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## RESEARCH ARTICLE

### FORMULATION OF REVERSE MICELLAR FUEL MICROEMULSION: INVESTIGATION OF PHASE BEHAVIOUR, INTERFACIAL COMPOSITION, EFFECT OF CHAIN LENGTH OF CO-SURFACTANTS & CHARACTERIZATIONS

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#### ABSTRACT

Due to stringent environmental norms, a lot of research is going on to reduce exhaust emissions coming out from diesel engines. Diesel microemulsion is one of those alternate techniques. In fuel microemulsion, microexplosion triggers complete combustion of all the components and thus, high reduction in hazardous gases from diesel engines. The main focus of this research is to formulate and characterize diesel-based reverse micellar microemulsion. In a blend of two non-ionic surfactants, hydrophilic surfactant dominates the effect of lipophilic surfactant. The interfacial composition of fuel microemulsion was also investigated by Schulman's method of co-surfactant titration. During the investigation of the effect of chain length of co-surfactants, it was found that the efficiency of microemulsion increases with increasing chain length of co-surfactants. The chain structure of surfactant and co-surfactant also plays a paramount role in microemulsion formulation. The fuel properties like viscosity, cloud and pour points also get affected by chain length and structure of co-surfactants.

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#### INTRODUCTION

Diesel is a major contributor in today's energy source. The demand for the diesel engines has been increasing day by day due to their thermal efficiency, fuel economy, simple structure etc. Thus, they have been being a big competitor to petrol based energy sources. Diesel engines are widely used in heavy vehicles, marine transportation, power plants in industries. The exhaust gas, however, coming out of diesel engines contains the health and the environment hazardous components. These emissions consist of NO<sub>x</sub>, CO, particulate matters, ash etc. These exhaust gas emissions could be reduced by incorporating water in diesel. But, diesel and water, the immiscible components, would not give significant results. Thus, emulsification of diesel and water could be the better solution (Patil *et al.*, 2015a, 2015b; Lif and Holmberg, 2006; Chandra and Kumar, 2007). Microemulsion is an isotropic system in which two immiscible phases i.e. diesel (oil phase) and water are mixed with the help of surfactant and co-surfactant (amphiphile). Amphiphile helps to reduce the interfacial tension to make droplet size in the range of 10-100nm. Co-surfactants are short chain alcohols like butanol, pentanol, hexanol, octanol etc. They assist surfactant to lower interfacial tension to make a formulation more stable.

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Co-surfactant screens the electrostatic repulsion between the head groups of the surfactants and acts as a spacer. Nature of the surfactant used for a fuel microemulsion preparation is very crucial. Generally, biodegradable surfactant should be used. Most of the non-ionic surfactants are non-toxic and biodegradable. Additionally, non-ionic surfactants, unlike ionic surfactants, do not require any salt for formulating reverse micellar microemulsion. Further, the ionic surfactants lead to the emission of sulphur containing gases and particles due to the combustion of their group of SO<sub>4</sub><sup>-2</sup>, SO<sub>3</sub><sup>-</sup>. The co-surfactant also performs very important role in microemulsion formation. Therefore, it is very important to understand the composition of co-surfactant at interfacial region and at bulk region. Though it is highly recommended to evaluate the internal composition of W/O microemulsion, very few researchers have studied it (Moulik *et al.*, 2000; Bayrak, 2004; Paul and Nandy, 2007). The main focus of this study is to formulate single phase reverse micellar microemulsion of diesel using dilution method. The non-ionic surfactants are used for this study. The objectives of this work are i) to investigate the phase behaviour of reverse micellar fuel microemulsion ii) to determine the effect of surfactant and chain length of various co-surfactants i.e. alkanols (C<sub>4</sub>-C<sub>8</sub>) on microemulsion. iii) to investigate interfacial composition of fuel microemulsion. iv) to evaluate kinematic viscosity and pour and cloud points of water-in-diesel microemulsion.

