were used. For DDA (dodecanoic acid) and Brij 35, the force field parameters were adapted from the publication of Shirley W. I. Siu et al<sup>83</sup>. The force fields and the partial charges of surfactant molecules as were obtained via quantum mechanical calculations were adapted from literature<sup>88</sup>. Finally, for water, a SPC/F<sub>w</sub> model, which is a 3 site simple point-charge water model with flexible O-H bonds and H-O-H angle was adapted from literature<sup>85-88</sup>. Here, the energy of the initial structure of each component, as mentioned above, was first minimized using the steepest descent algorithm, followed by 1 ns pre-equilibration under the condition of constant pressure and temperature (NPT).

Subsequent simulations were performed at a temperature of 298 K that was coupled to a Nose–Hoover algorithm using a 3d periodic boundary conditions (PBC). The short-range Coulomb interactions were calculated up to a distance of 1.2 nm with the long-range interactions calculated using the particle mesh Ewald (PME) reciprocal sum method. The short-range van der Waals (vdW) interactions were computed using the Lennard-Jones 12–6 potential that were calculated up to a distance of 1.2 nm, which accounts for the long-range dispersion correction for energy and pressure. All chemical covalent bonds were constrained by means of the Linear constraint solver (LINCS) algorithm.

The simulations (DPD-MD) combined dissipative particle dynamics (DPD) and molecular dynamics (MD), which were carried out for a duration of 300 ns using a simulation box with the lateral dimensions fixed at 10 nm x 10 nm laterally, while the vertical dimension changed according the stresses developed in the system, in accordance with the interfacial tensions  $\gamma$ . The interfacial tensions  $\gamma = \frac{1}{2}L_z \left[ \langle p_{zz} \rangle - \frac{1}{2}(\langle p_{xx} \rangle + \langle p_{yy} \rangle) \right]$  was calculated using MD-DPD M106 source code (Version 2017.V1.2.3), where  $L_z$  is the characteristic length of the interface in the z-axis and  $\langle p_{xx} \rangle$ ,  $\langle p_{yy} \rangle$ , and  $\langle p_{zz} \rangle$  are the time averaged diagonal components of the pressure tensor. These calculations yielded the surface tension of water as 72 mN/m, and the interfacial tensions of water against Dodecane and Decane as 52 mN/m, and 50.4 mN/m, respectively. The interfacial tensions of various interfaces are summarized in Table S2.

Returning to the details in performing the simulations, let us first emphasize that the radial distribution function  $g(r)$  was calculated for both the equilibrium and nonequilibrium systems using the program RDF28 for each atom. This method characterizes the hydration behavior of each species and identifies the total number of H-bonds and the hydration number of any

component<sup>79,85-86</sup>. In the radial distribution profiles, the characteristic peaks corresponding to the HB distance signifies whether the hydrogen bond forms between molecules of interest, namely dodecanoic acids, water and poly(oxyethylene) ether. The coordination numbers (CN) were estimated for each species by integrating the radial density function, up to a value that corresponds to its first minimum.

**Aggregation of Surfactant in various Solvents.** We extended the standard DPD simulations for estimating the repulsion parameter for different solvent systems in order to identify the interaction parameter for the surfactants in both organic and aqueous phases with oil and water being the respective implicit solvents. Figure 3 (D-F) shows the results of such a simulation where the self-assembling behaviors of DDA, Brij-35 and the mixture were studied with dodecane as implicit solvent. Similar studies with water as the implicit solvent are presented in Figure 7.

Let us now explain how we carried out the DPD-MD simulations. To begin with, a coarse grained DPD simulation was carried out for the surfactant molecules in the organic and water phases individually<sup>85,87,88</sup>. In order to carry out these simulations, all the particles were placed at random positions within the rectangular box of 100x100x100 nm<sup>3</sup> and using a grant size as 1 nm<sup>3</sup>. These simulations allowed us to estimate the repulsion parameters (Table 4) between components.

These new repulsion parameters were integrated into the MD simulation using LAMMPS, where we could obtain the atomistic radial distribution of the individual molecule. Figure 8 (C) illustrates how these new parameters integrated with Non-equilibrium DPD-MD simulation (as discussed below) allowed the estimation of cross-sectional anatomy of various structures: vesicles, inverted emulsion and emulsion, which were performed in the NVE ensemble within a periodic boundary condition.

