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Surfactant-free alternative fuel: Phase behavior and diffusion properties

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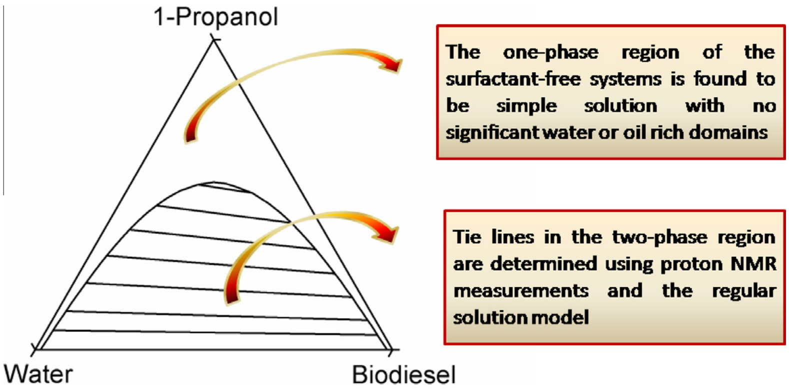
GRAPHICAL ABSTRACT



The one-phase region of the surfactant-free systems is found to be simple solution with no significant water or oil rich domains

Tie lines in the two-phase region are determined using proton NMR measurements and the regular solution model

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ABSTRACT

Phase behavior of the three components, 1-propanol, water and oil is studied at 10, 25, and 40 °C. Biodiesel, limonene and diesel are used as oil phases. NMR self-diffusion measurements are performed to investigate the microstructure of the one-phase regions. Tie lines in the two-phase regions are determined both by proton NMR analysis and compared with theoretical calculations. NMR self-diffusion results for the different components in these systems do not show any sign of confinement or obstructions, demonstrating these mixtures to be structureless solutions. A good agreement between the experimental and calculated phase behavior is obtained. The determined tie lines in the two-phase regions show higher affinity of 1-propanol to water than to oil.

1. Introduction

The concern over environmental pollution and the expected depletion of fossil fuel have raised the attention toward finding alternative renewable fuel. Several promising non-fossil oxygenated fuels with the potential of reducing the pollutant emissions like soot, NO_x, CO and CO_2 have been investigated. The methyl ester of fatty acids made from different vegetable oils, commonly known as biodiesel, is one of the candidates that actually has been tested as an alternative and as an additive to ordinary diesel [1]. The fatty acid composition corresponds to that of its parent oil. Several specifications like cold-flow, cetane number and oxidative stability can vary according to this difference in composition [2]. For example, the cetane number, which is related to the ignition quality, increases with increasing chain length and saturation of the parent fatty acids. Viscosity, which is the main reason why oils can't be used directly as fuel and have to be esterified, usually increases with increasing number of carbons in the chain and decreases with increasing unsaturation. Oxidative stability

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depends on the number of double bonds present in the unsaturated fatty acids. Oleic acid, which constitute 52–65% of rapeseed oil, has relatively higher oxidative stability than linoleic acid, which is a main constituent of soybean oil. Therefore the enrichment of biodiesel with methyl oleate would improve its stability [3]. Alcohol is another attractive non-fossil oxygenated renewable resource [4]. The use of ethanol as a 10 % dry ethanol (E10) in gasoline is a common practice in order to reduce vehicle exhaust emissions. Blending ethanol with diesel reduces the soot formation substantially [5]. However adding ethanol to diesel can also lower the cetane number, decrease the energy content and have limited miscibility at lower temperatures. Adding a suitable emulsifier will solve the problem of miscibility and will contribute positively toward improving the cetane number [4].

Limonene oil extracted from citrus peel has also been investigated as a renewable source of fuel. Combustion experiments with 30 % orange oil-diesel blend resulted in reducing the CO, the hydrocarbon and smoke emissions while increasing NO_x emissions [6].

The use of water in fuel emulsion and microemulsion in combustion engines has also been investigated [7]. The presence of water facilitated atomization of fuel through the microexplosions, therefore improving the combustion efficiency. For water in diesel microemulsion, significant reduction in soot, NO_x, CO and CO_2 emissions were observed compared to neat diesel [8]. On the nanometer length scale, microemulsion has a structure with oil and water domains separated by surfactant films at the interface [9]. Microemulsion may consist of water droplets in oil (W/O), oil droplets in water (O/W) or they can be bicontinuous, in which both oil and water form domains that are continuous in all three dimensions. Due to the high interfacial volume in microemulsion, high amount of surfactants are needed in the formulation. In addition, the surfactant to be used should burn readily without forming smoke and should not contain nitrogen or sulfur [10].