## MATERIALS

Non-ionic surfactants Span 80 (Sorbitan monooleate), Tween 80 (polyoxyethylene-20 sorbitan monnooleate) and Brij 35 (polyoxyethylene-23 lauryl ether) were obtained from Croda Pvt. Ltd. The HLB values of these non-ionic surfactants are 4.3, 15 and 17, respectively. Alcohols like n-butanol (>99% purity) and i-butanol (>99% purity) were purchased from Thomas Baker Chemicals Pvt. Ltd and n-hexanol (>99% purity) and n-octanol (>99% purity) were procured from Himedia Laboratories. All these solvents were of AR grade and were used without further purification. Diesel (fuel no 2) was bought from local gas station. Doubled distilled water was used throughout the experiment.

## METHODS

### Microemulsion preparation

Microemulsion was formulated using dilution method i.e. Schulman's method of co-surfactant titration (Bowcott and Schulmann, 1955). The required quantity of surfactant/blend of surfactants, water and diesel were mixed properly. Two blends were prepared Span 80/Tween 80 and Span 80/Brij 35. Span 80 was kept constant in both the blends to check the role of hydrophilic surfactant in microemulsion formation. The alcohol, i.e. co-surfactant, was added using a burette till the turbid solution got cleared. This is the end point of microemulsion formulation. The assessment of microemulsion was checked by the solution absorbance measured at 320nm (Abulin *et al.*, 2004). There was a sharp decrease in the absorbance while titrating the mixture with alkanol. The amounts of mixed surfactant, diesel were 7 mmol and 70 mmol, respectively. The quantity of water was 10% (by vol.) of the final concentration.

### Phase behaviour study

For the phase behaviour study, we have adopted different method mentioned by (Nguyen *et al.*, 2010). The ratio of diesel to water was maintained at 1:1. The mass ratio of surfactant and co-surfactant (S/C) were kept constant at 1:2. The mixture containing a surfactant or a blend of surfactant (Span 80/Tween 80 or Span 80/Brij 80), co-surfactants (alcohols), were mixed in mixture of diesel and water at different proportions in vials. All the solutions were shaken gently and kept at constant temperature controlled bath to allow the systems to reach the equilibrium.

### Particle size analysis

All the microemulsion solutions that are formulated were subjected to particle size analysis to confirm the size of the emulsion droplets present in the formulation and to compare the effect of chain length of the alkanol on emulsion droplet size. The instrument used for this study was Hydro 2000MU. The analysis was carried out at 303 K.

### Viscosity measurement

The viscosity of fuel microemulsion was measured using Brookfield Viscometer- DV-E at 313 K. A sample was taken into beaker in such a way that the spindle should sufficiently be dipped into the solution without touching the base. The values obtained as dynamic viscosity in centipoises (cP) which then converted to kinematic viscosity in centistokes (cSt) by using equation 1.

$$v = \frac{\mu}{\rho} \quad (1)$$

Where  $v$  is a kinematic viscosity in (cSt),  $\mu$  is dynamic viscosity in (cP) and  $\rho$  is density of the solution.

