The Effect of AOT and Octanoic Acid on the Formation of Stable Water-in-diesel Microemulsion

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Abstract. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and octanoic acid (OA) were used as surfactants to prepare water-in-diesel microemulsion. The effect of mixed surfactants ratio on the phase behavior of water-in-diesel microemulsion was investigated. The $R_0$-T plot phase diagrams for the diesel/AOT and OA/water system with different surfactant ratios were constructed at 30-80 °C. The results indicate that the largest single phase region could be obtained when OA to AOT molar ratio was 1. The temperature had a significant influence on phase transformation behavior. The single phase separated into two immiscible phases with the increase of temperature when $R_0$ value was above 10. Compared with applying AOT alone, mixing AOT with appropriate amount of OA is benefit to form smaller nanosized W/O droplets. The determination of particle size was performed to verify the phase transformation behavior, and the results were consistent with the phase diagrams.

1. Introduction
The increasing demand for fuel energy, continuing consumption of reserved petroleum and environmental pollution problems such as the emission of NOX, particulate matter (PM) and CO2 due to the combustion of fuels have challenged the existing fuel energy [1-3]. Recently, more attention has been paid to the development of cleaner, alternative and sustainable fuels in order to meet higher emission standards and to reduce the dependence on pure fossil fuels.

The addition of water into diesel to form water-in-diesel microemulsion fuel exhibits several benefits. First of all, it has been proved that the vaporization of water and the mixing process can effectively reduce soot, PM and NOx emissions [4-6]. Another benefit is that water in the form of microstructure droplets can exert some positive influences on the combustion process of fuels. When microemulsion fuel is heated, the vaporization of water will cause continuous hydrocarbon phase to “explode” [7]. This phenomenon helps in improving fuel combustion process and combustion efficiency [8]. Furthermore, since water droplets are wrapped by diesel fuel, there is no direct contact between water and engine cylinder, which can eliminate the negative effect of water on lubricating oil contamination and engine wear [9]. There is no doubt that water-in-diesel microemulsion fuel is energy saving and environmental protection.

Sharon et al. investigated the co-surfactant chain length, alcohol isomerism, solution salinity, CTAB/alcohol ratio and the effect of combining various alcohols were studied [10]. Ochoterena et al. investigated physical properties, spray behavior and combustion characteristics of water-in-diesel
emulsion, water-in-diesel microemulsion and conventional diesel fuel [11]. Spray behavior studies demonstrated droplets of water-containing fuels penetrated further than droplets of regular diesel fuel. Combustion studies showed that water-in-diesel fuels yielded to flames with lower temperature and lowered soot concentrations than diesel fuel. Kannan and Anand reported that the emission characteristics like carbon monoxide (CO), carbon dioxide (CO₂), nitric oxide (NO) and smoke emissions for biodiesel and microemulsion fuels were lower than diesel fuel[12]. Bülent and Mudhafar investigated the effects of water concentration in a biodiesel nanoemulsion fuel on engine performance and exhaust emissions of a 4-cylinder diesel engine [13]. Biodiesel nanoemulsions containing 5%, 10% and 15% water were used for the engine tests. They concluded that increasing water concentrations in biodiesel nanoemulsions increased the engine brake specific fuel consumption and CO emissions. The rate of NOₓ reduction was greater than the rate of CO increase when the water concentration in biodiesel nanoemulsions increased from 10% to 15%.

However, papers have been reported were mainly concerning combustion properties, spray behavior and reduction of emissions. In our previous studies, several kinds of nonionic surfactants were used to form water-in-diesel emulsions, whereas the stability of such emulsions was not satisfactory. Hence, we embarked on the study of phase behavior of water-in-diesel microemulsion. The objective of this research is to experimentally study the effect of AOT and octanoic acid on the formation of water-in-diesel microemulsion. AOT is a popular surfactant used for the formation of water-in-oil microemulsion droplets containing large amount of water under wide range of conditions (such as water content, temperature, solvent, electrolyte type and concentrations)[14-16]. OA is used as co-surfactant and its role is to enhance AOT surfactant property and compatibility with diesel at the interface.

2. Materials and methods

2.1. Materials
Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) with 98% purity was purchased from Fluka. Octanoic acid (OA) with 98% purity was purchased from Sigma-Aldrich. Double distilled de-ionized water was used in sample preparations. Diesel was purchased from local Petronas petrol station (national oil company of Malaysia).

