Corrigendum: Phase Behavior of Bicontinuous and Water/Diesel Fuel Micro emulsions Using Nonionic Surfactants...
Journal of Dispersion Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/ldis20

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Accepted author version posted online: 10 Feb 2014. Published online: 10 Feb 2014.

To cite this article: Journal of Dispersion Science and Technology (2014): Phase Behavior of Bicontinuous and Water/Diesel Fuel Microemulsions using Nonionic Surfactants Combined with Hydrophilic Alcohol Ethoxylates, Journal of Dispersion Science and Technology, DOI: 10.1080/01932691.2014.886513
To link to this article: http://dx.doi.org/10.1080/01932691.2014.886513

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Received 10 January 2014; accepted 20 January 2014.

Abstract

Bicontinuous and water in diesel microemulsions were formulated using single nonionic alkyl poly glycol ethers combined with hydrophilic alcohol ethoxylates. The phase behavior at temperatures ranging from 0° to 50° was investigated. Visual inspection as well as cross polarizers were used to detect anisotropy. The fish phase diagrams were determined. The presence of the hydrophilic alcohol ethoxylates was necessary to initiate both types of microemulsions. Increasing the hydrophobic chain length of the surfactant led to a wider range of temperature stability at lower surfactant concentration. Meanwhile increasing the ethylene oxide units in the head group by two units led to a phase diagram that is dominated by lyotropic liquid crystal. The formulated water in diesel microemulsions were tested experimentally in a 4-cylinder diesel engine, from which it is observed that the emissions of NOₓ, soot, and CO₂ were reduced substantially compared to neat diesel, while for the CO the reduction occurs just at low load.
KEYWORDS: Diesel, microemulsion, alternative fuel, emissions, phase behavior

1. INTRODUCTION

Microemulsions as diesel fuels have been investigated more than 30 years ago and were proved to lower the exhaust smoke level as well as the concentration of nitrogen oxides compared to regular diesel. Microemulsions for fuel use have also been described in the patent literature. Water incorporated in the range of 5-15 wt. % in either fuel emulsion or microemulsion has been found to reduce drastically the particulate matter emission from a direct injection diesel engine.

Fuel emulsion can be formulated with a relatively small amount of surfactant, however it is thermodynamically unstable and there is always the risk of phase separation depending on the storage and handling conditions. Microemulsions, on the other hand, are homogeneous and thermodynamically stable isotropic liquid solution. On the nanometer
length scale, microemulsions have a structure with water and oil domains separated by surfactant films at the interface, they can be bicontinuous, in which both oil and water form domains that are continuous in all three dimensions. They may also consist of water droplets in oil (w/o) or oil droplets in water (o/w). The kind of surfactant used as well as the ratio of water to oil can determine which structure will be formed. The volume of the interface in microemulsions is considerably higher than the one present in emulsion droplets. This means that large amounts of surfactants are needed to formulate microemulsions.

Microemulsion fuel systems have been formulated using anionic, cationic and nonionic surfactants. However for practical use and environmental concerns, the surfactants used should burn readily without forming smoke and should not contain sulfur or nitrogen. Therefore the choices are limited to surfactants that contain only carbon, hydrogen and oxygen atoms. These requirements put the nonionic surfactants as prime candidates, namely the alkyl polyglycol ether (CₙEₗ, where i is the number of carbon atoms in the alkyl chain and j the number of ethoxy units in the head group) and polyol surfactants including polyglycerol esters and the different kinds of sugar surfactants.

In order to reduce the amount of surfactant needed to formulate microemulsion, thus increasing the efficiency of surfactant, various attempts were reported in the literature. Using minute amount of the block copolymer, poly alkane-poly ethylene oxide (PA-PEO), enhances drastically the efficiency of the CₙEₗ surfactant in formulating microemulsions with equal volume fractions of water and decane. The lamellar liquid
crystal, \(L_\alpha\) that usually forms as surfactants become more efficient, was suppressed at such very low polymer concentration. It was later found that at higher polymer concentrations, the \(L_\alpha\) phase region was enlarged compared to the original system without the polymer addition.\[^{12,13}\] Further increase of polymer concentration led to the formation of additional liquid crystal phases namely the hexagonal, \(H_1\) and the reverse hexagonal, \(H_2\) phases surrounding the \(L_\alpha\) region.\[^{12,13}\]