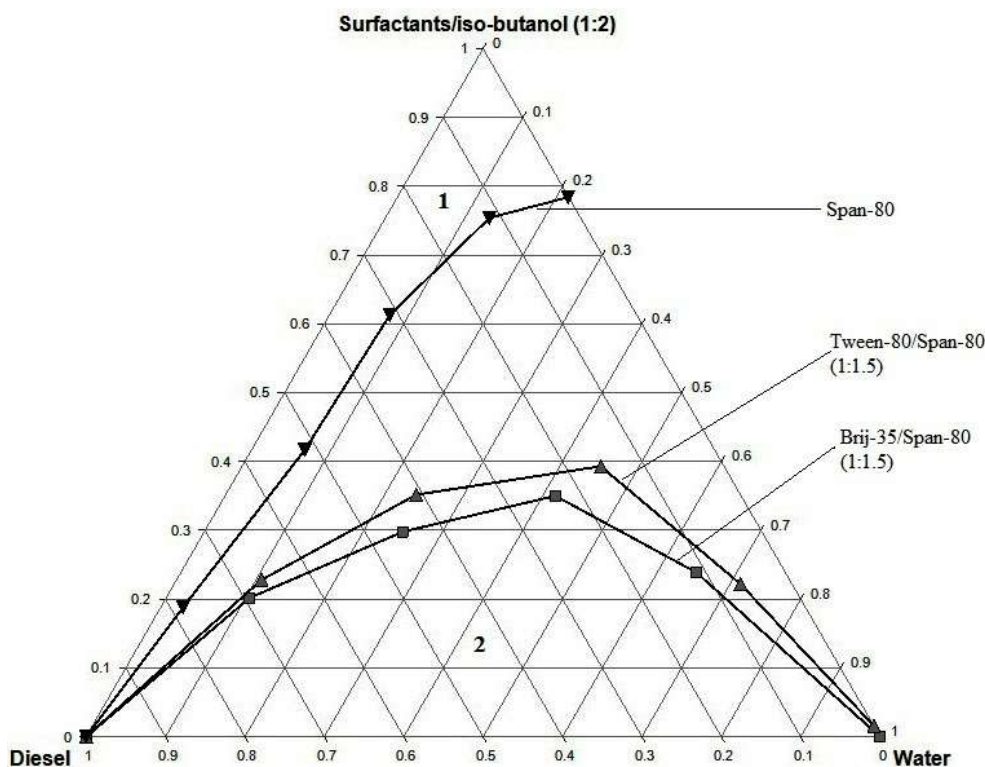


Figure 1. Pseudo-ternary phase diagram of fuel microemulsion containing diesel, water, blend of surfactants and iso-butanol (as co-surfactant) at 303 K. Surfactant: Co-surfactant (1:2)

## Cloud and Pour point

The cloud and Pour points are essential parameters in fuel. It is the temperature at which fuel stops flowing. They measured by placing the fuel samples at various low temperatures and observe the samples for cloudiness and solidification. When sample turns cloudy, the temperature was noted as the cloud point whereas the solidification temperature is the pour point of the fuel.

## RESULTS AND DISCUSSION

### Phase behaviour study

#### Effect of surfactant

The pseudo-ternary phase diagram of W/D fuel microemulsion was drawn by for different surfactant systems. Three surfactant systems were used for study viz. blend of Span 80 and Tween 80 (S80/T80), blend of Span 80 and Brij 35 (S80/B35) and Span 80. Since the hydrophilic, lipophilic values of the surfactants are significantly different, their interactions towards oil and water phases would be completely different. Therefore, we had examined the effect of hydrophilic surfactant on lipophilic surfactant's performance. Fig. 1 shows the pseudo-ternary phase diagram for W/D fuel microemulsion system containing diesel as an oil, water, different surfactants and iso-butanol as a co-surfactant.

The single phase microemulsion area is represented by number 1 and multilayer region is represented by number 2. As expected, the system containing single Span 80 surfactant forms much smaller monophasic area than that of blends. The hydrophilic surfactant significantly influences the performance of a lipophilic surfactant. It drags the separation line down and forms large monophasic region. Therefore, the amount of surfactant required to form a microemulsion is much lower for surfactant blends than that of single surfactants. We also compared the performance of Tween 80 and Brij 35 (both hydrophilic surfactants). The experiment was performed thrice and it's investigated that the amount of surfactant required to form a microemulsion is lower for Brij 35 than Tween 80.

Though Brij 35 contains 3 extra ethoxylated groups than Tween 80 or, in other words, Brij 35 is more hydrophilic (HLB-17) than Tween 80 (HLB-15), Brij 35 forms microemulsion at lower quantity that contradicts the statements made by other researchers (Dunn and Bagby, 1994; Rosen, 2004; Arpornpong *et al.*, 2014) which state that as the hydrophilicity increases, surfactant quantity required to form emulsion increases. This could be because of the chain structure of these surfactants. Brij 35 is a completely linear structure while Tween 80 is a branched structure with a ring sorbitan group present within the chain. This chain structure may dominate the effect of polyethoxylated (PEO) groups present within Tween 80.

