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INVESTIGATING OIL-IN-WATER EMULSIONS: A CASE STUDY OF 1-HEXANOL AND 1-OCTANOL

Gülsüm GÜNDOĞDU [1]

[1] *Turkish-German University, Department of Energy Science and Technology, Istanbul, Türkiye,*

gulsum.gundogdu@tau.edu.tr

ABSTRACT

Alcohols like 1-hexanol ($C_6H_{14}OH$) and 1-octanol ($C_8H_{18}OH$) possess both a hydrophobic alkyl tail (the hexyl group) and a hydrophilic hydroxyl head, allowing them to interact with both water and oil phases. This dual affinity helps reduce the interfacial tension between oil and water, promoting the formation of stable nanoemulsions of hexadecane in water, as confirmed by zeta potential measurements. The effects of non-ionic surfactants, 1-hexanol and 1-octanol on oil nanodroplets are examined through concentration-dependent fluorescence measurements using Nile Red. This fluorescence spectrum also provides valuable information for estimating the critical micelle concentration (CMC), which is crucial for understanding surfactant behavior, as well as the stability and performance of nanoemulsions. Optimizing oil nanoemulsions containing alcohols is essential for various applications, including drug delivery, emulsification, enhanced oil recovery (EOR), food processing, cosmetics and energy storage technologies.

Keywords: Surfactant adsorption, Oil-water interface, Oil nanodroplet, Nanoemulsion, Critical micelle concentration.

1 INTRODUCTION

Alcohols play a crucial role by acting as surfactants or co-surfactants in the formation of oil-in-water emulsions. By reducing interfacial tension of the oil-water interfaces, they offer exciting possibilities in various industrial, biomedical and environmental applications [1–5]. This reduction is due to the perturbation of the dielectric properties at the interface between oil and water, as the alcohol molecules alter the orientation of the molecules at the interface. Being amphiphilic alcohol molecules can be adsorbed and align at the oil-water interface, with their hydrophilic (water-attracting) part in the water phase and their hydrophobic (oil-attracting) part in the oil phase, thereby stabilizing long-term the emulsion droplets by preventing their coalescence [6],[7]. This property is important in various applications, such as in drug delivery, emulsification, enhanced oil recovery (EOR) techniques, food processing, cosmetics and could potentially be used in energy storage technologies [8–16].

Alcohols like 1-hexanol ($C_6H_{14}OH$) and 1-octanol ($C_8H_{18}OH$) used as surfactant in this study significantly affect the behavior of oil-water interfaces due to their unique molecular structure. 1-Hexanol consists of a six-carbon chain with a hydroxyl group (-OH) attached to the first carbon in the chain, where 1-octanol is a straight-chain higher alcohol with an eight-carbon alkyl chain and a hydroxyl group (-OH) at the terminal position (on the first carbon). Having both a hydrophobic alkyl tail (the hexyl group) and a hydrophilic head (the hydroxyl group), gives them the ability to interact with both water and oil phases. This property alters the local dielectric properties at the oil-water interface, thereby reducing the interfacial tension and facilitating the formation of more stable emulsions [17–19].

Determining the critical micelle concentration (CMC) of surfactants is essential for understanding their interfacial behavior, particularly in complex systems such as nanoemulsion. Conventional methods, including time-dependent static light scattering (TDSLS) and conductivity [20–23], Interfacial Tension (IFT) measurements [24–26], interfacial-sensitive spectroscopies like static light-scattering techniques [27], nonlinear light scattering [28] and sum-frequency (SF) [29] are widely used methods, but present limitations: such as conductivity applies only to ionic surfactants, and tension-based methods often lack molecular-level sensitivity, while light scattering requires complex setups. In contrast, the low sample volume requirement and rapid data acquisition make fluorescence emission spectroscopy a powerful, accessible, and practical alternative for estimating CMC value in oil-in-water emulsions, as an original approach proposed in this study.

The solvatochromic behavior of Nile Red dye is observed through fluorescence measurements, which are dependent on alcohol concentrations and controlled to examine its effect on oil-in-water emulsions. These measurements demonstrate that the concentrations of 1-hexanol and 1-octanol significantly impact the emission spectrum of hexadecane in water nanoemulsions, offering an effective and practical method for monitoring changes in oil nanodroplet formation and stability.