Water soluble polymers, having highly hydrophilic alcohol ethoxylates, have been also tried as additives to enhance the efficiency of the surfactants.\[^{14}\] For an equal volume fraction of water and decane, using \(C_{12}E_5\) surfactant, the phase diagram showed a one phase microemulsion region at surfactant concentration above 14 % and a lamellar region starting at 22 %. Adding the hydrophilic alcohol ethoxylate (\(C_{12}E_{93}\)) at a polymer mass fraction in the surfactant/polymer mixture, \(\delta = 0.10\), the one phase microemulsion region was shifted to a smaller surfactant concentration while the \(L_\alpha\) region became closer to the fish tail point but has smaller temperature extension compared to the microemulsion without additives.\[^{14}\]

Diesel is composed of a broad range of paraffinic and aromatic hydrocarbons making it difficult for a single surfactant to do the job specially at low concentrations. Combining more than one surfactant can facilitate the formulation of microemulsion that is stable over a wide range of temperatures. Water in diesel microemulsions phase behavior has been investigated using the nonionic surfactant \(C_{11}E_5\) and sorbitanmonooleate with total amount of surfactants varied between 10 to 20 % in temperature range of 17 to 50 °C.\[^{8}\]
Microemulsions based on Fisher-Tropsch diesel have been also studied [15]. A mixture of 14.6 % sorbitanmonooleate, 6.2% C_{16-18}E5 and 7.6 % C_{9-11}E8 produces a microemulsion with 10 wt% water that was stable over a temperature range of 14-53°C. When a propoxylatedethoxylated ethyl hexane ( abbreviated C_{8}P_{2}E_{4} ) was used as co-surfactant together with sorbitanmonooleate, a microemulsion could be formulated with a total amount of surfactants of about 18 % at around 40°C. When C_{8}P_{2}E_{4} was combined with etheramine surfactant, the total amount of surfactants required to produce microemulsion at 25°C dropped to about 14 % [15].

In the present contribution we investigate the role of hydrophilic alcohol ethoxylates in formulating both the bicontinuous and the water in oil diesel microemulsions using nonionic alkyl poly glycol ethers. Phase behavior studied as a function of temperature and surfactant concentration will be presented in the form of the well known ‘fish’ diagram which is a vertical section taken from the ternary phase diagram at constant water/oil ratio. The emission from the formulated water in diesel fuel microemulsions during combustion in a 4 –cylinder engine is compared with those from neat diesel.

2. EXPERIMENTAL

2.1. Materials

The surfactants Berol 533 ( tri(ethylene glycol) mono undecyl ether, C_{11}E_{3} ) and Berol 535 ( penta(ethylene glycol) mono undecyl ether, C_{11}E_{5} ) and the hydrophilic alkylethoxylate C_{16-18}E_{140} ( M Wt ~ 6300 ) were all from Akzo Nobel surface Chemistry AB Sweden. Alfonic1214 GC-3 ethoxylate surfactant (C_{14}E_{3}) was from Sasol North.
America, Westlake, Louisiana, USA. All surfactants and co-surfactants were of technical grade and used as received. Polyoxyethylene (100) stearyl ether, C_{18}E_{100}, Brij S 100 (M Wt \sim 4670) was obtained from Sigma-Aldrich, Sweden. Heptane, 99 %, was obtained from Alfa Aesar, Sweden. European ultra lowsulphur diesel was obtained from a local gasoline station in Lund, Sweden. Millipore water was used in all formulations.

2.2. Preparation Of Microemulsion

1- The samples were prepared by weighing appropriate amounts of surfactant, co-surfactant and water in 10 mm glass test tubes with screw caps, shake with a vortex for 1-2 minutes. The appearance of the solution was checked visually for transparency and between cross polarizers for birefringence. After that heptane or diesel were added at water/oil wt. ratio of 1:1 for bicontinuous microemulsion and at 1:9 wt. ratio for w/o droplet microemulsion. The determinations of the phase diagrams were carried out in a thermostated water bath with temperature control up to 0.1 °C. Samples at a given compositions were checked as a function of temperature by visual inspection in transmitted light and between cross polarizers to detect the presence of anisotropic phases.