2.2. Preparation of microemulsion and phase diagram
The microemulsions were prepared by mixing given concentration of AOT and OA solution with diesel oil. Then different volumes of water were added into the mixture. The samples were mixed by using Minishaker for 10 s. The phase diagram was constructed by calculating ratios of water concentration ([H₂O]) to surfactant concentration ([Surf]) [17] (formula 1). By plotting different R₀ values with respect to temperatures, the phase diagram was obtained. For all the samples, the total surfactant concentration was kept constant as 0.222 mol/L (the total surfactant concentration = [AOT] + [OA]). The phase behaviors of samples were observed with eyes after pulled out 30 s, and then the phase numbers were recorded.

\[ R_0 = \frac{[H_2O]}{[Surf]} \]  

(1)

2.3. Instrumentation
The water-in-diesel microemulsion samples were prepared in 3.5 mL vials sealed with caps. The phase behaviors of samples under different temperatures were investigated by changing temperature in the range of 30-80 °C in a Thermo Haake water bath, which accuracy is ±1.0 °C. Water content was measured by Karl Fisher Titrator (Mettler Toledo DL38). Dynamic Light scattering (DLS) experiments were performed to obtain the mean diameter of the water-in-diesel microemulsion droplets. The measurements were carried out by using a Zeta Sizer Nano Series (Malvern). All measurements were performed at the temperature of 40°C. Each sample was monitored for 3 times.
3. Results and discussion

3.1. Water content and $R_0$ values
In order to confirm actual water content in the samples, Karl Fisher Titrator was employed to determine the water quantity, and then the water concentration could be calculated. After the water concentrations were figured out, $R_0$ values could be calculated according to formula 1. Results of $R_0$ values for all the samples with different surfactant ratios were listed in Table 1.

Table 1. $R_0$ values of samples with different surfactant ratios.

| Water volume of addition (μL) | AOT alone | $n_{OA}$ : $n_{AOT}$ = 1:4 | $n_{OA}$ : $n_{AOT}$ = 1:2 | $n_{OA}$ : $n_{AOT}$ = 1:1 | $n_{OA}$ : $n_{AOT}$ = 4:3 | $n_{OA}$ : $n_{AOT}$ = 2:1 | $n_{OA}$ : $n_{AOT}$ = 4:1 |
|-------------------------------|-----------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| 50                            | 5.23      | 5.38                        | 4.05                        | 4.66                        | 5.17                        | 4.15                        | 4.39                        |
| 100                           | 7.66      | 9.00                        | 9.18                        | 9.00                        | 9.05                        | 8.97                        | 8.87                        |
| 150                           | 10.17     | 14.50                       | 13.27                       | 13.11                       | 13.90                       | 13.99                       | 14.99                       |
| 200                           | 15.94     | 17.35                       | 19.14                       | 17.34                       | 17.81                       | 19.43                       | 18.15                       |
| 250                           | 22.36     | 23.54                       | 23.36                       | 20.50                       | 21.87                       | 23.09                       | 23.19                       |
| 300                           | 25.78     | 28.38                       | 27.05                       | 27.91                       | 26.33                       | 28.52                       | 27.54                       |
| 350                           | 32.04     | 33.44                       | 34.69                       | 32.03                       | 31.94                       | 32.68                       | 31.64                       |
| 400                           | 38.13     | 36.27                       | 38.96                       | 39.96                       | 37.34                       | 36.08                       | 38.29                       |

3.2. Construction of phase diagrams
The molar ratio of surfactant OA and AOT is an important factor that influences the phase behavior of microemulsion. The phase behavior was divided into several categories as shown in figure 1. The single phase seemed to be clear and transparent, while the phase behavior of two-phase or three-phase altered with variation of conditions, such as surfactant ratio, water content and temperature. To investigate the effect of surfactant ratios on the transformation of W/O microemulsion domain, $R_0$-T plot phase diagrams of diesel/surfactants/water system for different surfactant molar ratios at temperature range of 30-80 °C were presented in figure 2.

Figure 1. Schematic diagrams of phase behavior. (a) Phase behavior at lower water content; (b) Phase behavior at higher water content; (c) Phase behavior for samples with $n_{OA}$ : $n_{AOT}$ = 1:1; (d) Phase behavior for samples with $n_{OA}$ : $n_{AOT}$ = 4:1.

Figure 2 (a) reveals that single phase separated into two immiscible phases with the increase of temperature for all cases. The highest $R_0$ value for single phase boundary was 20.50 when $n_{OA}$/$n_{AOT}$ was 1 at 30 °C, and the corresponding water content was 10.8 %. Figure 2 (b) reveals the three-phase region (inside the boundary) transformation process with the increase of OA amount. For $n_{OA}$/$n_{AOT}$ below 1, the three-phase region transformed from lower $R_0$ value to higher $R_0$ value. When $n_{OA}$/$n_{AOT}$ was increased to 2, the phase diagram appeared the minimum three-phase region area. However, the three-phase region not only transformed to higher $R_0$ value but also expanded again when $n_{OA}$/$n_{AOT}$
was 4. Furthermore, the single phase region disappeared at this ratio. The results illustrate that it is not suitable to form stable water-in-diesel microemulsion by applying AOT alone, and the addition of appropriate amount of OA is benefit to increase water content in water-in-diesel microemulsion. This is due to almost 70% of the components in diesel are saturated linear alkanes with C₆–C₁₆ [18–19], while the carbon number of AOT hydrophobic tail is six and the shape of AOT molecule is wedge. This may lead to an unfavorable interface between AOT and diesel oil. The presence of OA will effectively reduce the interfacial energy of water-oil surface and stabilize the water-oil surface [20]. Consequently, the optimum molar ratio of OA to AOT was 1 in this experiment.

