Quantifying the Influence of Salinity on Spontaneous Emulsification of Hydrocarbons

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ABSTRACT

This study has investigated the process of spontaneous emulsification of oil in water using the hydrophobic force of a non-ionic surfactant (Triton X-114) and inorganic salt additive (NaCl). The cloud point of surfactant solutions with different salt concentrations was examined and show a gradual decrease from 27 ^{o}C to 18.5 ^{o}C when increasing the salinity from 0 to 5 M. The surface excess concentration of oil droplet has been enlarged spontaneously in the system due to the adsorption of Triton X-114 into the oil-water interface leading to the decrease in surface tension and the spontaneous formation of oil droplets in water. Increasing the concentration of salt additive caused an increment in ions' penetration into the hydrophilic layer of surfactants, resulting in the formation of smaller droplets. Increasing the chain-length of the oil from C7 (n-heptane) to C16 (n-hexadecane) produced a decrease of 58.6 % in droplet diameter. According, a newly-proposed model was developed and fitted against experimental data to obtain the best-fitted parameters of maximum droplet size (D_0) and ion adsorbent constant (K_{ion}). The data and modelling results verify the influence of the interfacial layer on the emulsions' size and stability.

Keywords: spontaneous emulsification, Triton X-114, NaCl

INTRODUCTION

Emulsions are mixtures of two immiscible liquids such as water and oil in the form of small droplets. In the petroleum industry, both oil-in-water emulsions, where the oil is the dispersed phase, and water-in-oil emulsions, where the oil is the external phase can be found [1–3]. The formation and separation of oil-in-water emulsions, nano-sized emulsions of hydrocarbon particularly have been investigated due to growing environmental concerns as well as its critical applications in oil production and water treatment [4–6]. For instance, it has been widely reported that oil spills and the resulted oil-in-water emulsions have posed detrimental effects on aquatic ecology, water management and coastal marsh production [7–9]. Although a wide range of cleaning techniques, such as gravity separation, skimming and dissolved air flotation has been introduced, these approaches are proved ineffective for separating nano-sized emulsions [5,10,11]. Hence, understanding the mechanism of stabilizing emulsions is critically important in both scientific and industrial aspects.

In addition to mechanical pathways, the droplets of the dispersed phase can be formed spontaneously by contacting two non-equilibrium immiscible liquids placed in a closed system without external energy [12–14]. The earliest spontaneous emulsification was reported by Gad [15,16], which is attributed to the interaction between sodium hydroxide in water and a carboxylic acid in the oil. Various possible mechanisms have been suggested to describe the phenomena of spontaneous emulsification based on diffusion and stranding, and interfacial turbulence. Alternatively, water-alcohol-oil emulsions are formed via the "diffusion and stranding" mechanism [17]. The theoretical treatment was further extended by Ruschak and Miller [18] and Granek et al. [19]. It has been proposed that spontaneous emulsification can be formed by the interfacial turbulence. A mathematical model and established criteria were introduced by Scriven and Sternling [20] to predict interfacial turbulence occurrence based on the Marangoni effect. This mechanism then has been hypothesized as a possible mechanism for spontaneous emulsification by many other researchers [21,22]. It has been showed that spontaneous emulsification requires the formation of the bilayer phase [23]. Consequently, the size of the resulting emulsion is controlled by the hydrophilic-lipophilic balance (HLB) of the surfactant [24].

While the HLB of the surfactants can be varied by changing the chemical structure, such changes are too dramatic for studying the emulsification-structure correlation. On the other hand, varying salinity can offer a gradual change in the interfacial properties of the surfactant layer. For example, emulsions stabilized by different surfactant types can be affected by salting in and salting out phenomenon in several industrial processes [25]. A number of researchers have reported emulsion behavior when changing its salinity to match manufacturing requirements [25–27]. These studies show that the rate of oil exchange is decreased by increasing the salt concentration of the mixture. This observation indicates the dependence of droplet size on the salinity of the aqueous phase.