At low temperature o/w type coexists with excess oil (denoted by I). At high temperature, w/o type coexists with excess water (II). At intermediate temperature the three phasemicroemulsion appears (III). At higher surfactant concentrations, at the fish tail, the one phase region appears (IV). The surfactant concentration at which this first occurs is denoted by ~. Phase separation between the regions (I) and (II) is usually very slow in
such systems and may take weeks. In the present work these regions were not studied in
details, instead the investigations were directed towards the fish tail region where the
three- phase and the one phase regions meet.

2.3. Engine Test

A 4-cylinder, 4- stroke naturally aspirated Diesel engine (Perkins 1760 cc) was used as
the test engine for this study. The engine data is presented in table(1), the engine is
equipped with an hydraulic dynamometer ( Froude SG14, 110kW capacity), it is used to
measure the torque in N.m. A tachometer of Plint C102 type to measure its speed in
revelations per minute. A special sight glass with 50 ml volume fuel consumption using a
stop watch was used to measure fuel consumption in ml/s. A smoke meter of Poket
smoke 310-0332 type for measuring diesel smoke in percentage was connected through
exhaust manifold. And an exhaust gas analyzer of Kane OIML class 1(N 0356) was
used to measure exhaust emissions, namely, NOx, CO, and CO2.

Commercial diesel that is sold in the market was used for the comparison with the
microemulsion. The engine was run until it reached steady state for about 20 minutes,
then the throttle is set to the required value, ( for the test convenience 2 throttles were set
to compare performance, i.e 30% and 40% throttles respectively), the hydraulic
dynamometer which sets engine load was set to minimum, this gave the highest engine
speed at this throttle, the engine is left to settle down on this sitting, then readings are
taken, after that; load is increased slightly for a certain lower speed, the procedure is
repeated for 4 points between the maximum and minimum available speeds at each
throttle. A comparison between diesel and microemulsion at the same engine throttle and speed took place. Fuel consumption, torque, smoke, and exhaust gas emissions were measured.

3. RESULTS AND DISCUSSION

The phase behavior of nonionic surfactants, namely $C_{11}E_3$, $C_{11}E_5$ and $C_{14}E_3$ as a function of surfactant concentrations while varying temperature is described here. The role of two hydrophilic alkyl ethoxylates, $C_{16-18}E_{140}$ and $C_{18}E_{100}$ as co-surfactants is illustrated. The presence of such co-surfactants was required in order to formulate either the bicontinuous or the droplet microemulsions using a single surfactant.

3.1. Bicontinuous microemulsion Using $C_{11}E_3$.

Formulating the one phase microemulsions at water to oil wt. ratio of 1:1 using different surfactant concentrations (1-30%) was not successful even at high temperatures reaching 50°C. Instead more than one phase was present. The situation changed drastically when the co-surfactant was added in a mass fraction of co-surfactant in the surfactant/co-surfactant mixture, $\delta=0.10$.

The phase diagram of water-heptane-$C_{11}E_3$ at water:heptane wt. ratio of unity with $C_{16-18}E_{140}$ at $\delta=0.10$ is shown in Fig. 1. The one phase region denoted as IV was reached at a minimum surfactant concentration of 10% and temperature of 25°C. The temperature window at 15 wt % surfactant varied from 12.5 to 32.5°C.
When commercial diesel was used as the oil phase also with 1:1 ratio to water, the minimum surfactant concentration shifted to 11.5 wt. % at 25 °C and the temperature window at 15 wt % surfactant was between 20.0 to 32.5 °C as shown in Fig. 2. As expected, increasing the surfactant concentration to 25 wt % led to a much wider window ranging between 10 to 40 °C. Surprisingly, liquid crystal was not detected in either phase diagrams even at surfactant concentrations as high as 30 wt. %. The relatively short hydrophobic chain of surfactant and short hydrophilic head, E3, together with the nature of the co-surfactant seem to help the suppression of liquid crystal phase.

### 3.2. W/O Droplet Microemulsions

Water in oil microemulsions were formulated with C11 E3 at water to diesel wt. ratio of 1:9 using C16-18 E140 at δ=0.10 as a co-surfactant. Again only two phase emulsions were produced in the absence of the co-surfactant. Fig. 3 shows the minimum amount of surfactant needed to reach the one phase microemulsions to be also 11.5 wt. % at 25 °C with the temperature window widening between 1.0 to 42.5 °C at 23 wt. % surfactant. Again here no sign of liquid crystals appearance up to 25 wt. % surfactant.

