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Water-in-gasoline microemulsions stabilized by polyglycerol esters

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Abstract

Synergistic effect for the mixtures of polyglycerol esters of fatty acids (PGEFs) [including triglycerol diisostearate (TGDIS), pentaglycerol distearate (PGDS), triglycerol monostearate (TGMS) and triglycerol monooleate (TGMO)] with sodium oleate solubilizing water in gasoline has been investigated. The effect of a series of alcohols on the water amounts solubilized in the microemulsion systems of TGDIS/sodium oleate/alcohol/gasoline/water has been studied. It was shown that the microemulsion system of TGDIS/sodium oleate/1-butanol/gasoline/water exhibited better behavior in solubilizing water than the other systems studied. The best weight ratio of TGDIS/sodium oleate was 6:4, in which the maximum solubilization capacity of water was 2.402 g at 16 °C, when the amount of the mixed surfactants and gasoline were 0.740 and 6.000 g respectively. In addition, the microemulsion system of TGDIS/sodium oleate/1-butanol/gasoline/water was more water soluble and less temperature sensitive, in comparison with the microemulsion system of TGDIS/lauryl polyoxyethylene (9) ether (AEO_9)/gasoline/water.

Keywords: Water-in-gasoline microemulsion; Polyglycerol esters; Solubilization capacity

1. Introduction

According to Danielsson and Lindman [1], microemulsions are single isotropic and thermodynamically stable liquid solutions. The formation of microemulsions usually involves a combination of oil, water, surfactant and cosurfactant. There are three kinds of microemulsions: oil-in-water microemulsion (normal microemulsion), bicontinuous microemulsion and water-in-oil microemulsion (reverse microemulsion). The water molecules solubilized in the interior of the water pool have properties different from those of bulk water. This makes reverse microemulsions applicable to many fields such as fuels [2], pharmaceuticals [3–5], metal extractions [6,7], media for chemical reactions [8,9] and nanoparticle syntheses [10–12].

Since the combustion characteristics of such fuel has been found to be considerably different from the unmodified one [13]. Differences in combustion between microemulsion fuel and fuel have been attributed to the presence of low molecular weight immiscible compound such as water in fuel as well as to the structural changes, which accompany micellization of the surfactants employed. Water incorporated in fuel vaporizes during combustion and acts as a heat sink. This lowers the peak combustion temperatures, which results in a drastic reduction in nitrogen oxides (NO_x) emissions. In the case of combustion of fuel in an internal combustion engine, water is also expected to assist in fuel atomization due to microexplosions, which occur during the evaporation of the water inside droplets of fuel. This reduces the particulate soot formation and improves the combustion efficiency [14,15]. There are many reports about microemulsion fuel systems containing anionic, cationic or nonionic surfactant, usually containing a mixture blend of surfactants [16–18]. In previous studies AOT [sodium di (2-ethylhexyl) sulfosuccinate], CTAB (cetyltrimethylammonium

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bromide), and D0821 [dialkyl (C_8–C_{10}) dimethylammonium chloride] exhibit high solubilization capacity of water in microemulsion fuel, however combustion of AOT results in sulfur oxide in the vapor, whereas combustion of CTAB and D0821 leads to nitrogen oxides [16].

Polyglycerol esters of fatty acids (PGEFs), which can be prepared from renewable resources such as plant or animal oils, have received much attention in pharmaceutics [19,20], food [21,22], cosmetics [23,24], and detergent [25]. Extensive studies of PGEFs will lead to better utilizations in industrial applications.

In most cases, right blend of low and high HLB surfactants can lead to the formation of microemulsions. In this study, sodium oleate was selected as a high HLB surfactant because of its convenience, its eco-friendly, nontoxicity, and especial its ability of neutralizing sulfur acids formed by the oxidation of sulfur in gasoline during combustion [14]. Lauryl polyoxyethylene (9) ether (AEO_9) was also chosen as a high HLB surfactant because of its convenience and its eco-friendly. Four PGEFs (including TGDIS, PGDS, TGMS and TGMO) (nonionic surfactants with lower HLB values) were studied to investigate their synergistic effects with sodium oleate (a anionic surfactant with a higher HLB value) and 1-butanol in solubilizing water in gasoline. The effect of alcohols (1-butanol, 2-butanol, 1-propanol and 2-propanol) on the solubilization capacity of water in the microemulsion systems of TGDIS/sodium oleate/alcohol/gasoline/water was also investigated, because alcohol is sometimes required to adjust the spontaneous packing property of microemulsion, or to increase the fluidity of the interfacial film, thus allowing the formation of microemulsion [26]. In addition, the effect of the total concentration of the two mixed surfactants, TGDIS/sodium oleate and TGDIS/AEO_9, and temperature on the solubilization capacity of water in the two microemulsion systems of TGDIS/sodium oleate/1-butanol/gasoline/water and TGDIS/AEO_9/gasoline/water were studied.