Other studies [28–30] showed that the interior structure of micelles as well as nano-scale oil droplets is significantly dependent on the surfactant structure and the dispersed oil phase as the chain length of these hydrophobic molecules would alter the average number of hydrophobic hydration shell dangling OH groups, leading to the alteration in micelles' or droplets' composition and size [31]. It has been well-accepted that the H-bonds structure of the oil/brine interface would be perturbed significantly by the presence of ions within the interface [32].

In spite of numerous mechanisms as well as research methods proposed in the literature, a rigorous investigation on parameters related to emulsions' formation is not available. In particular, the influences of the salinity and the structure of hydrogen bonds in the interface, which play important roles in dealing with current environmental issues [33], are not understood.

This study investigates the effect of oil molecule structure and salinity on the droplet size of spontaneous emulsions. Two different chain-length alkanes (n-heptane ad n-hexadecane) were used for the oil phase, while brine solutions with various NaCl concentrations were used for the aqueous phase. A newly-proposed theoretical model was developed and fitted against obtained experimental data to reveal the effects of the oil molecular structure and the salinity of aqueous phase on the size of spontaneous emulsions.

THEORETICAL MODEL

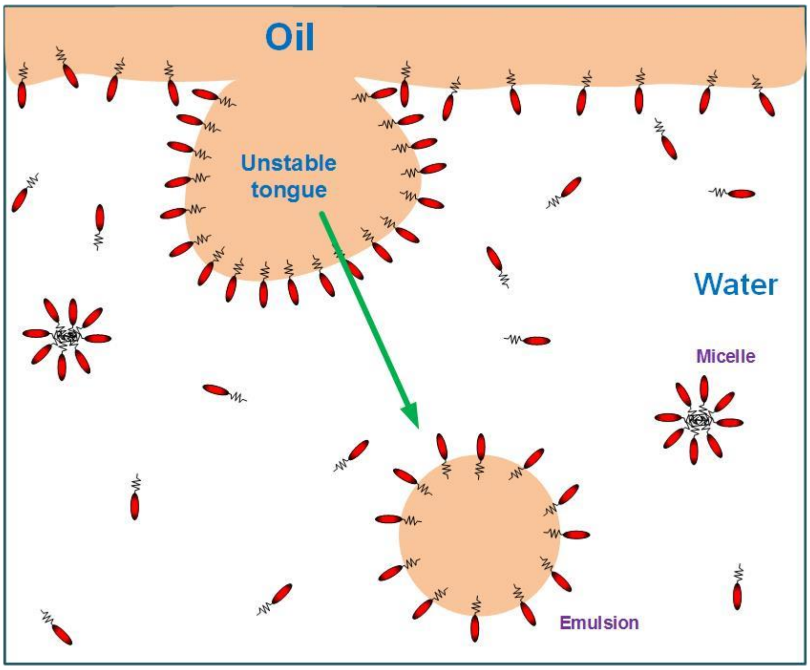

Fig. 1. Spontaneous emulsification.

Previous experimental observation has verified that the spontaneous emulsification undertook several steps [23], as demonstrated in Fig.1. First, the bilayer at the interface was swollen to form tongue-like bodies. The breaking of the oil bodies is then governed by the thinning of the necking region. It should be noted that the optical observation was practical for octane/C5E8 surfactants, which produced larger than 100-micron droplet. For other hydrocarbons, the droplets are too small for optical validation. From the mechanism, the size of the resulting droplet should be determined by the overall deformation time, which depends on the tensile strength of the surfactant layer, and the mass transfer of the hydrocarbons from the bulk to the detached body. Consequently, it can be expected that a longer mass transfer produces larger droplets.