The same formula was tried with changing the co-surfactant, reducing the ethylene oxide length to 100 while maintaining the length of the hydrophobic unit. Fig. 4 shows the phase diagram using C18E100 also at δ= 0.10. The minimum amount of surfactant is shifted to 12.5 wt. %, however the temperature window is wider, ranging between 0 to 47 °C at 19 wt. % surfactant.
As pointed out earlier, the interaction of these hydrophilic alcohol ethoxylates with nonionic surfactants were investigated in details (14). The long polyethylene oxide (PEO) can decorate the surfactant film, coiling into the aqueous domain. The hydrophobic part, with its relatively short chain has been found to be sufficient to anchor the PEO at the interface. It has been found that the longer the PEO chain, the smaller the minimum amount of surfactant needed to formulate the one phase microemulsions. The length of PEO was also found to influence the appearance of LC. For systems of water-decane-C_{10}E_{4} with a co-surfactant of very long PEO chains, no LC appeared up to 18 wt. % surfactant.

Reduction of the minimum amount of surfactant, needed to form the w/o microemulsions by adding various amounts of co-surfactant, C_{16-18}E_{140} is shown in Fig. 5. Increasing the amount of co-surfactant yielded only a moderate decrease in \( \delta \) specially beyond \( \delta = 0.10 \). This particular mass fraction of the additive in the amphiphilemixture have been also used before (11,14). The appearance of the bicontinuous diesel microemulsion at 11.5 wt. % C_{11}E_{3} with C_{16}E_{140} at \( \delta = 0.10 \) is shown in Fig. 6(A). A typical bluish transparent microemulsion resulted from such a combination. Meanwhile, the appearance of the w/diesel microemulsion system, Fig. 6(B), was so similar to the neat diesel, Fig. 6(C), that it was so difficult to distinguish between them by visual inspection. The formulation of w/diesel without the addition of co-surfactant resulted in a two phase system as shown in Fig. 6(D).
As stated earlier, increasing the surfactant chain length while maintaining the size of the head group will increase the efficiency of the surfactant. When C\textsubscript{14} E\textsubscript{3} was used to formulate w/diesel microemulsion with the addition of C\textsubscript{16-18} E\textsubscript{140} at $\delta=0.10$, $\sim=10.0$ wt. % and the microemulsion produced was stable at the temperature range of 10-45 at 15 wt. % surfactant. The size of the head group has a less pronounced effect than the chain length as was demonstrated earlier (16). However in our experiments, using C\textsubscript{11} E\textsubscript{5} surfactant to formulate the w/diesel microemulsion were not successful even with the addition of co-surfactant. Instead, the phase diagram was dominated by lyotropic liquid crystal. Fig. 7 shows a sample between cross polarizers with 20 wt. % surfactant and the co-surfactant C\textsubscript{16-18} E\textsubscript{140} at $\delta=0.10$.

3.3. Combustion Experiments

Diesel engine performance and emission levels using w/diesel microemulsion were measured and compared to that using neat diesel at the same throttle and speed. The obtained results showed a significant reduction in all types of emissions for various loads and speeds. NO\textsubscript{x} emissions presented a high range of percent reduction, between 16 and 54% at 30% throttle, and between 3 and 71% at 40% throttle (Figures 8 and 9), the low speeds showed a small reduction while at higher speeds; the reduction is very high, this might be due to reduction in maximum combustion temperature inside the cylinder as a result of short time combustion at each revolution.

Figures 10 and 11 shows the comparison between diesel and microemulsion for percent soot, the range of soot reduction using microemulsion is between 51 and 86% for the
30% throttle, and between 22 and 75% for the 40% throttle. In Figures 12 and 13, the CO2% is presented for the comparison between the two fuels, the reduction in CO2% is between 18 and 30%, at 30% throttle, and between 18 and 32% for the 40% throttle.

CO emission is a very limited pollutant in diesel engines. Despite its low values it was reduced with microemulsion at low speeds with both throttles. but with high speeds its value was slightly increased, this might be due to small combustion interval due to high speed, which leads to incomplete combustion. Figures 14 and 15 present CO values for both diesel and emulsion at 30 and 40% throttles.