2 MATERIAL AND METHOD

2.1 Chemicals

Hexadecane (99.9%, analytical grade, Sigma-Aldrich), 1-Octanol (≥99%, anhydrous, Sigma-Aldrich), 1-Hexanol (≥99%, anhydrous, Sigma-Aldrich), and methanol (≥99.8%, ACS reagent, Sigma-Aldrich), along with Nile Red (Sigma-Aldrich), were all obtained from Sigma-Aldrich and used without further purification. Millipore deionized water (resistivity: 18 MΩ cm−1) was employed in all experiments.

2.2 Nanoemulsions

Oil nanoemulsions, composed of bare oil nanodroplets, were prepared in an aqueous solution using a standardized protocol with surfactants 1-Octanol and 1-Hexanol at varying concentrations. A 2% hexadecane solution was introduced into the aqueous phase, which was then homogenized for 5 minutes with a hand-held homogenizer (TH, OMNI International). The mixture was further treated in an ultrasonic bath Bandelin brand (35 kHz, 400 W) for an additional 5 minutes [30–32]. The droplet size, polydispersity index (PDI), and zeta potential of the nanodroplets were measured using dynamic light scattering (Malvern, Zetasizer Nano ZS). The nanodroplets consistently exhibited an average size between 205 and 300 nm, with a PDI under 0.25. Measurements of particle size and zeta potential were conducted in triplicate to ensure reproducibility.

2.3 Measurements

The nanoemulsion samples were diluted in a 1:40 ratio with the appropriate surfactant solution (water for the untreated nanoemulsion samples), and Nile Red solution was incorporated to reach a final concentration of 0.12 µM. Fluorescence measurements were performed using a Varian Cary Eclipse Fluorescence Spectrometer, with excitation at 490 nm and emission detected within the 500–800 nm wavelength range. The Fluorescence measurements at each surfactant concentration were carried out using at least two independently prepared sample batches. Consistency in peak positions was observed between batches, indicating reproducibility of the spectral features. However, variations in fluorescence intensity were noted, likely due to inherent difficulties in achieving uniform nanoemulsion size and particle distribution with the preparation method employed.

3 RESULTS AND DISCUSSION

A novel fluorescence-based technique known as Fluorescence Multivariate-Curve-Resolution (FMCR) Spectroscopy, which probes the oil-water interface dielectric perturbations was presented [33]. The prominent band near 640 nm, linked to the oil-water interface fluorescence peak of hexadecane nanoemulsions, shifts to longer wavelengths (red shift) when anionic surfactants are present, indicating an increase in dielectric properties. On the other hand, the band progressively shifts to shorter wavelengths (blue shift) as the concentration of cationic surfactants increases, indicating a reduction in the dielectric properties of the interface. The fluorescence emission spectrum of Nile Red was examined in hexadecane-in-water nanoemulsions. Three main spectral components were identified: from the primary bulk liquid phase (hexadecane and water) at 532 nm and 571 nm, and a distinct band around 640 nm, which is attributed to the oil-water interfacial component. This band was confirmed to be useful for probing the dielectric properties of the oil-water interface [33]. The two from the primary liquid phases are shifted in this study toward 540 and 573 nm with 1-hexanol and to 542 and 571 nm with 1-octanol surfactants (Figure 1). At an intermediate concentration value which can be defined as critical concentration value the three peaks are overlapped (pink layer Figure 1) 29 mM (for 1-hexanol) and 0.58 mM (for 1-octanol), as can be seen in Figure 1. Above the critical concentration values approaching the critical micelle concentration (CMC) of the surfactants, the permeability of the oil-water interface increased due to the formation of micelles, occurred which first with 1-octanol (after 0.58 mM) and with 1-hexanol at concentrations exceeding 40 mM. So the surfactant concentration in the bulk increases. The fluorescence band intensity increased to 50 mM (626 nm) and 58 mM (629 nm) with hexanol and to 1.15 mM (600 nm), 1.5 mM (611 nm), and 2.3 mM (621.6 nm) with octanol. The fluorescence emission spectrum of the alcohols with Nile red in water (Figure 2), in the absence of oil droplets, to 29 mM (636 nm), 40 mM (633 nm), 50 mM (630 nm) and 58 mM (631 nm) with hexanol and to 1.15 mM (629 nm), 1.5 mM (628 nm) and 2.3 mM (629 nm) with octanol show distinct intense band.

