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Formulation of Microemulsions Based on Sugar Surfactant as an Alternative Fuel

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Abstract

Microemulsion systems that serve as water in diesel fuel were formulated using minimum amount of sucrose laurate at 25°C. Comparative experiments were also conducted using n-heptane. It was found that in order to formulate diesel and microemulsions a cosurfactant should be added. Alcohols such as 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol served as cosurfactants. The area of the one phase microemulsion region varies depending on the cosurfactant structure and composition. A continuous microemulsion region was observed with 1-butanol and 1-pentanol. Water solubilization capacity and thermodynamics as a function of alcohol chain length was determined.

KEYWORDS: water-diesel fuel, hydrophilic sugar ester surfactant, fuel microemulsion, alternative fuel

INTRODUCTION

Microemulsion, based on nonionic surfactants, has been extensively investigated^[1]. In almost all nonionic microemulsions the nonionic surfactants used were single surfactants. However, mixed nonionic surfactants were also used^[2]. Any co-surfactants used are usually grouped together with the surfactant at a fixed ratio and treated as a pseudo-component^[3]. It was found that sucrose esters were not able to form water-in-oil microemulsion with cosurfactants^[4].

Microemulsions have found numerous applications in different fields due to their unique properties that are low interfacial tension, high thermodynamic stability, high interfacial area, and the ability to dissolve immiscible liquids^[5]. On the microstructural level, the water molecules solubilized in the interior of the water pool have properties different from those of bulk water. This makes reverse microemulsion applicable to many fields such as water –diesel fuels^[6,7].

The investigations of different groups^[8-12] have shown that the increase of the oxygen content in blend fuels with additives such as ester, ether, acetals, alcohols etc. causes the reduction of soot emissions, hence the addition of water leads to a reduction of nitrogen oxide and soot emissions simultaneously, and an important criterion for a microemulsion to be used as fuel is that the one-phase region extends over a wide temperature range⁹. Nonionic surfactants based on aliphatic hydrocarbon tails, such as alcohol ethoxylates, fatty acid ethoxylates and sugar esters of fatty acids, are typical surfactant candidates^[10-12].

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Combining more than one surfactant can facilitate the formulation of microemulsion that is stable over a wide range of temperatures^[13]. Ding *et al.* investigated synergistic effect for the mixtures of polyglycerol esters of fatty acids (PGEFs) with sodium oleate solubilizing water in gasoline meanwhile they studied the effect of series of alcohols on water amounts solubilized in the microemulsion^[6].

In this study we aimed to prepare stable microemulsion formula that serves as water-diesel fuel and detect the optimum water solubilization capacity and thermodynamics of the formulated microemulsion systems.

EXPERIMENTAL

Materials

Sucrose laurate (sucrose dodecanoate) (L1695) was obtained from Mitsubishi-Kasei Food Corp., (Mie, Japan). n-heptane was obtained from Fink leman LTD Chemical. 1-pentanol, was obtained from MP Biomedicals, Inc. 1-butanol, 1-hexanol and 1-heptanol were purchased from Sigma Chemicals Co (ST.Louis,USA). Diesel was obtained from a local gas station in Bethlehem, Palestine. All components were used as supplied without further purification. Double distilled water was used.

Method

Pseudoternary Phase Behavior At Constant Temperature

The phase behavior of a system consisting of water, oil, mixture of surfactants and cosurfactant may be described in a phase tetrahedron whose apexes represent the pure components. 1g of a mixture consisting of oil, cosurfactant, and surfactant at different

weight ratios were prepared in culture tubes sealed with Viton lined screw caps. Titrating these samples with double distilled water which was added dropwise until its solubilization limit was reached. Vigorous stirring followed all of the aqueous phase additions on a vortex mixer. The time for equilibration between each addition was typically from a few minutes up to 24 h. Phase diagrams were investigated at 25°C. Detecting the number of phases was done by bare eyes. Anisotropic lamellar and hexagonal liquid crystal were determined by the cross polarizers and polarizing microscope. The single isotropic sample which appears dark under cross polarizers may be regarded as either cubic or micelle; which can be distinguished by its viscosity.