![Figure 2. R₀-T plot phase diagram of diesel/surfactants/water system with different OA/AOT molar ratios: (i) AOT alone; (ii) n_{OA} : n_{AOT} = 1:4; (iii) n_{OA} : n_{AOT} = 1:2; (iv) n_{OA} : n_{AOT} = 1:1; (v) n_{OA} : n_{AOT} = 4:3; (vi) n_{OA} : n_{AOT} = 2:1; (vii) n_{OA} : n_{AOT} = 4:1. (b) boundary of two-phase and three-phase.](Image)

### 3.3. Particle size and polydispersity index

The surfactant ratio has an important influence on the particle size, and then the particle size of the droplet determines the phase behavior of the samples. In order to identify the relation between particle size and phase behavior, the particle size of clear water-in-oil (W/O) region in samples has been measured. As shown in figure 3, the curves for different surfactant ratios were fluctuated with the increase of added water volume. The variation of particle size was consistent with phase behavior, the phase boundary of single phase and multiphase could be deduced. For example, the particle size at point 4 and point 5 in the case of n_{OA} : n_{AOT} = 1:1, corresponding to R₀ value of 17.34 and 20.50, were not linear increase. This tendency exactly indicates a phase transition, which also can be seen in figure 2. Point 4 was the phase boundary of single phase and multiphase, and point 5 was the phase boundary of two-phase and three-phase. The particle size at point 5 decreased to 21.7 nm, which was mainly due to the formation of a clear phase on the top of the sample (see figure 1c). Figure 3 also reveals that the addition of excessive OA is more feasible to form larger size droplets. This may be due to AOT is interfacial active to increase the interfacial energy, which favors to form negative curvature. However, OA is not so interfacial active as AOT that it will lower the interfacial energy. With an overdose of OA is added to the mixture, there is an increase in the magnitude of the spontaneous curvature of the surfactant monolayer, and then the droplets swell in size [21].

In an emulsion-based solution, polydispersity index (PDI) is one of the key characteristics, as PDI contributes to physical stability and rheological properties of the solution [22]. PDI values of the samples with different surfactant molar ratios were listed in Table 2. The PDI value provides a measure of the narrowness of particle size distribution, with values ≤0.1 indicating a very narrow distribution [23]. That means it is more possible to obtain stable and monodisperse samples at lower PDI value. As shown in Table 2, the stability of the samples decreased with the increase of OA.
amount. Moreover, the lowest PDI values for all the cases were exactly corresponded to particle size transition points in figure 3.

![Figure 3](image)

**Figure 3.** Particle size of droplets in water-in-oil region as a function of water volume of addition. The samples were soaked in water bath with temperature of 40°C, and the measurement of particle size was done immediately after the sample was taken out.

| Water volume of addition (μL) | AOT alone | n<sub>OA</sub> : n<sub>AOT</sub> = 1:4 | n<sub>OA</sub> : n<sub>AOT</sub> = 1:1 | n<sub>OA</sub> : n<sub>AOT</sub> = 2:1 |
|-----------------------------|-----------|------------------|------------------|------------------|
| 50                          | 0.195±0.007 | 0.213±0.095      | 0.162±0.002      | 0.102±0.005      |
| 100                         | 0.070±0.010 | 0.078±0.029      | 0.049±0.012      | 0.139±0.050      |
| 150                         | 0.033±0.007 | 0.026±0.010      | 0.051±0.013      | 0.053±0.017      |
| 200                         | 0.062±0.016 | 0.025±0.012      | 0.036±0.005      | 0.182±0.043      |
| 250                         | 0.099±0.020 | 0.026±0.003      | 0.058±0.014      | 0.349±0.059      |
| 300                         | 0.483±0.149 | 0.068±0.030      | 0.451±0.240      | 0.519±0.154      |

4. **Conclusions**

In this work, the effect of mixed molar ratio of surfactant AOT and OA on the phase behavior of water-in-diesel microemulsion was tested. The results confirmed that nanosized water-in-diesel droplets formed by using the mixture of AOT and OA. The largest single phase region could be obtained when the molar ratio of OA to AOT was 1. The single phase separated into two immiscible phases with the increase of temperature when the R<sub>0</sub> value was above 10. It is not suitable to form homogeneous and stable water-in-diesel microemulsion by applying AOT alone. The addition of appropriate amount of OA is benefit to form clear and transparent microemulsion with smaller nanosized droplets. The measurement of particle size and PDI was performed to verify the phase transformation behavior, and the results were consistent with the phase diagrams.