**Table 3.** Bead Notation and Repulsion Strength Parameters Used in the MD-DPD Simulation

| $a_{ij} = \frac{k_B T}{r_c}$ (eV/Å) |           |     |     |     |    |     |     |     |     |     |
|-------------------------------------|-----------|-----|-----|-----|----|-----|-----|-----|-----|-----|
| molecular prototype                 | bead name | P1  | P2  | P3  | D1 | D2  | B1  | B2  | E1  | W1  |
| PTBS (aliphatic tail)               | P1        | 30  | 45  | 27  | 40 | 66  | 149 | 122 | 104 | 93  |
| PTBS (aromatic)                     | P2        | 68  | 52  | 70  | 24 | 108 | 74  | 25  | 35  | 26  |
| PTBS (aliphatic head group)         | P3        | 27  | 70  | 25  | 51 | 70  | 65  | 115 | 32  | 60  |
| Carboxylic acid group               | D1        | 35  | 24  | 39  | 54 | 89  | 84  | 47  | 45  | 145 |
| Aliphatic tail (DDA)                | D2        | 80  | 107 | 50  | 58 | 15  | 40  | 167 | 154 | 125 |
| Ethylene oxide group (Brij-35)      | B1        | 187 | 45  | 104 | 72 | 48  | 63  | 45  | 70  | 57  |
| Aliphatic tail (Brij-35)            | B2        | 145 | 38  | 115 | 47 | 125 | 82  | 54  | 43  | 45  |
| Dodecane                            | E1        | 109 | 158 | 89  | 21 | 154 | 65  | 12  | 25  | 30  |
| Water                               | W1        | 50  | 15  | 89  | 78 | 135 | 43  | 45  | 30  | 25  |

Having discussed about the specifics of the DPD-MD simulation above, we now move to the DPD-MD simulations for the non-equilibrium emulsion formation kinetic studies. These non-equilibrium simulations were performed with periodic boundary conditions under a non-isothermal ensemble. The reaction field corrections were applied for compensating the mean effect of electrostatic interactions beyond 1.2 nm distance, using a dielectric permittivity of 60 as appropriate for the SPC water model. All the systems were ensured to have an effective solvent density by controlling the volume ratios of the solute to the solvent. The simulations were carried out for a duration of 300 ns (as mentioned above) with the trajectory capture of 20 ns for further analysis.

In the Non-equilibrium DPD-MD simulation, we obtained the trajectory of a system as a function of time in an NVE ensemble. The system traverses through multiple microstates before it finally reaches an equilibrium. While an equilibrium DPD-MD simulation was performed with a widely used Nose-Hover thermostat, this does not have the capability to ascertain the path of the system that reaches the final state when the system is coupled with the hydrodynamic forces. We used DPD-MD simulations with a non-isothermal algorithm to understand the mechanism of emulsification. This NVE ensemble fails to converge within the scope of the first-fluctuation

dissipation theorem. Hence these simulations were performed with a modified DPD algorithm (using the Second fluctuation-dissipation theorem allowing the kinetic temperature to evolve). A velocity verlet method is also adopted in these simulations in order to prevent the self-penetration of the molecules within each other.

**Ionization strength – information from MD simulations.** Poisson-Boltzmann (PB) method was used in order to ensure that the protonation and de-protonation strengths have been estimated correctly in the above NEMD simulations. This method combined with DPD-MD simulations were used for analyzing the anatomy of the components of emulsification. In the estimation of ionization strength, the artifacts due to multiple bond formation in a head - head interaction were eliminated by constraining the bond angle in the system by standard method using LINCS algorithm<sup>4-5</sup>. In the aggregation of surfactants in various solvents we found that the DDA forms lateral bonds with the neighboring DDA molecules. It also forms head on bonding with Brij-35 molecule and water molecule.