RESULTS AND DISCUSSION

Phase Behavior At Constant Temperature

Water/Sucrose Laurate /Oil Phase Behavior

Figure 1 presents the phase behavior of water /sucrose laurate /n-heptane ternary system at 25°C. Semisolid anisotropic liquid crystal phase was observed along N60 for water contents below 37 wt %. Then a multiphase region separates the liquid crystal region from a water-in-heptane bicontinuous one phase microemulsion region that extends to the water apex where an oil-in-water microemulsion region is observed.

Figure 2 presents the phase behavior of water /sucrose laurate /diesel oil system. At high surfactant content (above 60 wt %) liquid crystal phase is observed and an oil-in-water microemulsions are observed at high water and surfactant contents. The difference in behavior between n-heptane and diesel oil could be explained by the difference in

molecular volume of both oils. The molecular volume of n-heptane is 0.244 nm³/molecule, while that of diesel oil is 0.344 nm³ / molecule. The diesel oil is bulky, thick and contains a range of hydrocarbon molecules varying from C₁₀H₂₂ to C₁₅H₃₂ with an average molecular formula of C₁₂H₂₆ and an average density of 0.845 g/cm³, compared to n-heptane with a density of 0.6795 g/cm³ and although the sucrose laurate is a highly efficient surfactant it could not deal with diesel oil and cannot permit the formation of microemulsions with water. Similar behavior of bulky oils was reported elsewhere^[4,14].

Water/Sucrose Laurate /(Diesel/1-Butanol(1/1)) System Phase Behavior

In order to improve the solubilization of diesel oil in water sucrose laurate was mixed with another hydrophilic surfactant. Water in diesel microemulsion was formulated using single nonionic alkyl poly glycol ethers combined with hydrophilic alcohol ethoxylates (C18E100) at $\delta = 0.10$ as a co-surfactant^[13]. Small quantities of hydrophilic alcohol ethoxylates were added to surfactant caused a drastic shift of the one-phase region to lower surfactant concentration^[15].

Fig 3 presents the phase diagram of the water/sucrose laurate (L1695)/ (diesel/ 1-butanol (1:1)) at 25°C. The phase diagram indicates the presence of low viscous isotropic micremulsion and semisolid anisotropic LC regions. Oil keeps turbid region based on visual identification. As shown in the figure the one phase microemulsion region extends from the water-in-oil through a bicontinuous region to an oil-in-water region. Butanol is known of its effect in reducing the interfacial tension between oil and water as reported by Garti et al.^[17]. A chain length compatibility indicating that the mixture of oil and

butanol chain length is compatible with the chain length of the surfactant, something that leads to the improvement of surfactant/oil interactions and hence improved oil-in-water solubilization and the formation of continuous microemulsion region^[18,19,20].

Water/Sucrose Laurate (L1695)/ (Diesel Oil /1-Pentanol(1/1)) System Phase Behavior

Fig 4 presents the phase diagram of the water/sucrose laurate (L1695)/ (diesel/1-pentanol (1/1)) at 25°C. The phase diagram indicates the presence of low viscous isotropic and semisolid anisotropic LC regions. The remainder of the phase diagram represents the turbid region based on visual identification.

As shown in figure 4, the one phase microemulsion region with 1-pentanol as the cosurfactant is the wider compared to 1-butanol as cosurfactants. It is clear that the principle of chain length compatibility is the factor affecting the extent of mutual oil and water solubilization. Increasing the chain length of cosurfactant from 4 carbons in the case of 1-butanol to 5 carbons for 1-pentanol increases the area of the one phase region(microemulsions and liquid crystals). This means that the best hydrophobic interactions between diesel oil and surfactant are achieved in the presence of 1-pentanol. The OH group in 1-pentanol will mainly be at the interface something that enables the oil to arrange itself further from the interface interacting with the surfactant hydrophobic chain. The results in this study are in accordance with the previously published works^[18-20].

Water /Sucrose Laurate (L1695) /(Diesel Oil /1-Hexanol(1/1)) System Phase Behavior

Fig 5 presents the phase diagram of the water/sucrose laurate (L1695)/ (diesel/1-hexanol (1/1)) at 25°C. The phase diagram indicates the presence of L₁, L₂ and semisolid anisotropic LC regions. However, w/o microemulsion (L₂) was obtained at low surfactant concentration equals~ 20%. 1-hexanol interaction with the diesel oil and the surfactant reduced the interfacial tension between oil and water and enabled better arrangement of diesel oil molecules at the interface.