Specific fuel consumption (sfc) is defined as the mass flow rate divided by the power output of the engine, the lower the specific fuel consumption the better the engine performance, for the comparison between microemulsion and diesel fuels there is a slight increase in (sfc) at low speeds, while a significant increase in (sfc) at high engine speeds, this might be due to the lower heating value of microemulsion than that of pure diesel. Figures 16 and 17 show the comparison.

4. CONCLUSIONS

This work shows that the addition of hydrophilic alcohol ethoxylates as a co-surfactant was necessary to initiate the formation of both continuous and w/diesel microemulsions in the formula of water, diesel and the nonionic surfactant C1Ej. Varying the mass fraction of co-surfactant in the surfactant/co-surfactant mixture, δ, between 0.05 to 0.16
gave approximately similar surfactant efficiency. In the present work microemulsions were formulated at $\delta=0.10$.

The length of ethylene oxide units in the surfactant head group was crucial to avoid the dominance of the liquid crystalline phase in the fish phase diagram. For C$_{11}$ E$_3$ surfactant, no liquid crystal was detected up to 25 wt. % surfactant in the temperature range between 0-50$^\circ$C. For C$_{11}$ E$_5$ surfactant, a single microemulsion phase could not be formed, instead liquid crystalline phase dominated the phase diagram specially at surfactant concentrations above 20 wt. %. When the length of the hydrophobic chain of surfactant was increased while maintaining the length of the head group, (C$_{14}$E$_3$), the efficiency was improved and the temperature window was wider at lower surfactant concentration.

Combustion experiments, using a diesel engine without any modification, performed on the water/diesel microemulsion showed emissions with lower levels of nitrogen oxides, soot, and CO$_2$, both at low and medium loads compared to neat diesel. At low speeds, CO emission was also reduced. Although there was a small reduction in engine efficiency, specially at high speeds, there is a significant advantages regarding environmental pollution. The reasonable amount of surfactant required to form w/diesel microemulsion provides realistic options in the search for alternative fuel that would reduce the level of major air pollutants resulting from diesel engines exhaust emission.

ACKNOWLEDGMENTS

This work was supported by the Swedish Research Council.
REFERENCES


Table 1. Test engine data

<table>
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<td>Stroke</td>
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<td>Compression ratio</td>
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</tr>
<tr>
<td>Maximum speed</td>
<td>3000 rev/min</td>
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</table>
Figure 1. Phase diagram of water-heptane-\( \text{C}_{11} \) \( \text{E}_3 \) at water to heptane wt. ratio of 1:1 with \( \text{C}_{16-18} \) \( \text{E}_{140} \) at \( \delta = 0.10 \).
Figure 2. Phase diagram of water-diesel-C$_{11}$ E$_3$ at water to diesel wt. ratio of 1:1 with C$_{16}$-18 E$_{140}$ at $\delta=0.10$. 
Figure 3. Phase diagram of water-diesel-C_{11}E_3 at water to diesel wt. ratio of 1:9 with C_{16-18} E_{140} at δ=0.10.
Figure 4. Phase diagram of water-diesel-C_{11}E_3 at water to diesel wt. ratio of 1:9 with C_{18}E_{100} at $\delta=0.10$. 
Figure 5. Reduction of minimum amounts of surfactant, ~, needed for solubilizing 10 wt. % of water in diesel by adding the co-surfactant C_{16-18} E_{140}.
Figure 6. Photos for samples representing bicontinuous microemulsion (A), water in diesel microemulsion (B), neat diesel (C), and a two phase mixture in the absence of the co-surfactant (D).
Figure 7. photo for a sample between cross polarizers prepared with C_{11} E_5 surfactant.
Figure 8. NOx levels as a function of engine speed at constant 30% throttle.
Figure 9. NOx levels as a function of engine speed at constant 40% throttle.
Figure 10. Soot levels as a function of engine speed at constant 30% throttle.
Figure 11. Soot levels as a function of engine speed at constant 40% throttle.
Figure 12. CO$_2$ levels as a function of engine speed at constant 30% throttle.
Figure 13. CO$_2$ levels as a function of engine speed at constant 40% throttle.
Figure 14. CO levels as a function of engine speed at constant 30% throttle.
Figure 15. CO levels as a function of engine speed at constant 40% throttle.
Figure 16. SFC levels as a function of engine speed at constant 30% throttle.
Figure 17. SFC levels as a function of engine speed at constant 40% throttle.