In the literature, the interfacial deformation is often characterized via either viscoelasticity [34] and interfacial tension [35]. For the spontaneous emulsification, the interfacial deformation strength is a function of both properties and not fully described [36]. On the other hand, it is reasonable to assume that the strength is proportional to the number of H-bonds between the surfactant molecules within the adsorption layer, n [37]. A lower H-bonds number results in a weaker layer, and thus faster deformation (that is shorter breaking-up time) and a smaller size. Quantitatively, the droplet size (D_e) is correlated to the H-bonds density of the surfactant layer (n). Since a mathematical formulation is not available, a linear correlation is assumed between D_e and n. The presence of salt will affect the H-bonds [38] and the droplet size as a consequence:

$$D_e = D_\mathrm{o} \; \frac{n}{n_0} \qquad [1]$$

Where n_0 is H-bonds density (mol/m^2) and D_o is the droplet size in the absence of salt, respectively. The relationship between n and n_0 is defined by the number of adsorbed ions within the surfactant layer [32]:

$$n = n_0 - r_{ion}\, \Gamma_{ion} \qquad [2]$$

where Γ_{ion} and r_{ion} are the ionic adsorption (mol/m^2) and the number of disrupted H-bonds per ion respectively.

According to Langmuir isotherm, the ions are adsorbed into the interface depending on its concentration in the bulk and an adsorption factor, that is considered in this study the main parameter effecting oil droplet sizes. Consequently, the ionic adsorption on surfactant layer is given by:

$$\frac{\Gamma_{ion}}{\Gamma_{m,ion}} = \frac{K_{ion} \cdot C_{ion}}{1+K_{ion} \cdot C_{ion}} \qquad [3]$$

where C_{ion} is ion concentration in the bulk; K_{ion} is the ion adsorbent constant; and $\Gamma_{m,ion}$ is maximum adsorbing rate of ions.

Combining Eqs (2) and (3), one gets:

$$n = n_0 - r_{ion}\, \Gamma_{m,ion}\, \frac{K_{ion}.C_{ion}}{1+K_{ion}.C_{ion}} \qquad [4]$$

Substituting into Eq.(1), the overall model gives the droplet diameter in presence of salt as:

$$D_e = D_0 \left(1 - \frac{r_{ion}}{n_0} \Gamma_{m,ion}\, \frac{K_{ion}.C_{ion}}{1+K_{ion}.C_{ion}}\right) \qquad [5]$$

The equation can be further simplified as:

$$D_e = D_o \left(1 - H\, \frac{K_{ion}.C_{ion}}{1+K_{ion}.C_{ion}}\right) \qquad [6]$$

Where H is a parameter accounting for the maximum number of H-bonds in the surfactant layer:

$$H = \frac{r_{ion}}{n_0}\, \Gamma_{m,ion} \qquad [7]$$

It is physically feasible that at the maximum adsorbing rate of ions, all H-bonds of the surfactant layer will be disrupted. Thus, the value of H can be assumed of 1, and the above equations has only two parameters: K_{ion} and D_o. The values of these parameters can be obtained by fitting the above equation to the experimental data. It should be noted that the above model is limited to the tension-driven emulsification without fluid flows. Secondly, the model requires that formation is sufficiently slow so that the surfactant adsorption is always saturated.

MATERIALS AND METHOD

Materials

The chemical materials, including n-heptane (anhydrous, 99%), n-hexadecane (anhydrous, 99%) and sodium chloride (anhydrous, ≥ 99%) were purchased from Sigma-Aldrich. Triton X-114 (polyethylene glycol tert-octylphenyl ether (Fig. 2)) was also purchased from Sigma-Aldrich. All chemicals were used without further purification. Pure water was obtained from a

Milli-Q system, consisting of a pre-filter, a carbon cartridge, two mixed-bed ion exchange cartridges, and an ultrafiltration cartridge. It is noted that other Triton surfactants including Triton X-45, Triton X-100, and Triton X-405 were tried. However, none of them can produce spontaneous emulsions at room temperature.