**Table 4.** Interfacial tension and Molecular Surface area estimate using MD-DPD simulation with a Grain size of 0.1 nm<sup>3</sup>.

| <i>Component</i>      | <i>Interfacial Tension, mN/m</i> | <i>Total Area A (nm<sup>2</sup>)</i> | $N_{DDA}$ | $N_{Brij}$ | $\frac{N_{DDA}}{N_{Brij}}$ | $\frac{A}{N_{DDA}+N_{Brij}}$<br><i>nm<sup>2</sup></i> |
|-----------------------|----------------------------------|--------------------------------------|-----------|------------|----------------------------|-------------------------------------------------------|
| Flat interface        | 7.6                              | 10,000                               | 6745      | 6012       | 1.12                       | 0.78                                                  |
| Oil in Water Emulsion | 1.4                              | 493                                  | 950       | 650        | 1.46                       | 0.31                                                  |
| Water in Oil Emulsion | 2.1                              | 1319                                 | 1901      | 1450       | 1.31                       | 0.39                                                  |
| Vesicle               | 2.3                              | 1256                                 | 1865      | 1542       | 1.21                       | 0.37                                                  |

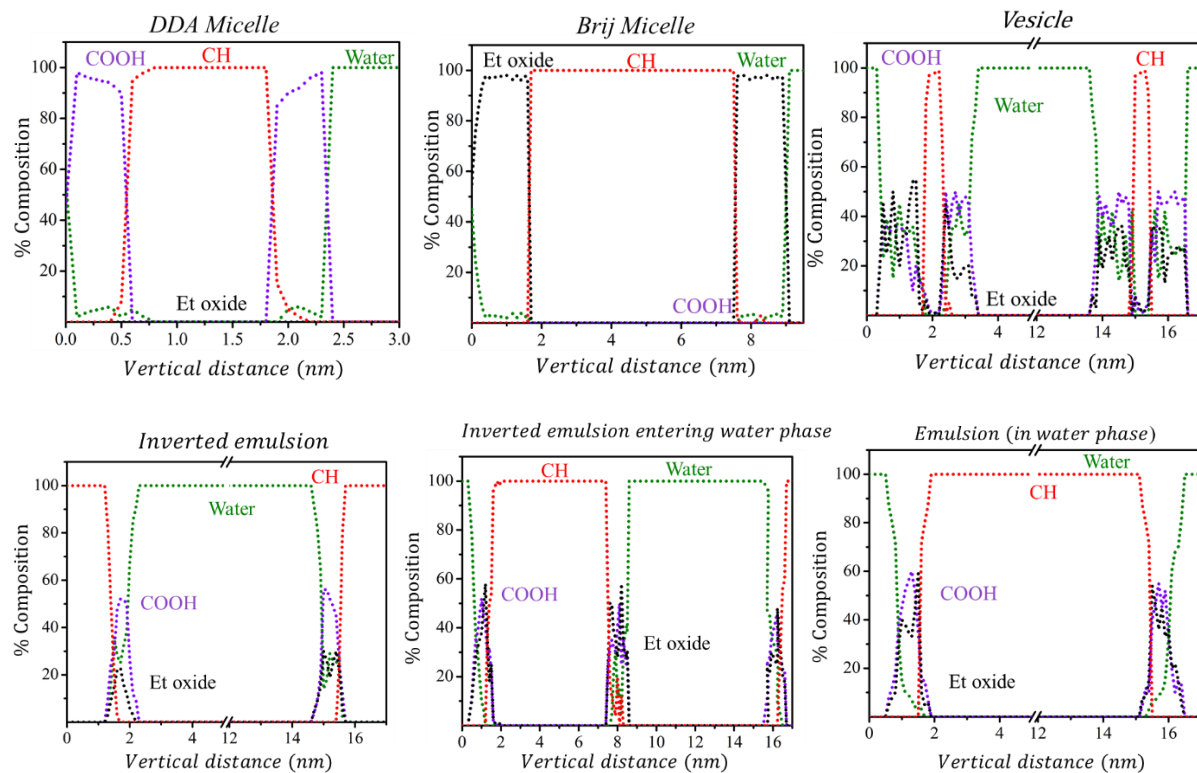


**Figure 10.** The anatomy of the vesicle like structures can be visualized when the concentrations of water, hydrocarbon, carboxylic acid and water are plotted across it. Along with these structures, the composition profile of these groups is shown for a micelle, vesicle, water-in-oil and oil-water emulsions.