#### Effect of co-surfactants and its interfacial composition

#### Important aspects of dilution method

In microemulsion system, the dispersed phase (water) is stabilized in continuous diesel phase with the help of surfactants and co-surfactant (alkanols). The distribution of alkanol between oil and the interface decides the extent of stability of the microemulsion. Thus, for fixed Brij 35/Span 80 surfactant blend, a critical concentration of alkanol is required to stabilise the microemulsion. Further addition of a oil phase destabilises the microemulsion system due to alteration of interfacial concentration of co-surfactant. The stability can be regained by the addition more co-surfactant. The following equations would help to calculate the transfer of co-surfactant from continuous oil phase to interface. The derivation of these equations is described in the literature (Moulik *et al.*, 2000; Bayrak, 2004; Paul and Nandy, 2007).

$$\frac{n_a}{n_s} = \frac{n_a^w + n_a^i}{n_s} + k \frac{n_o}{n_s} \quad (1)$$

$$K_d = \frac{X_a^i}{X_a^o} = \frac{\frac{n_a^i}{n_a^i + n_s}}{\frac{n_a^o}{n_a^o + n_o}} \quad (2)$$

$$\Delta G_t^o = -RT \ln K_d \quad (3)$$

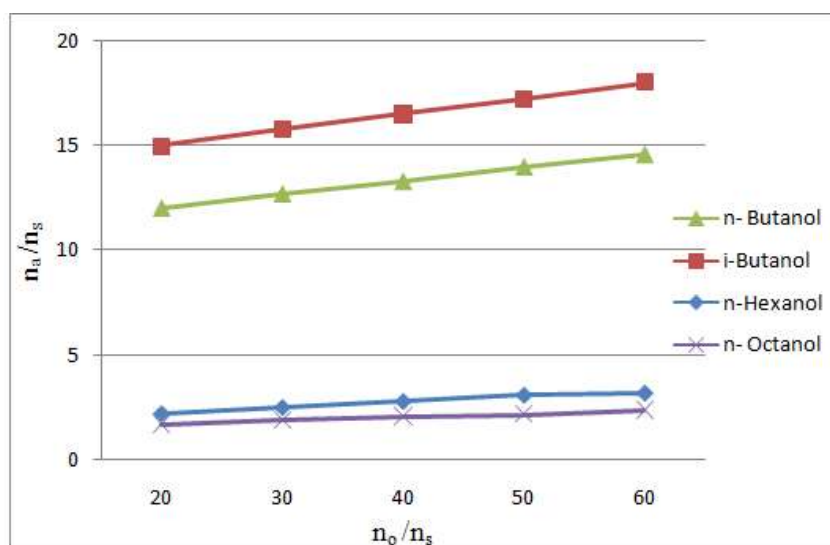


Figure 2. Graphical representation of  $\frac{n_a}{n_c}$  Vs  $\frac{n_o}{n_s}$  for diesel/water/blend of Brij35 and Tween80/alkanol system at 303K

Here,  $n_a$ ,  $n_s$ ,  $n_o$  are number of moles of alkanol, surfactant and diesel (oil), respectively. Furthermore,  $n_a^i, n_a^w, n_a^o$  are number of moles of alkanol at interface, water phase and oil phase, respectively.  $K_d$  is the distribution constant of alkanol.  $X_a^i, X_a^o$  are mole fractions of alkanol at interface and oil phase, respectively.  $\Delta G_t^o$  represents the standard Gibb's free energy of transfer of alkanol from the oil phase to interface.