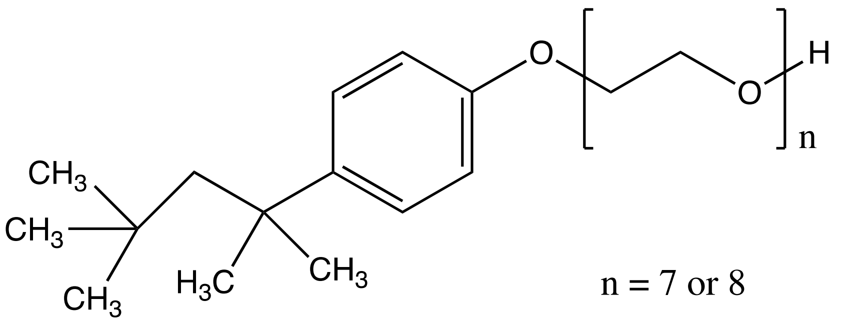

Fig. 2. Chemical structure of Triton X-114 (polyethylene glycol tert-octylphenyl ether)

Experimental procedure

All experiments were carried out with Triton X-114 at the concentration of 1 %, w/w while the concentration of sodium chloride was varied from 0 to 5 M. Spontaneous emulsions were prepared by pouring approximate 50 ml surfactant solution (with different salt concentrations) in 70 ml plastic bottles (55 (H) × 44 (D) mm) at first. Then around 1 ml of oil (n-heptane or n-hexadecane) was added on the top of each solution to form a thin oil layer. All the samples were kept in a static state without any external energy for 72 hours to allow spontaneous emulsification process. It is worth reminding that the formed emulsions are in nanoscale and cannot be validated optically. However, other physical techniques such as Dynamic light scattering (DSL) can be beneficial to determine the size distribution profile of these small emulsions. Finally, the middle layer of samples (Fig. 3) was taken out by a pipette for analyzing oil droplet size. The droplet size distributions of oil-in-water emulsions were measured by using a ZetaSizer Nano ZS (ZEN3600), which employs laser light scattering to determine the droplet's diameter.

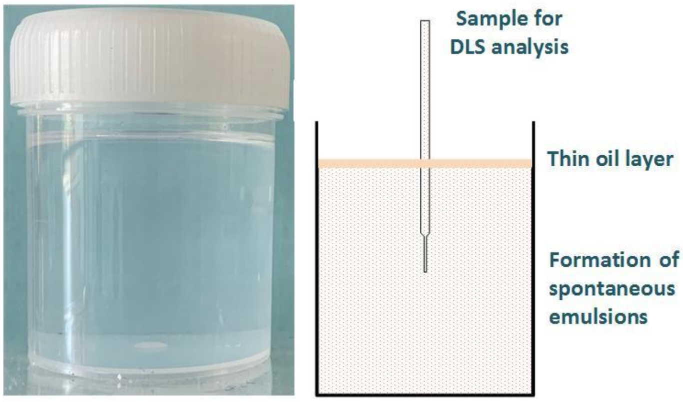

Fig. 3. Experimental setup for spontaneous emulsification process (left) and the position where samples were collected for DLS measurements

The cloud point of Triton X-114 in sodium chloride solution was measured visually by gradually changing the solution's temperature. With the presence of salt, the cloud point of Triton X-114 would be lower than room temperature (25 ^{o}C). Therefore, the samples were firstly cooled down to 15 °C (the temperature at which all solutions were clear and exhibited a single phase) and then heated up slowly by using a plate heater until the solutions first became cloudy. All experiments were performed three times to obtain average cloud points.

RESULTS AND DISCUSSION

Cloud Point

For non-ionic surfactants, common observations show that the solution tends to become visibly turbid at a specific temperature called cloud point. Above this temperature, the system separates into a micelle-free dilute solution and a surfactant-rich micellar phase [39]. This separation is caused by a sharp increase in the aggregation number of surfactant. The presence of salt in the solution of nonionic surfactant leads to a lower interaction between surfactant molecules and a lower cloud point of the solution. Consequently, the cloud point is a good indicator of the salt penetration into the hydrophilic layer of the surfactant [40].