5. **Acknowledgments**

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6. **References**

[1] Sheehan J, Cambreco V, Duffield J, Garboski M and Shapouri H 1998 *A report by US Department of Agriculture and Energy* 1–35
[2] Salvi B, Subramanian K and Panwar N. Alternative fuels for transportation vehicles: A technical review 2013 Renewable & Sustainable Energy Reviews 25 404–419

[3] Zhang Z, Cheung C, Chan T and Yao C Experimental investigation of regulated and unregulated emissions from a diesel engine fueled with Euro V diesel fuel and fumigation methanol 2010 Atmos. Environ. 44 1054–1061

[4] Lin C and Wang K The fuel properties of three-phase emulsions as an alternative fuel for diesel engines 2003 Fuel 82 1367–1375

[5] Subramanian K A comparison of water–diesel emulsion and timed injection of water into the intake manifold of a diesel engine for simultaneous control of NO and smoke emissions 2011 Energy Convers. Manage. 52 849–857

[6] Armas O, Ballesteros R, Martos F and Agudelo J Characterization of light duty Diesel engine pollutant emissions using water-emulsified fuel 2005 Fuel 84 1011–1018.

[7] Anna L and Krister H Water-in-diesel emulsions and related systems 2006 Adv. Colloid Interface Sci. 123–126

[8] Kadota T and Yamasaki H Recent advances in the combustion of water emulsion fuel 2002 Prog. Energy Combust. Sci. 28 385–404

[9] Yang W, An H, Chou S, Chua K, Chua K, Maghbouli A and Li J Impact of emulsion fuel with nano-organic additives on the performance of diesel engine 2013 Appl. Energy

[10] Sharon L, Deane T and Simon B The formation of water-in-oil microemulsions using a concentrated saline aqueous phase 1998 Colloid Surf. A-Physicochem. Eng. Asp 137 25–33

[11] Raúl O, Anna L, Magnus N, Sven A and Ingemar D Optical studies of spray development and combustion of water-in-diesel emulsion and microemulsion fuels 2010 Fuel 89 122–132

[12] Kannan G and Anand R Experimental investigation on diesel engine with diestrol-water micro emulsions 2011 Energy 36 1680–1687

[13] Bulent K and Mudhafar A Performance and NOx emissions of a diesel engine fueled with biodiesel-diesel-water nanoemulsions 2013 Fuel Processing Tech. 109 70–77

[14] Sujan C, Rajib K, Bidyut K and Subhash C Interface of AOT/Brij mixed reverse micellar systems: Conductometric and spectrophotometric investigations 2006 J Colloid Interf. Sci. 298 935–941

[15] Li Q, Li T and Wu J Water solubilization capacity and conductance behaviors of AOT and NaDEHP systems in the presence of additives 2002 Colloid Surf. A-Physicochem. Eng. Asp. 197 101–109

[16] García R, Mejuto J and Pérez L Ester aminolysis by morpholine in AOT-based water-in-oil microemulsions 2006 J Colloid Interf. Sci. 301 624–630

[17] Alireza S, Julian E, Kevin J and Rico F Tuning aggregation of microemulsion droplets and silica nanoparticles using solvent mixtures 2008 J Colloid Interf. Sci 318 244–251

[18] Shinya S, Yoshikazu S, Kinya S, Ikuo S and Sok Y Diesel quality and molecular structure of bitumen-derived middle distillates 2004 Fuel 83 1915–1927

[19] John Holladay Thermochemical Conversion Processes to Aviation Fuels 2012 A report by US Department of Energy 1–28

[20] Catherine E, Sharon J and Matthew J Unique crystal morphologies of glycine grown from octanoic acid-in-water emulsions 2006 J Am Chem Soc 128 7718–7719

[21] Catherine M, Justin W and Stephanie R Effect of added α-lactalbumin protein on the phase behavior of AOT–brine–isooctane systems 2003 J Colloid Interf. Sci 261514–523

[22] Hamed M, Chin P, Nazimah S and Salmah Y Optimization of the contents of Arabic gum, xanthan gum and orange oil affecting turbidity, average particle size, polydispersity index and density in orange beverage emulsion 2008 Food Hydrocolloids 22 1212–1223

[23] Amir H, Yuan F and David J Fabrication of vitamin E-enriched nanoemulsions: Factors affecting particle size using spontaneous emulsification 2013 J Colloid Interf. Sci 391 95–102