Water /Sucrose Laurate (L1695) /(Diesel Oil /1-Heptanol(1/1)) System Phase Behavior

Fig 6 presents the phase diagram of the water/sucrose laurate (L1695)/ (diesel/1-heptanol (1/1)) at 25°C. The phase diagram indicates the presence of L₁, L₂ and semisolid anisotropic LC regions. However, w/o microemulsion (L₂) was obtained at lower surfactant concentration (~ 10%) than that in case of 1-hexanol. 1-heptanol interaction with the diesel oil and the surfactant reduced the interfacial tension between oil and water and enabled better arrangement of diesel oil molecules at the interface.

Alcohol Chain Length N_A

The solubilization capacity of the systems studied above using different chain length alcohols ($N_A=4-7$), was estimated as the monophasic area (A_T) of the relevant pseudoternary phase diagrams, and shown in table 1. The solubilization behavior is shown in figure 7. The results show that the solubilization capacity expressed as A_T % of the system increases with the increase in chain length of alcohol up to n-pentanol, then decreases. These results are in accordance with Garti et al's results when sucrose monolaurate (L1695) surfactant was used^[19].

Thermodynamics Of Water Solubilization

The corresponding free energy of dissolution (ΔG°_s) at a constant temperature can be obtained from the relation $\Delta G^{\circ}_s = -RT \ln X_d$, where X_d is the mole fraction of the dispersed phase (in our case water in case of water-in-oil microemulsions, and diesel in case of oil-in-water microemulsions) and R is the gas constant (J/mol.K). The free energy of solubilization (ΔG°_s) for water-in-oil microemulsions studied were calculated and the values are given in Table 2. It is found that the ΔG°_s values decrease with water content in the water-in-oil microemulsions indicating that adding water to the water-in-oil microemulsions disrupts their organization. The ΔG°_s values increase with water content in the oil-in-water microemulsions indicating that adding water to the oil-in-water microemulsions improves their organization. In the water-in-oil microemulsion region, ΔG°_s values depend also on the alcohol carbon number. ΔG°_s values decrease with increasing the alcohol chain length indicating that the emulsification process becomes less easy with the increase in the chain length in accordance with Fanun's results^[21].

CONCLUSION

The addition of medium chain alcohol as a cosurfactant in the diesel /alcohol mixture is necessary to initiate the formation of water in diesel microemulsions in the formula of water, diesel and sugar ester nonionic surfactant.

Water in diesel microemulsions were formulated using 10 wt% of single sugar ester surfactant (L1695); combined with 1-pentanol as a co-surfactant. At last the reasonable

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amount of surfactant required to form water in diesel microemulsion provides realistic options in the search for alternative fuel that would reduce the level of both nitrogen oxides and soot in the emission.

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REFERENCES

- [1] Fanun, M. (Ed) (2009) *Microemulsions: Properties and Applications*, Taylor and Francis/CRC Press, USA, 144:349-385.
- [2] Fanun, M. (2008) *J. Dispersion Science and Technology*, 29:1043–1052.
- [3] Cosima, S. (2009) *Microemulsions Background, New Concepts, Applications, Perspectives*, 1st Ed., A John Wiley and Sons Ltd., Inc., New Delhi, India.
- [4] Ruiz, C. (2009) *Suger-Based Surfactant: Fundamentals and Applications, 1 st Ed.*, Taylor & Francis Group London.
- [5] Moulik, S. and Rakshit, A. (2006) *J. of Surface Sci. Technology*, 22(3-4):159-186.
- [6] Ding, Z., Hao, A., and Wang, Z. (2007) *Fuel*, 86: 597–602.
- [7] Kayali, I., Qamhieh, K., Olsson, U., Berment, L., and Strey, R., (2012) *J. Disp. Sci. and Technology*, 33: 516-520.
- [8] Lee, S., Speight, J., and Loyalka, S. (2007) *Handbook of Alternative Fuel Technologies*, 1st Ed., Taylor & Francis Group, LLC., New York, London.