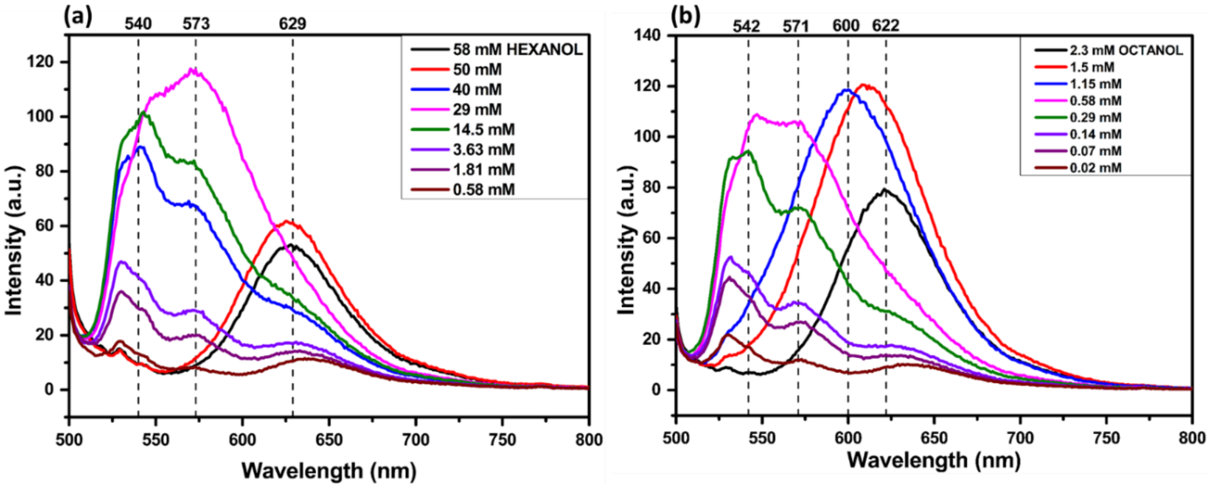

Figure 1. Fluorescence emission spectra of Nile Red the nanoemulsion samples with (a) 58 mM (black), 50 mM (red), 40 mM (blue), 29 mM (pink), 14.5 mM (green), 3.63 mM (violet), 1.81 mM (purple), 0.58 mM (brown) concentration of 1-Hexanol and (b) 2.3 mM (black), 1.5 mM (red), 1.15 mM (blue), 0.58 mM (pink), 0.29 mM (green), 0.14 mM (violet), 0.07 mM (purple), 0.02 mM (brown) concentration of 1-Octanol, clear changes are observed with increasing the concentration. The excitation wavelength is 490 nm.