In this study, the cloud point of surfactant solution (1 % w/w of triton X-114 in pure water) without NaCl was determined at 27 °C, which is consistent with the literature value [41]. By adding NaCl to this solution, the cloud point was decreased as a function of salt concentration and depicted in Fig. 4.

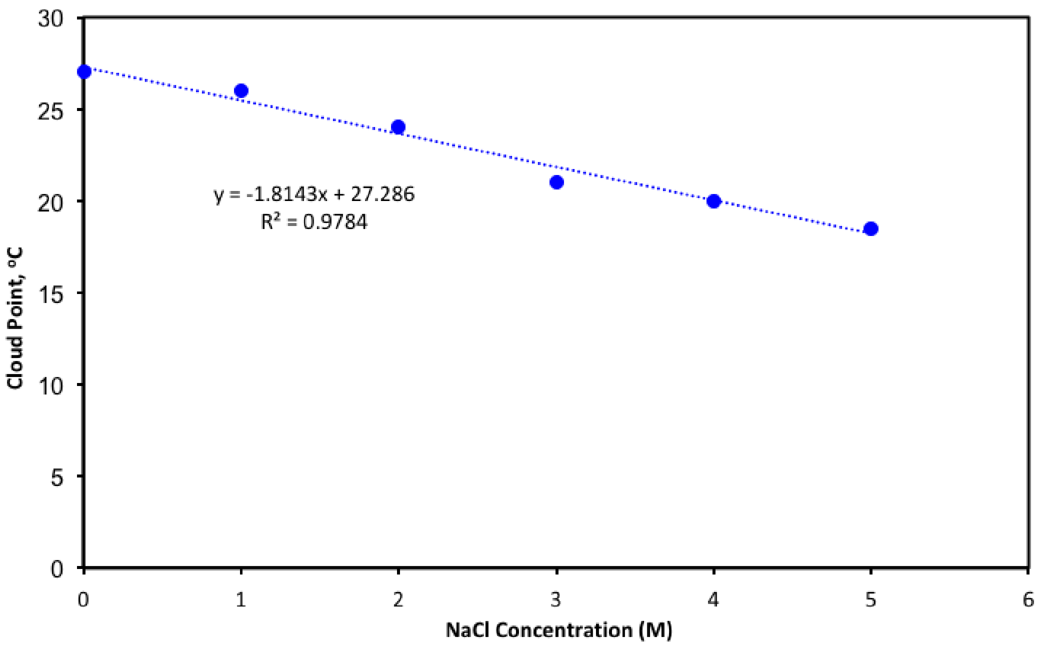

Fig. 4. Cloud point of triton X-114 solution (1 % w/w) as a function of NaCl concentration

This linear decrease of cloud point was often referred to as a "salting out" effect [41,42]. In other words, water molecules have a tendency to preferentially interact with electrolytes, which results in dehydration of the polyethylene oxide chain. This will lead to closer interaction between surfactant molecules and the formation of aggregates. The effect of electrolytes on the cloud point is indicative of electrolytes' influence on the spontaneous emulsification processes.

Size analysis of emulsion droplets

As mentioned in the experimental procedure, the size of oil droplets was measured by dynamic light scattering technique, with examples are plotted in Fig. 5. It is obvious that oil-in-water emulsions were obtained in both cases of oil phase with the presence of non-ionic surfactant. Narrow size distributions of oil droplets in brine is indicative of a spontaneous emulsification process. All measurements were conducted three times and the average diameters, as well as standard deviations were depicted in Fig. 6.