- [9] Bemert, L., Engelskirchen, S., Simon, C., and Strey, R. (2009) *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem*, 54(1): 290-291.
- [10] Lif, A., Stark, M., Nydén, M., and Holmberg, K. (2010) *Colloids and Surfaces A*, 354:91–98.
- [11] Lif, A., and Holmberg, K. (2006) *Adv. Colloid Interface Sci.*, 123-126: 231–239.
- [12] Ochoterena, R., Lif, A., Nydén, M., Andersson, S., and Denbratt, I. (2010) *Fuel*, 89:122–132.
- [13] Kayali, I., Qamhieh, K., and Olsson, U. (2014) *J. Disp. Science and Technology*. (In press).
- [14] Fanun, M. (2007) *Journal of Molecular Liquids*, 133:22–27.
- [15] Frank, C., Frielinghaus, H., Allgaier, J., and Ichter, D. (2008) *Langmuir*, 24: 6036–6043.
- [16] Shakarnah, A. (2012) *Thesis presented to the graduate faculty of Al-Quds University*.
- [17] Garti, N., Aserin, A., Tiunova, I., and Fanun, M. (2000) *Colloids and Surfaces A*, 170:1 -18.
- [18] Bental, V., Shah, D., and O'cornell, J. (1980) *J. Colloid Interface Sci.*, 75:462.
- [19] Garti, N., Aserin, A., and Fanun, M. (2000) *Colloids and Surfaces A*, 164: 27-38.
- [20] Garti, N., Aserin, A., Ezrabi, S., and Wachtal, E. (1995) *J. Colloid Interface Sci.*, 169: 428.
- [21] Fanun, M. (2011) *Colloids and Surfaces A*, 382:226-231

TABLE 1. Solubilization capacity of the systems water /L1695 /(diesel /alcohol (1:1)) as a function of alcohol chain length at 25°C

Alcohol	wt(in grams) of total area of one phase region A_T	wt(in grams) of total area of phase diagram	A_T %
butanol	0.2819	0.6991	40.32
pentanol	0.3786	0.6126	61.80
hexanol	0.1952	0.6220	31.38
heptanol	0.1342	0.5952	22.54

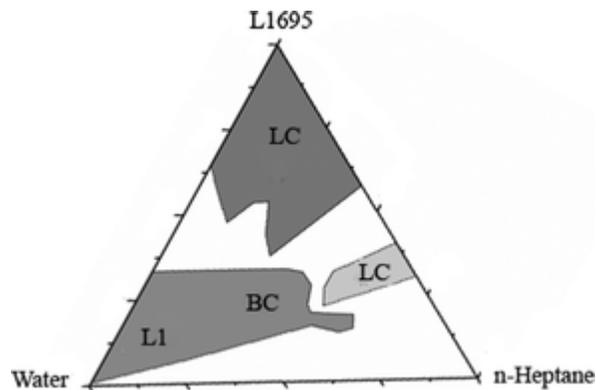
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TABLE 2. ΔG_s° values of the water / L1695/ diesel: alcohol (1:1) systems at 25°C for different alcohols at different water contents (L1695 /diesel:alcohol is 60:40 w/w)

			ΔG_s°	(kJ/mol)	
water wt%	composition	butanol	pentanol	Hexanol	Heptanol
	Water-in-oil microemulsions Water/ L1695/ Diesel: alcohol (1:1)				
5	5/57/19:19	2.43	2.29	2.18	2.10
10	10/54/18:18	1.44	1.34	1.27	1.21
15	15/51/17:17	1.00	0.93	0.87	0.83
20	20/48/16:16	0.75	0.69	0.65	0.62
	Oil-in-water microemulsions Water/ L1695/ Diesel: pentanol (1:1)				
80	80/12/4:4		13		
85	85/9/3:3		13.8		
90	90/6/2:2		15		
95	95/3/1:1		16.9		

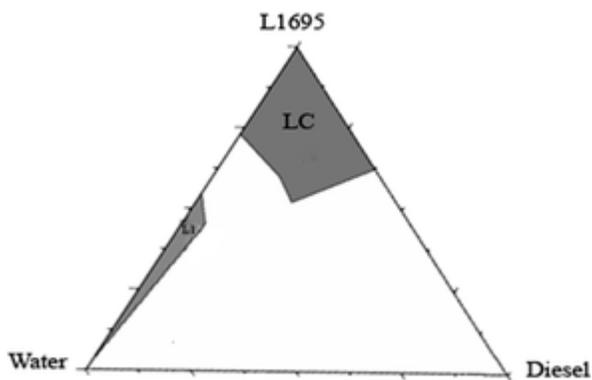
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FIG. 1. Phase diagram of water/sucrose laurate (L1695)/n-heptane system at 25°C. The LC. indicates a liquid crystal phase, BC indicates a bicontinuous microemulsion phase and L1 indicates an oil-in-water microemulsion.