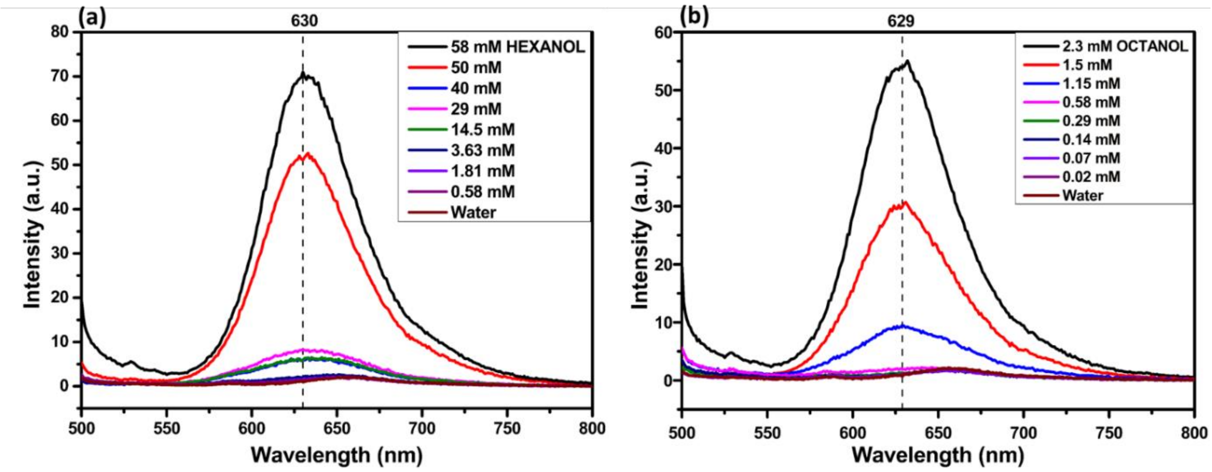

Figure 2. Fluorescence emission spectra of Nile Red with (a) 58 mM (black), 50 mM (red), 40 mM (blue), 29 mM (pink), 14.5 mM (green), 3.63 mM (dark blue), 1.81 mM (violet), 0.58 mM (purple) concentration of 1-Hexanol, pure water (brown) and (b) 2.3 mM (black), 1.5 mM (red), 1.15 mM (blue), 0.58 mM (pink), 0.29 mM (green), 0.14 mM (dark blue), 0.07 mM (violet), 0.02 mM (purple) concentration of 1-Octanol and pure water (brown). The Intensity increases with increasing the concentration in the absence of hexadecane oil. The excitation wavelength is 490 nm.

The CMC value of hexanol in oil-in-water emulsions is estimated to range between 40 mM and 50 mM, while for octanol, the CMC value in oil-in-water emulsions is estimated to range between 0.58 mM and 1.15 mM. Longer-chain alcohols, like octanol, may have a better ability to orient themselves at the oil-water interface, leading to more stable emulsions and a lower CMC. Hexanol, with its shorter chain, might be less tightly packed at the interface and thus have a higher CMC. Surfactant concentrations above the critical micelle concentration (CMC) lead to the formation of surfactant micelles. This study provides a crucial guide for identifying the appropriate working concentration range of the surfactants, which should be below the CMC value, for surfactant-based investigations of the oil-water interface and for estimating the CMC value. This study is the first in the literature to estimate the CMC of the surfactant at the oil-water interface using the fluorescence emission spectrum.

The fluorescence emission spectrum clearly shows that at concentrations where peak intensity starts to rise significantly (Figure 2), the signal from the oil-water interface becomes indistinguishable (Figure 1), indicating a weak fluorescence signal around 635-640 nm. In contrast, ionic surfactants tend to form stable, well-ordered micelles that efficiently solubilize the fluorophore and reduce quenching effects, resulting in higher fluorescence emission intensity of oil-water interface band [33]. When studying the oil-water interface, it is more critical to carefully adjust surfactant concentration (below CMC) changes with non-ionic surfactants compared to ionic ones.

To confirm the stable formation of the nanoemulsion, the zeta potential (ζ) is measured (Figure 3). The Zeta potential of the nanoemulsion samples with increasing the concentration of 1-hexanol and 1-octanol at pH 7 changes in the range of (-45.23 mV, at 58 mM)-(-53.87 mV, at 40 mM) and (-47.03 mV, at 0.023 mM)-(-52.87 mV, at 0.29 mM), respectively. As shown in Figure 3, nanoemulsions containing 1-hexanol exhibited slightly greater fluctuation in zeta potential, whereas those with 1-octanol demonstrated increased stability. It can be concluded that no significant change in zeta potential was observed compared to the bare nanoemulsions, which had a ζ-potential of -55 mV. No significant or linear change in the zeta potential is observed as the alcohol concentration increases, confirming the stability of the prepared nanoemulsions [33].

This behavior aligns with the non-ionic nature of the alcohols, which are not expected to contribute directly to the surface charge. Overall, both 1-hexanol and 1-octanol may affect the oil-water interfacial microenvironment by altering their surfactant packing and the dielectric properties. These alcohols can also contribute to slight charge shielding, reducing the expression of existing surface charges of nanoemulsion without introducing new ones. However, these effects are subtle and do not result in significant changes in zeta potential, especially in the absence of ionic surfactants. Additionally, the resolution limits of the measurement instrument may prevent detection of very small shifts in zeta potential, particularly in nanoemulsions stabilized primarily by non-ionic surfactants. Therefore, the role of 1-hexanol and 1-octanol in stabilization is attributed more to steric contributions than to electrostatic interactions.