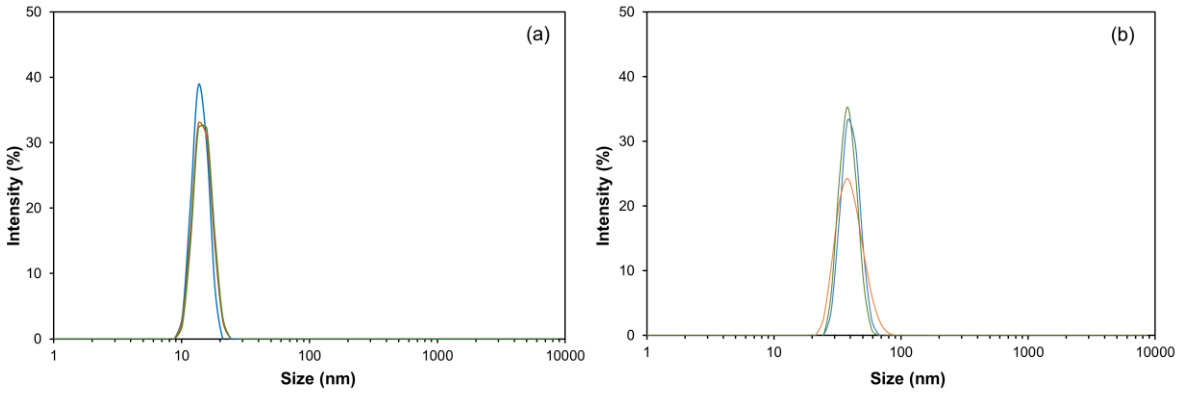

Fig. 5. n-Hexadecane (a) and n-heptane (b) droplet size distribution in the solution of 5 M NaCl and 1 %(w/w) Triton X-114