### Investigation of interfacial composition

By considering the Equation 1 the results obtained from dilution experiment are summarised by plotting  $\frac{n_a}{n_s}$  verses  $\frac{n_o}{n_s}$ . Figure 2 represents the graphical representation of data investigated in dilution experiment at the temperature of 303 K. The graph is linear in nature. The value of slop ( $S$ ) and intercept ( $I$ ) can easily be obtained from Fig. 2. These results are summarised in Table 1. The solubility of alkanols (Carbon No. > 3) into the aqueous phase is negligible therefore it is ignored for all the alkanols. From the experiment, it was observed that the amount of  $I$  and  $n_a^i$  decreases with an increase in alkanol chain length which means that the quantity of alkanol required forming microemulsion decreases with an increase in alkanol chain length. Furthermore, it was investigated that the branched alkanol takes higher quantity than that of linear alkanol of same chain length. This could be due to the smaller penetration of branched alkanol molecule into the interfacial region. It can be proved from the distribution constant ( $K_d$ ) mentioned in Table 1. The distribution constant ( $K_d$ ) is smaller for iso-butanol than that of n-butanol.

**Table 1. Effect of alkanol chain length on interfacial and oil phase composition of W/D microemulsion**

Co-surfactant	$S (n_a^o/n_s)$	$I (n_a^i/n_s)$	$n_s (10^3)$ (mol)	$n_a^i (10^3)$ (mol)	$n_a^o (10^3)$ (mol)	$k_d$	$\Delta G$ (KJ/mol)
i-Butanol	0.74	14.28	7	99.96	5.18	2.198	-1.984
n-Butanol	0.65	11.37	7	79.59	4.55	2.333	-2.134
n-Hexanol	0.26	1.98	7	13.86	1.82	3.22	-2.946
n-Octanol	0.17	1.55	7	10.85	1.19	4.183	-3.605

**Table 2. Comparison of the size and size distribution of the five microemulsion formulations at 303 K**

Sample	Size Distribution		
	$D_{1\text{ mean}}$ (nm)/ (%Intensity)	$D_{2\text{ mean}}$ (nm)/ (% Intensity)	$D_{3\text{ mean}}$ (nm)/ (% Intensity)
n-butanol	30.28/81%	645.30 <sup>a</sup> /12%	4185 <sup>a</sup> /7%
iso-butanol	34.86/97.64%	-	4570 <sup>a</sup> /2.36%
n-pentanol	27.65/74%	486.71 <sup>a</sup> /15%	4470 <sup>a</sup> /11%
n-hexanol	23.75/70%	300 <sup>a</sup> /20%	2275 <sup>a</sup> /10%
n-octanol	19.39/65%	258 <sup>a</sup> /23%	2130 <sup>a</sup> /12%

$D_{1\text{ mean}}, D_{2\text{ mean}}, D_{3\text{ mean}}$  represent main droplet size distributions in the system. Blend of Span 80/Brij 35 (1:1.5), Surfactant= 7mmol, Co-surfactant till solution gets cleared, Water= 10% (by total volume).

The value of  $S$  and  $I$  are highest for i-butanol than all the other alkanols used for the experiment. This indicates that the number of moles of i-butanol in the interface and in the oil (diesel) phase were highest than other alkanols. The negative values of Gibb's free energy suggest that the microemulsion is a spontaneous process. The data from Table 1 indicates that the spontaneity in transfer of alkanol from continuous diesel phase into interface increases with increasing the chain length of alkanol. This means that the spontaneity of microemulsion formation is directly proportional to the chain length of the alkanol. On the conclusive note, the amount of alkanols required to develop microemulsion follows the following descending order:

iso-butanol > n-butanol > n-hexanol > n-octanol.

### Particle size analysis

All the microemulsion formulations were undergone particle size analysis to confirm and compare the effect of co-surfactants on the emulsion droplet size. All the emulsion formulation's droplet size lies between 20-200 nm which confirms the micro (1-200 nm) nature of the emulsion. Further, chain length of the co-surfactants has positive effect on the microemulsion droplet size. Higher chain alkanol develops smaller emulsion droplets as compared to low chain alkanol. Droplet size decreases with increasing the chain length of the alkanols. Though this is the case, the intensity of smaller droplets in higher chain alkanols is lower. This means that higher chain alkanols do not able to convert all the droplets in microemulsion to smaller size. The size distributions of all microemulsion formulations are presented in tabular form in Table 2.