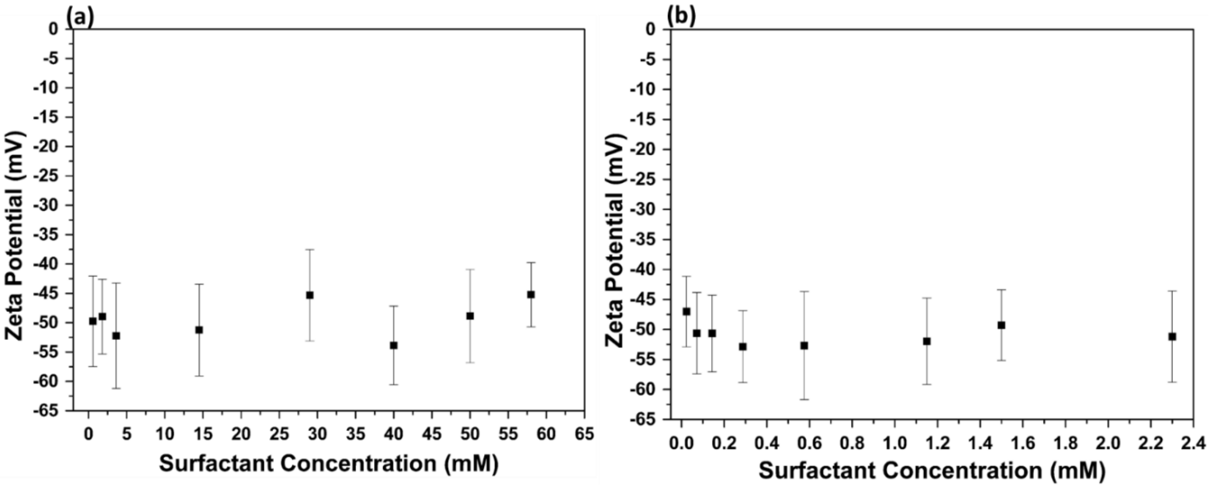

Figure 3. Zeta potential values of the nanoemulsion samples with (a) 58 mM, 50 mM, 40 mM, 29 mM, 14.5 mM, 3.63 mM, 1.81 mM, 0.58 mM with 1-Hexanol and (b) 2.3 mM, 1.5 mM, 1.15 mM, 0.58 mM, 0.29 mM, 0.14 mM, 0.07 mM, 0.02 mM with 1-Octanol by increasing the concentration at pH 7 with error bars, confirming the stability.

4 CONCLUSION

This study demonstrated that the fluorescence spectrum provides critical data for estimating the critical micelle concentration (CMC), which is key to understanding surfactant behavior and the stability and performance of nanoemulsions. This kind of study has been conducted for the first time in the literature. 1-Hexanol maintains a higher concentration range for studying the oil-water interface with fluorescence measurements because of its ability to form smaller, less stable micelles, which allows it to remain active at the interface over a broader concentration range. In contrast, 1-octanol forms larger, more stable micelles at lower concentrations, which can obscure the fluorescence signal from the interface, thereby limiting the concentration range in which the oil-water interface can be studied effectively. No significant shift was observed in the fluorescence band of the oil-water interface. This study demonstrated that stable nanoemulsions can be prepared using 1-hexanol and 1-octanol without the need for additional surfactants.

Beyond its applicability to oil-water interfaces, the method proposed in this study offers considerable potential for investigating interfacial concentration variations of various surfactants across a wide range of soft interfaces, including those in synthetic and biological systems. This broad applicability extends to practical uses in areas such as drug delivery, emulsification, enhanced oil recovery, food technology, cosmetics, and energy storage or fuel emulsion technologies [8–16].

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Statement of Research and Publication Ethics

The study is complied with research and publication ethics.

Artificial Intelligence (AI) Contribution Statement

This manuscript was entirely written, edited, analyzed, and prepared without the assistance of any artificial intelligence (AI) tools. An AI-based grammar checker was used to correct spelling and grammar mistakes. All content, including text, data analysis, and figures, was solely generated by the authors.

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