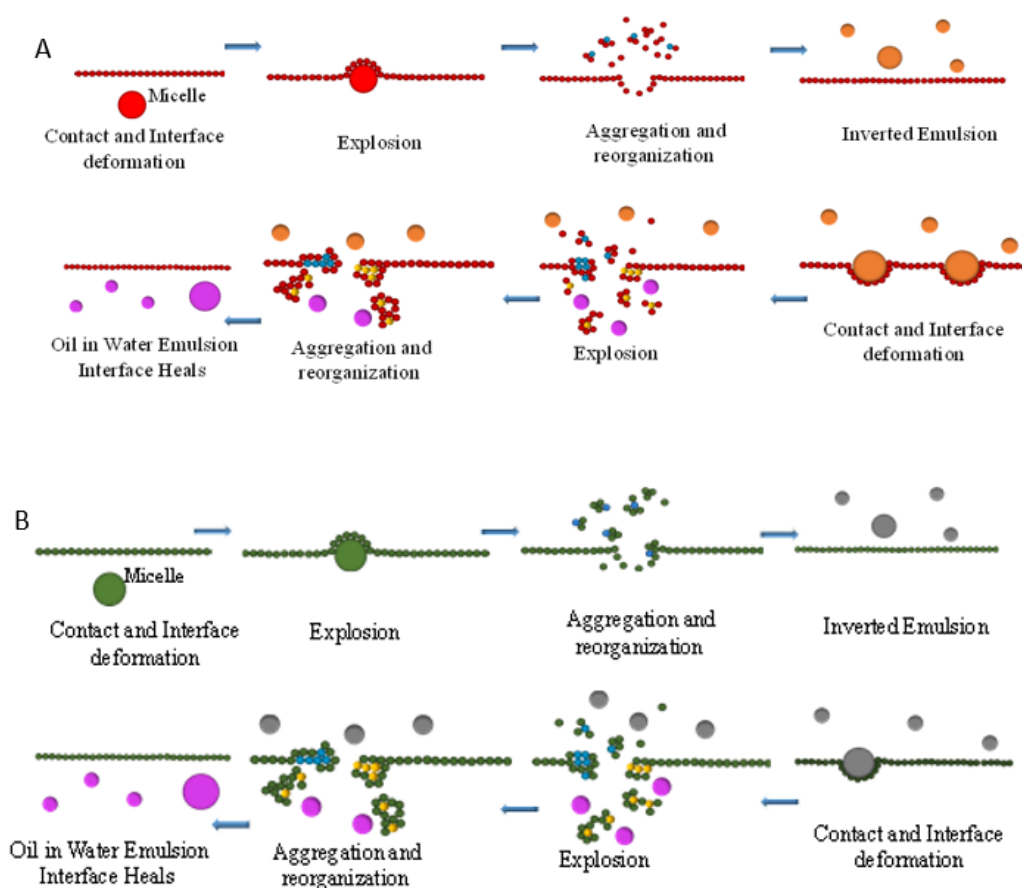


**Figure 11. (A and B)** Formation of water-in oil and oil-in-water emulsions. When the (A) dodecanoic acid (A) and Brij-35 (B) form micelles in the aqueous phase, it eventually comes into contact with the interface and explodes. The fragments resulting from this explosion cluster together and forms the inverted (i.e. water-in-oil) emulsion. When such an inverted emulsion comes into contact with the interface, another explosion occurs, following which the fragments cluster together and transform into oil-in-water emulsions. (Note: the color coding for different components are as follows, Red: DDA, Green: Brij-35, Blue: water, Yellow: Oil, Grey and Orange: inverted emulsion and Pink: Emulsion)

**Table 5a.** Diffusivity of emulsion as obtained from Figure 10 is plotted against the value ( $D_e$ ) obtained from the Stokes-Einstein relation:  $D_e = k_B T / (6\pi\eta r)$ , where  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $\eta$  is the viscosity of the aqueous phase.  $r$  is the average radius of the droplet, which was estimated using CHDF (capillary hydrodynamic flow chromatography, Figure S10).