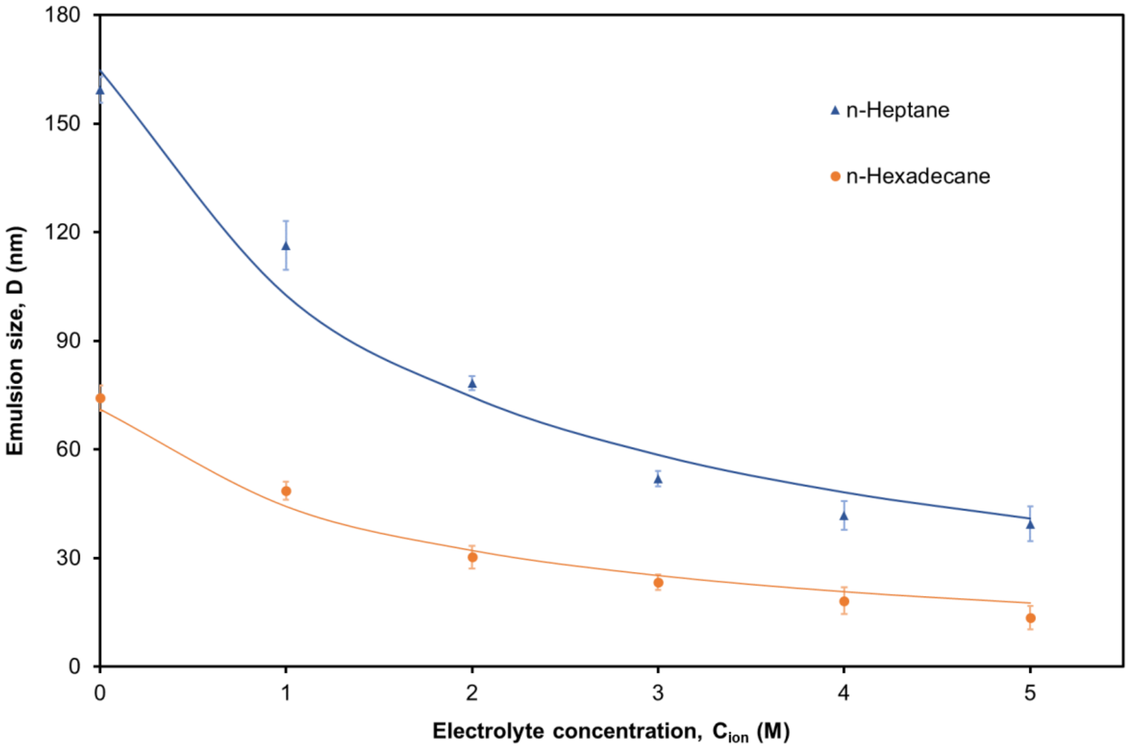

Fig. 6. Diameter of n-hexadecane-in-water (orange) and n-heptane-in-water (blue) emulsions as a function of NaCl concentration. Lines are fits described in theoretical model section.

It can be seen clearly from Fig. 6 that with both hydrocarbons, the emulsion's diameters are decreased gradually with increasing salt concentration. More specifically, n-heptane and n-hexadecane can form spontaneous emulsions without NaCl, with D_o as of 164.74 nm and 71.17 nm respectively. The addition of NaCl to this surfactant solution reduced the oil droplet size and reached the diameter of 40.88 nm and 17.65 nm for n-heptane and n-hexadecane respectively when the concentration of NaCl increased to 5 M. The reduction was more dramatic at lower electrolyte concentrations and tends to flat out when the salt concentration approaches its solubility point (~ 6 M). It is noteworthy that the emulsions formed from short oil molecules are always larger than those from long ones regardless of salt concentrations. This observation exhibits the independent effects of electrolytes and the nature of the oil phase on the diameter of spontaneous emulsions. Similar to the cloud point reduction, electrolytes penetrated into the hydrophilic layer of surfactants and decreased its hydrophilicity as showed in **Fig. 1**, leading to smaller droplet size.

Modelling

The experimental data was fitted against the proposed theoretical model. It is noted that K_{ion} is independent of the oil phase. Furthermore, D_0 can be directly obtained from the experimental values. Consequently, the model has only one fitting parameter for both hydrocarbons. The best-fitted value K_{ion} was obtained as 0.61 M^{-1}. As can be seen in Fig. 6, the model fitted the data very well. The curves validate the physical mechanism of spontaneous emulsion formation. Impressively, the model can apparently distinguish the effect of alkane length on the spontaneous emulsion.

It should be noted that the chain length of alkanes has a very weak impact on the interfacial tension [43]. Hence, one has to consider the dynamic steps to explain the influence of hydrocarbon in emulsion size. The final droplet size depends on the mass transfer or viscosity of the oil, which is positively correlated to the carbon length [44]. Consequently, the longer hydrocarbon (C16) transfers slower. For the same deformation period, the longer oil has transferred less and thus has a smaller final volume. The mechanism can be investigated further by molecular dynamics simulation.

CONCLUSION

The emulsification process of oil in water has taken place spontaneously for nonionic surfactant type Triton X-114 with NaCl additive. At first, the cloud point of surfactant solutions with different salt concentrations was determined and showed that increasing the salinity from 0 to 5 M reduced the cloud point of Triton X-114 from 27 ^{o}C to 18.5 ^{o}C. Then, the effect of oil chain-length, as well as NaCl concentration on the size of oil droplets was investigated. It is found that the longer the oil molecule, the smaller the spontaneous emulsions can be formed in spite of the variation of NaCl concentration. The increase in the oil molecule's length from C7 to C16 resulted in a decrease of 56.8 % in emulsions' diameter. A theoretical model was developed from the adsorption of ions onto the surfactant layer to fit against the experimental data. The model was fitted very well, with a single parameter on the ion adsorbent constant K_{ion}. The results lead to a simple theory to predict the oil droplet size, a critical factor for determining emulsion's stability and transportation via the structure of the oil phase and the salinity of the aqueous phase. Studies on the impact of other inorganic salts and other oil mixtures should be carried out in the future by experimental and computational methods to gain insights into their influences on emulsion's stability.

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