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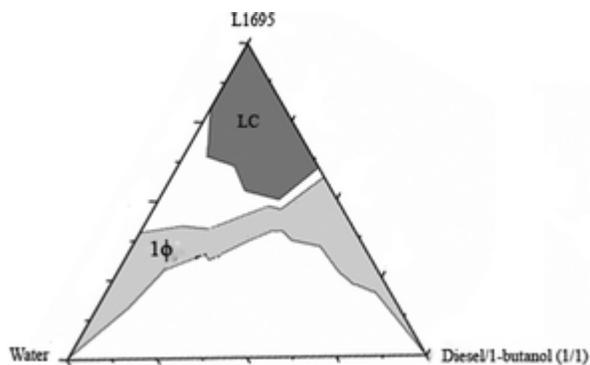
FIG. 2. Phase diagram of water/sucrose laurate (L1695)/diesel oil system at 25°C. LC indicates a liquid crystal phase, L_1 indicates an oil-in-water microemulsion region.



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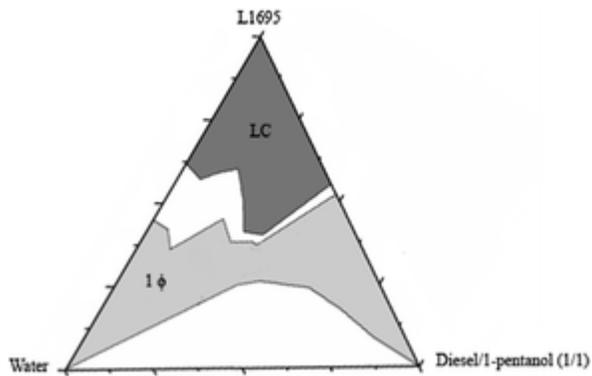
FIG. 3. Water /sucrose laurate (L1695) /(diesel/1- butanol (1/1)) phase behavior at 25°C.

LC indicates a liquid crystal region and 1ϕ indicates a continuous microemulsion region.



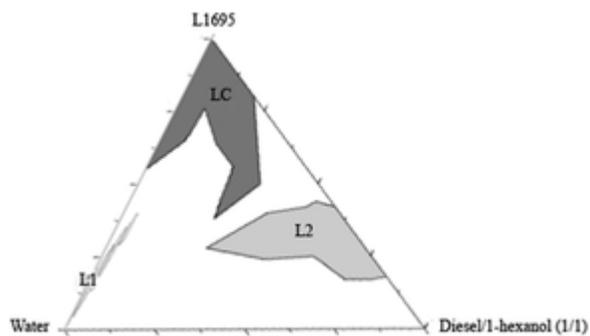
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FIG. 4. Water /sucrose laurate /(diesel oil /1-pentanol(1/1)) phase behavior at 25°C. The LC indicates a liquid crystal region with 1 ϕ indicates a microemulsion region.



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FIG. 5. Water /sucrose laurate (L1695) /(diesel/1-hexanol (1/1)) system phase behavior at 25°C. LC indicates a liquid crystal phase, L₂ and L₁ indicate water-in-oil and oil-in-water microemulsion region respectively.



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FIG. 6. Water /sucrose laurate (L1695) /(diesel /1-heptanol (1/1)) system phase behavior at 25°C. LC indicates a liquid crystal phase, L₂ and L₁ indicate water-in-oil and oil-in-water microemulsion region respectively.

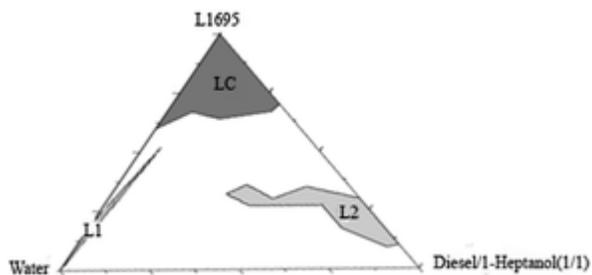


FIG. 7. Variation of monophasic area, $A_T\%$ vs the carbon number of alcohol, N_A 