<sup>a</sup> microemulsion size range (>200 nm) (Arpornpong *et al.*, 2014).

### Viscosity measurement

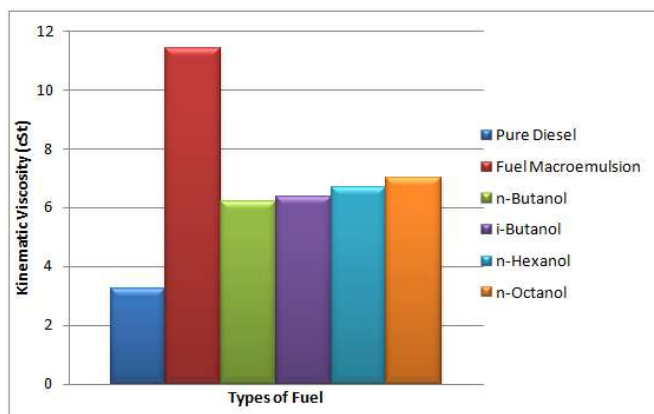
The viscosities of all the fuel microemulsion samples were analysed at 313K and compared with pure diesel and fuel macroemulsion (without co-surfactant). Fig. 3 shows the graphical representation of results obtained from viscosity measurement. The bar chart clearly indicates the viscosity of all fuel emulsion is higher than that of pure diesel. It is important to note that the fuel macroemulsion is more viscous than fuel microemulsions.

This means that co-surfactant lowers the viscosity of fuel emulsion. Furthermore, the viscosity of fuel microemulsion increases slightly (6.22 to 7.03 cSt) with an increase in co-surfactant chain length from C<sub>4</sub> to C<sub>8</sub>. Additionally, the branched co-surfactant forms more viscous fuel microemulsion than linear co-surfactant having same carbon number. In both the cases, the Vander Waals forces of hydrocarbon plays very important in Water-in-Diesel fuel microemulsion.

### Cloud and pour point

The fuel microemulsion, containing 70 mmol diesel, 7 mmol of a blend of Brij 35/Tween 80, iso-butanol and 10% (by volume) water, was formulated for cloud and pour point measurement.





**Figure 3. Kinematic viscosity of pure diesel, fuel emulsion (without co-surfactant) and fuel microemulsions containing co-surfactants with chain length (C<sub>4</sub>-C<sub>8</sub>)**

The cloud and pour point of water-in-diesel (W/D) microemulsion were measured by exposing the fuel microemulsion samples at various lowering temperatures. It was found that fuel microemulsion got cloudy at -1°C and cloudiness increased for further temperatures. The fuel microemulsion got completely solid at -3°C. Thus, the cloud and the pour point of the fuel microemulsion were -1°C and -3°C, respectively.

### Conclusion

The present study deals with the characterization of reverse micellar fuel microemulsion containing diesel as a continuous phase, water as a dispersed phase, a blend of surfactants (Span80/Tween80 and Span80/Brij35) and co-surfactants (alkanols). It is concluded from phase diagram that a blend of Span80/Brij35 is more efficient in developing a single phase fuel microemulsion than that of a blend of Span80/Tween 80 because of more linearity of Brij35 than Tween80. Hydrophilic non-ionic surfactants perform dominating role and lower the surfactant concentration required to form single phase microemulsion. The interfacial as well as oil phase composition was studied using Dilution method. The quantity of alkanol i.e. co-surfactant required to form microemulsion decreases with increasing the chain length of alkanol. The spontaneity of transfer of alkanol from the bulk phase to interface is directly proportional to alkanol chain length. n-octanol forms more spontaneous fuel microemulsion with minimum quantity. Linear chain alkanols possess more spontaneity than that of branched alkanol having same carbon numbers. Furthermore, the droplet size decreases with an increase in the chain length of alkanols. Additionally, co-surfactant has significant influence on a viscosity of the emulsion. By addition of co-surfactant the viscosity of emulsion decreases.

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