| Organic phase | $r$ (m)                          | $D$ , $m^2/s$                   | $D_e$ , $m^2/s$        | $D/De$             |
|---------------|----------------------------------|---------------------------------|------------------------|--------------------|
| Dodecane      | $1.10(\pm 0.002) \times 10^{-7}$ | $2.2(\pm 0.87) \times 10^{-10}$ | $1.81 \times 10^{-12}$ | $1.22 \times 10^2$ |
| Decane        | $1.00(\pm 0.05) \times 10^{-7}$  | $6.2(\pm 0.25) \times 10^{-10}$ | $1.99 \times 10^{-12}$ | $3.12 \times 10^2$ |
| Octane        | $2.50(\pm 0.12) \times 10^{-8}$  | $4.6(\pm 0.12) \times 10^{-10}$ | $7.95 \times 10^{-12}$ | $5.79 \times 10^1$ |
| Toluene       | $1.30(\pm 0.09) \times 10^{-7}$  | $1.6(\pm 0.01) \times 10^{-10}$ | $1.53 \times 10^{-12}$ | $1.05 \times 10^2$ |
| Styrene       | $1.50(\pm 0.24) \times 10^{-7}$  | $3.8(\pm 0.02) \times 10^{-10}$ | $1.32 \times 10^{-12}$ | $2.87 \times 10^2$ |
| Xylenes       | $5.00(\pm 0.14) \times 10^{-8}$  | $1.0(\pm 0.08) \times 10^{-11}$ | $3.97 \times 10^{-12}$ | $2.52 \times 10^0$ |

**Table 5b.** Diffusivity of emulsion as obtained from figure 10 is plotted against the value ( $D_e$ ) obtained from the Stokes-Einstein relation:  $D_e = k_B T / (6\pi\eta r)$ , where  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $\eta$  is the viscosity of the aqueous phase.  $r$  is the average radius of the droplet, which was estimated using CHDF (capillary hydrodynamic flow chromatography, figure S9. The ratio

| System                                   | $r$ (m)                          | $D$ , $m^2/s$                    | $D_e$ , $m^2/s$        | $D/De$             |
|------------------------------------------|----------------------------------|----------------------------------|------------------------|--------------------|
| Diesel w/ 500 ppm of S (●)               | $1.17(\pm 0.102) \times 10^{-7}$ | $1.67(\pm 0.25) \times 10^{-4}$  | $1.70 \times 10^{-12}$ | $9.84 \times 10^7$ |
| Diesel w/ 300 ppm of S (●)               | $4.14(\pm 0.215) \times 10^{-8}$ | $1.30(\pm 0.001) \times 10^{-4}$ | $4.80 \times 10^{-12}$ | $2.71 \times 10^7$ |
| Diesel w/ 200 ppm of S (●)               | $2.67(\pm 0.012) \times 10^{-7}$ | $1.10(\pm 0.26) \times 10^{-4}$  | $7.45 \times 10^{-13}$ | $1.48 \times 10^8$ |
| Diesel w/ 100 ppm of S (●)               | $1.11(\pm 0.202) \times 10^{-7}$ | $9.15(\pm 0.36) \times 10^{-5}$  | $1.79 \times 10^{-12}$ | $5.13 \times 10^7$ |