Surfactant-free microemulsions have also been suggested. Using conductivity measurements and visual examination, a micro emulsified ternary solution composed of water, hexane and 2-propanol was indicated [11]. A single-phase region composed of water, oleic acid and n-propanol was also studied [12]. The microstructure of the single-phase region investigated by electrical conductivity, showed the existence of three different micro regions, water in oleic acid, a bicontinuous and oleic acid in water region. The results were further confirmed by freeze-fracture and cryogenic transmission electron microscopy. The ternary system water/ethanol/octanol has been studied extensively by various scattering methods [13–15]. A microemulsion region, composed of water rich and octanol rich domains, respectively, has been proposed in the vicinity of the plait point. Concentration fluctuations, observed in small angle scattering as an Ornstein–Zernike behavior, increases upon approaching phase separation. Solutions near a plait point are clearly non-ideal. Whether the proposed “surfactant-free microemulsions” are not simply enhanced concentration fluctuations in near-critical conditions has not yet been clearly demonstrated. Mixtures of octanol, ethanol and water have also been studied by molecular dynamics simulations [16]. Recently, work has been extended to other polar solvent [17].

NMR self-diffusion studies can provide a reliable method to examine the internal structure of microemulsions [18]. In fact, the first experimental evidence that microemulsions may be bicontinuous came from NMR self-diffusion data [19]. The term bicontinuous has been used to imply the case where large fractions of both oil and water molecules form channels extending over macroscopic distances in all three dimensions. Multi-component self-diffusion measurements can also provide direct insight into other types, namely W/O and O/W droplet microemulsion. The solvent forming the continuous phase will have a diffusion coefficients near that of neat liquid while the other solvent confined to discrete, disconnected droplets will have a much lower diffusion coefficients due to confinement and obstruction of molecules.

In addition to the above three types of microemulsions, a fourth possibility of structureless solutions may exist when weak amphiphiles are being used [20]. Physical properties for these mixtures, such as surface tension and diffusion coefficients, have been found to be similar to those of conventional microemulsion [21]. Structureless microemulsion has also been reported for some non-aqueous systems even in the presence of surfactant [22,23]. Using self-diffusion coefficient measurements, the non-aqueous glycerol/hexanol/SDS isotropic system did not show any obvious confinement characteristics and the authors suggested a structureless simple solution. The same conclusion was also given for the four-component system with the added *p*-xylene.

Surfactant free mixtures of water, hexane and isopropanol have been used as a medium for enzymatic reactions [24]. In the ternary phase diagram, the one phase transparent region was suggested to consist of 3 different sub regions: a normal ternary solution with no detected microstructure, a microemulsion composed of aqueous microdroplets dispersed in hexane-rich continuous phase and an intermediate region of H-bonded aggregates of water and isopropanol dispersed in hexane-rich medium [25].

In this article, we have investigated the ternary phase diagrams of 1-propanol, water and oils. NMR self-diffusion measurements are conducted to elucidate the microstructure of the one-phase regions. Proton NMR measurements, as well as theoretical calculations, are used to determine the tie lines in the two-phase regions for these systems. NMR self-diffusion has been used previously to characterize self-assembly in near-critical mixtures [26], where it may be particularly useful as the self-diffusion often is not influenced by the composition fluctuations.

2. Materials and methods

2.1. Materials

1-propanol (99.8%) and R(+)-Limonene, technical grade (90%) were purchased from Sigma–Aldrich, Sweden. European ultra low sulfur diesel was obtained from a local gasoline station in Lund Sweden. The equivalent composition for diesel is $C_{12}H_{23}$. The fatty methyl ester, biodiesel, from rapeseed oil, with methyl oleate as its main constituent, was from Tecosol (Ochsenfurt, Germany). Millipore water was used in all experiments.

2.2. Methods

2.2.1. Ternary phase diagrams

In order to determine the location and boundaries of the different phases on the ternary phase diagrams, samples were prepared by adding water drop wise to pre-weighed mixtures from the other two components in glass test tubes with screw caps. Vigorous stirring followed all the aqueous phase additions using a vortex mixer. The time for equilibration between each addition was typically 1–2 min. Phase diagrams were investigated at 10, 25 and 40 °C. The number of phases were detected by bare eyes and between cross polarizers.

2.2.2. NMR self-diffusion experiments

Self-diffusion coefficients were measured by the stimulated echo pulsed field gradient (PGSE-NMR) method using a Bruker AVANCE II 200 spectrometer with Bruker field gradient probe operating at proton resonance frequency of 200 MHz. The temperature was kept at 25 °C with an accuracy of ±0.1 °C. The spin-echo amplitude, I, of a given NMR resonance is given by [27]:

$$I = I_0 \exp(-kD) \tag{1}$$