2. Experimental

2.1. Materials

Triglycerol diisostearate (TGDIS), pentaglycerol distearate (PGDS), triglycerol monostearate (TGMS), and triglycerol monooleate (TGMO) were gifts from Jinan Synwin Chemical Company. Their physical properties were listed in Table 1. The structures of PGEFs were shown in Fig. 1. Commercial grade gasoline (a mixture of straight and branched hydrocarbons with a boiling point rang of 70–205 °C, density of 0.7248 g ml^{-1} at 20 °C) was provided by SINOPEC Jinan Refinery. AEO_9 was a commercial grade material and used as such. Sodium oleate was reagent grade and used without further purification. Ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 1-pentanol were all reagent grades. Deionized water was used in this study.

Table 1
Physical properties of PGEFs

PGEFs	Appearance	Melting point (°C)	HLB[a]
Triglycerol diisostearate (TGDIS)	Pale yellow liquid	–	4.5
Pentaglycerol distearate (PGDS)	White solid	54–55	6.8
Triglycerol monostearate (TGMS)	White solid	55–56	8.4
Triglycerol monooleate (TGMO)	Pale yellow liquid	–	8.4

[a] HLB value of each PGEF was calculated from Griffin's equation [27].

R_1-CO-(OCH_2-CHOH-CH_2)$_m$-$OCOR_1$

R_2-CO-(OCH_2-CHOH-CH_2)$_n$-OH

Fig. 1. Structures of PGEFs. TGDIS, R_1: i-$C_{17}H_{35}$, m: 3; TGMS, R_2: n-$C_{17}H_{35}$, n: 3; PGDS, R_1: n-$C_{17}H_{35}$, m: 5; TGMO, R_2: $C_{17}H_{33}$, n: 3; m, n: the average number of glycerol.

2.2. Determination of the solubilization capacity of water and the optimum amount of alcohol used in the microemulsion system of PGEF/sodium oleate/alcohol/gasoline/water at different weight ratios of PGEF/sodium oleate

At different weigh ratios of PGEF/sodium oleate, the amount of water (W_{water}) solubilized and the optimum amounts of alcohol ($W_{alcohol}$) used in the microemulsion system of PGEF/sodium oleate/alcohol/gasoline/water were determined according to the literature [17].

At the weight ratio 6:4 of TGDIS/sodium oleate, and TGDIS/AEO_9, which was the optimum weight ratio of the two mixed surfactants, the effect of the total concentration of the mixed surfactants (TGDIS/sodium, and TGDIS/AEO_9) on the solubilization capacity of water in the two microemulsion systems of TGDIS/sodium oleate/1-butanol/gasoline/water and TGDIS/AEO_9/gasoline/water was investigated as described in the literature [17]. Of the TGDIS/AEO_9/gasoline/water system, no alcohol was used, because the presence of alcohol had little effect on the solubilization capacity of water (figure not shown). The experiments above all were done at temperature of 16 ± 0.5 °C.

At the optimum weight ratio 6:4 of TGDIS/sodium oleate, and TGDIS/AEO_9, W_{water} in the two microemulsion systems of TGDIS/sodium oleate/1-butanol/gasoline/water and TGDIS/AEO_9/gasoline/water was examined at 20, 25, 30, 35, 40, 45 ± 0.5 °C according to the literature [17], in order to investigate the effect of temperature on the solubilization capacity of water.

In all experiments, the amount of gasoline was fixed at 6.000 g. The appearance, viscosity and flow properties of the microemulsion system were so similar to 100% gasoline that it was difficult to distinguish one another by visual examination.