| Diesel w/ 50 ppm of S (●)                | $5.40(\pm 0.004) \times 10^{-7}$ | $1.90(\pm 0.15) \times 10^{-5}$  | $3.68 \times 10^{-13}$ | $5.17 \times 10^7$ |
| Diesel + 20 ppm PTBS w/ 100ppm of S (●)  | $3.26(\pm 0.001) \times 10^{-8}$ | $5.00(\pm 0.12) \times 10^{-9}$  | $6.10 \times 10^{-12}$ | $8.20 \times 10^2$ |
| Diesel + 40 ppm PTBS w/ 100 ppm of S (●) | $1.16(\pm 0.025) \times 10^{-7}$ | $1.40(\pm 0.01) \times 10^{-9}$  | $1.71 \times 10^{-12}$ | $8.20 \times 10^2$ |
| Diesel + 20 ppm PTBS w/ 500ppm of S (●)  | $1.00(\pm 0.010) \times 10^{-8}$ | $1.63(\pm 0.01) \times 10^{-4}$  | $1.99 \times 10^{-11}$ | $8.20 \times 10^6$ |
| Diesel + 40 ppm PTBS w/ 500ppm of S (●)  | $2.42(\pm 0.122) \times 10^{-9}$ | $1.55(\pm 0.01) \times 10^{-4}$  | $8.22 \times 10^{-11}$ | $1.89 \times 10^6$ |
| Diesel + 80 ppm PTBS w/ 500ppm of S (●)  | $1.16(\pm 0.090) \times 10^{-8}$ | $1.50(\pm 0.01) \times 10^{-4}$  | $1.71 \times 10^{-11}$ | $8.78 \times 10^6$ |
| Diesel + 100 ppm PTBS w/ 500ppm of S (●) | $8.00(\pm 0.325) \times 10^{-9}$ | $1.45(\pm 0.01) \times 10^{-4}$  | $2.48 \times 10^{-11}$ | $5.84 \times 10^6$ |
| Benzene w/ 500 ppm of S (■)              | $1.18(\pm 0.122) \times 10^{-8}$ | $1.68(\pm 0.01) \times 10^{-4}$  | $1.68 \times 10^{-11}$ | $1.00 \times 10^7$ |
| Toluene w/ 500 ppm of S (■)              | $3.49(\pm 0.101) \times 10^{-7}$ | $8.75(\pm 0.01) \times 10^{-5}$  | $5.69 \times 10^{-13}$ | $1.24 \times 10^8$ |
| Styrene w/ 500 ppm of S (■)              | $1.35(\pm 0.08) \times 10^{-7}$  | $7.50(\pm 0.16) \times 10^{-5}$  | $1.48 \times 10^{-12}$ | $5.08 \times 10^7$ |
| Xylenes w/ 500 ppm of S (■)              | $9.13(\pm 0.133) \times 10^{-8}$ | $5.00(\pm 0.25) \times 10^{-5}$  | $2.18 \times 10^{-12}$ | $2.30 \times 10^7$ |
| Octane w/ 500 ppm of S (■)               | $1.11(\pm 0.24) \times 10^{-8}$  | $8.50(\pm 0.46) \times 10^{-5}$  | $1.79 \times 10^{-11}$ | $4.74 \times 10^6$ |
| Decane w/ 500ppm of S (■)                | $9.29(\pm 0.43) \times 10^{-8}$  | $4.00(\pm 0.45) \times 10^{-5}$  | $2.14 \times 10^{-12}$ | $1.87 \times 10^7$ |
| Dodecane w/ 500ppm of S (■)              | $3.00(\pm 0.05) \times 10^{-7}$  | $2.00(\pm 0.37) \times 10^{-5}$  | $6.62 \times 10^{-13}$ | $3.02 \times 10^7$ |
| Benzene w/ 100 ppm of S (▲)              | $2.56(\pm 0.53) \times 10^{-8}$  | $1.50(\pm 0.11) \times 10^{-4}$  | $7.75 \times 10^{-12}$ | $1.94 \times 10^7$ |
| Cyclohexane w/ 100 ppm of S (◆)          | $2.80(\pm 0.126) \times 10^{-7}$ | $2.20(\pm 0.87) \times 10^{-6}$  | $7.10 \times 10^{-13}$ | $3.10 \times 10^6$ |

**Table 5b (continued)**

| System                                                      | $r\ (m)$                         | $D, m^2/s$                      | $D_e, m^2/s$           | $D/De$             |
|-------------------------------------------------------------|----------------------------------|---------------------------------|------------------------|--------------------|
| Cyclohexane+Dodecane w/ 100 ppm of S (◇)                    | $1.50(\pm 0.002) \times 10^{-7}$ | $2.00(\pm 0.13) \times 10^{-6}$ | $1.32 \times 10^{-12}$ | $1.51 \times 10^6$ |
| Diesel w/ 20 ppm of PAM with 100 ppm of S (▲)               | $2.62(\pm 0.04) \times 10^{-8}$  | $2.00(\pm 0.11) \times 10^{-8}$ | $7.57 \times 10^{-12}$ | $2.64 \times 10^3$ |
| Diesel w/ 40 ppm of PAM with 100 ppm of S (▲)               | $8.80(\pm 0.46) \times 10^{-8}$  | $2.00(\pm 0.10) \times 10^{-9}$ | $2.26 \times 10^{-12}$ | $8.86 \times 10^2$ |
| Benzene+Toluene w/ 100 ppm of S (□)                         | $1.20(\pm 0.16) \times 10^{-7}$  | $3.50(\pm 0.11) \times 10^{-6}$ | $1.66 \times 10^{-12}$ | $2.11 \times 10^6$ |
| Benzene+Styrene w/ 100 ppm of S (□)                         | $2.90(\pm 1.34) \times 10^{-7}$  | $2.50(\pm 0.25) \times 10^{-6}$ | $6.85 \times 10^{-13}$ | $3.65 \times 10^6$ |
| Benzene+Xylenes w/ 100 ppm of S (□)                         | $1.10(\pm 0.21) \times 10^{-7}$  | $1.20(\pm 0.59) \times 10^{-6}$ | $1.81 \times 10^{-12}$ | $6.64 \times 10^5$ |
| Simulated mixture w/ 100 ppm of S (○)                       | $2.25(\pm 0.536) \times 10^{-7}$ | $2.20(\pm 0.46) \times 10^{-6}$ | $8.83 \times 10^{-13}$ | $2.49 \times 10^6$ |
| Equal volume mixture of all solvents w/ 100 ppm of S (○)    | $2.70(\pm 0.26) \times 10^{-7}$  | $5.60(\pm 0.13) \times 10^{-6}$ | $7.36 \times 10^{-13}$ | $7.61 \times 10^6$ |
| Benzene+Ethanol w/ 100 ppm of S (★)                         | $4.00(\pm 0.33) \times 10^{-7}$  | $4.00(\pm 0.06) \times 10^{-5}$ | $4.97 \times 10^{-13}$ | $8.05 \times 10^7$ |
| Toluene+Ethanol w/ 100 ppm of S (★)                         | $6.54(\pm 0.01) \times 10^{-9}$  | $8.00(\pm 0.01) \times 10^{-4}$ | $3.04 \times 10^{-11}$ | $2.63 \times 10^7$ |
| Styrene+Ethanol w/ 100 ppm of S (★)                         | $1.00(\pm 0.08) \times 10^{-8}$  | $5.00(\pm 0.13) \times 10^{-4}$ | $1.99 \times 10^{-11}$ | $2.52 \times 10^7$ |
| Xylenes+Ethanol w/ 100 ppm of S (★)                         | $3.03(\pm 0.015) \times 10^{-9}$ | $4.65(\pm 0.09) \times 10^{-4}$ | $6.55 \times 10^{-11}$ | $7.09 \times 10^6$ |
| Octane+Ethanol w/ 100 ppm of S (★)                          | $3.80(\pm 0.01) \times 10^{-9}$  | $3.00(\pm 0.37) \times 10^{-4}$ | $5.23 \times 10^{-11}$ | $5.74 \times 10^6$ |
| Decane+Ethanol w/ 100 ppm of S (★)                          | $9.56(\pm 0.001) \times 10^{-9}$ | $4.52(\pm 0.23) \times 10^{-4}$ | $2.08 \times 10^{-11}$ | $2.17 \times 10^7$ |
| Dodecane+Ethanol w/ 100 ppm of S (★)                        | $1.16(\pm 0.002) \times 10^{-8}$ | $5.16(\pm 0.01) \times 10^{-4}$ | $1.71 \times 10^{-11}$ | $3.02 \times 10^7$ |
| Cyclohexane+Dodecane w/ 20 ppm of PAM with 100 ppm of S (▲) | $4.89(\pm 0.02) \times 10^{-8}$  | $1.50(\pm 0.08) \times 10^{-8}$ | $4.06 \times 10^{-12}$ | $3.69 \times 10^3$ |
| Cyclohexane+Dodecane /40 ppm of PAM with 100 ppm of S (▲)   | $2.80(\pm 0.54) \times 10^{-7}$  | $1.50(\pm 0.01) \times 10^{-9}$ | $7.10 \times 10^{-13}$ | $2.11 \times 10^3$ |
| Cyclohexane+Dodecane+20 ppm PTBS w/ 100 ppm of S (▲)        | $4.00(\pm 0.71) \times 10^{-7}$  | $2.50(\pm 0.68) \times 10^{-8}$ | $4.97 \times 10^{-13}$ | $5.03 \times 10^4$ |
| Cyclohexane+Dodecane+40 PPM PTBS w/100 ppm of S (▲)         | $3.90(\pm 437) \times 10^{-7}$   | $5.00(\pm 0.13) \times 10^{-9}$ | $5.10 \times 10^{-13}$ | $9.81 \times 10^3$ |
| Dodecane+Decane w/ 100 ppm of S (▲)                         | $1.40(\pm 0.002) \times 10^{-7}$ | $6.61(\pm 0.87) \times 10^{-5}$ | $1.42 \times 10^{-12}$ | $4.66 \times 10^7$ |
| Xylenes+Toluene w/ 100 ppm of S (▲)                         | $1.50(\pm 0.047) \times 10^{-7}$ | $1.21(\pm 0.89) \times 10^{-5}$ | $1.32 \times 10^{-12}$ | $9.13 \times 10^6$ |