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Properties and Phase Behavior of Water-in-Diesel Microemulsion Fuels Stabilized by Nonionic Surfactants in Combination with Aliphatic Alcohol

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ABSTRACT: We investigate the properties and phase behavior of the water−diesel fuel−Neonol AF 9-6/2-ethylhexanol system, which is regarded as a promising microemulsion fuel. A pseudoternary diagram of the system has been obtained. In the diesel fuel/water (DF/W) ratio ranging from 98:2 to 50:50 and the emulsifier concentration of 8−40 vol %, a region of microemulsions has been distinguished, generating particular interest as an alternative fuel. In the region under study, a reverse micellar phase L_2 has existed predominantly. Fish-cut diagrams have been obtained for the DF/W ratios in the emulsifier concentration−temperature coordinates. An increase in the water fraction in microemulsions significantly has narrowed the range of their stability. The critical changes of microemulsion properties have been identified using the fish-cut diagrams. We have established the empirical relationship among the phase inversion temperature, the emulsifier concentration in the phase inversion point, and the water fraction in microemulsions.

1. INTRODUCTION

Microemulsions are multicomponent liquid dispersion systems, characterized by thermodynamic stability. They are a mixture of two immiscible liquids (most often hydrocarbon compounds and water), stabilized by a surfactant and an additional component (cosurfactant). The diameter of dispersed-phase droplets in microemulsions varies from 1 to 100 nm, most often 10−50 nm, making them clear or slightly turbid liquids.[1−3] Over the last 70 years, the fundamentals of microemulsions have been widely studied alongside their practical applications, e.g., using them to increase oil recovery,[4−6] as new fuel types,[7−12] in the synthesis of nanoparticles,[13,14] in the technologies of pharmaceutical and cosmetic product preparations,[15−18] etc.

In this study, we focus on the properties and phase behavior of water-in-diesel microemulsion systems that can be used as an alternative fuel. Today, using fuel microemulsions, as compared to conventional fuels, is known to reduce the level of harmful emission, increase combustion efficiency, and save hydrocarbon fuel.[19−21] Microemulsion fuels (MFs) decrease the temperature of exhaust gases by 20−60% and cut down the emission of solid particles by 40−77% and of nitrogen oxides and carbon monoxide by 70−75%.[11,12,22] The increasing interest in water-containing diesel fuels is explained by the fact that adding water minimizes sooting due to the so-called microexplosions that eventually increase the efficiency of fuel−air mixture and overall combustion.[23,24] Another benefit of water-in-diesel microemulsions is that they can be used in diesel engines and power facilities without major modifications of fuel feeder systems, as opposed to the method of direct injection of water into the combustion chamber.[25]

Despite all of the advantages of MFs, fuel samples available today have one important disadvantage—high-temperature susceptibility. In the past, researchers neglected the issue of MF stability under changing external factors, in particular, temperature. At the same time, it is well known that microemulsions, especially those stabilized by nonionic surfactants, are highly susceptible to it. Over recent years, this issue has attracted considerable interest; studies have been published on the stability of MFs at temperatures other than room temperature.[3,9,11,26,27] When researching microemulsions as an alternative fuel, one should not forget about the significant temperature fluctuations in vast areas where diesel engines and power facilities are traditionally used. For countries and regions with cold and arctic climate (Russia, Canada, and Scandinavia), the low-temperature properties of liquid fuels and controlling them are of special significance. For diesel fuel, they involve such parameters as pour point, cloud point, and cold filter plugging point, which are regulated by industrial and state standards. The said properties characterize the fuel free flow ability or capability to remain a homogeneous system. From the physical and chemical perspectives, they are conditioned by an increase in the viscosity and crystallization of n-paraffins with a decrease in temperature. In the case of MFs, along with the above factors, there are additional phenomena that can be considered harmful for the fuel. They can be summarized as follows: a homogeneous microemulsion

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(Winsor IV) separates into two or three liquid phases (Winsor I, II, or III) under temperature variation. While negative factors like a critical increase in viscosity or crystallization of n-paraffins reveal themselves for common hydrocarbon fuels only at low temperatures, MFs have an additional problem of phase separation at high temperatures, as well.[27−30] This means that there is not only the lower but also the upper operating temperature range for such fuels. The macrophase separation of fuel composition is much unwanted and can have even more serious consequences than cold filter plugging or paraffin deposition. This indicates the high importance of understanding the phase behavior of MFs under varying temperatures.

Figure 1 presents the so-called fish-cut diagram of a microemulsion system, which is a vertical section through the phase prism at constant water−oil ratio.[31] Kahlweit's fish-cut diagrams are often used when analyzing the phase behavior of the water−oil−surfactant systems vs temperature.[31−34] The curves in the diagram show the boundaries of phase regions. When studying fuel microemulsions, the "tail" of the fish is of the most considerable interest. These are the curves coming from the phase inversion temperature point (PIT) and separating the single-phase region of microemulsion existence (Figure 1).

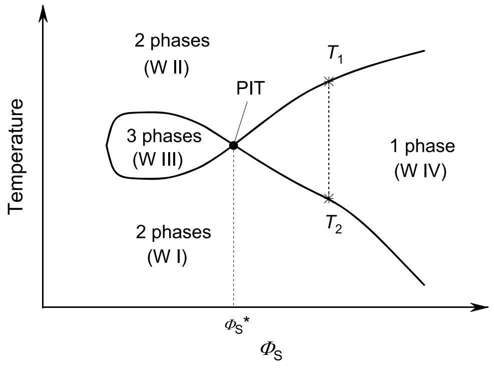


Figure 1. Schematic fish-cut diagram of the water−oil−surfactant system: PIT, phase inversion temperature; Φ_S, surfactant concentrations; Φ_S*, surfactant concentrations at PIT; T_1 and T_2, upper and lower cloud points, respectively; W I, II, III, IV, types of microemulsions using the Winsor's classification.

Thus, the operating temperature range of MFs is limited by the range of Winsor IV (W IV) microemulsion existence, i.e., a single-phase region (Figure 1). This range is usually much more narrow than that of a similar hydrocarbon fuel since the latter actually has only a lower limit. MF stability is affected by the following factors: the nature of the surfactant and cosurfactant, type of hydrocarbon, the composition of the water phase, and the component ratio in a microemulsion.[5,6]

Despite a wide variety of surfactants, the concept of MFs to be burned in the combustion chambers of power plants places significant constraints on the composition of such fuels. Obviously, using anionic surfactants, containing the ions of any metals, is totally futile since a large amount of noncombustible solid residue is formed under their thermal destruction, which will inevitably deposit on the chamber walls. It is also unacceptable to use the compounds with sulfur and halogens because of the high toxicity and corrosiveness of their combustion products. Nitrogen-containing compounds should be used with care as they increase the risk of the high content of NO_x in exhaust gases. In this study, we use commercial Neonol AF 9-6 as a nonionic surfactant. It is an oxyethylated isononylphenol, containing six oxyethyl groups on average. 2-Ethylhexanol is used as a cosurfactant. These compounds are basic chemicals that can be considered as components for promising MFs.

Thus, the aim of this study is to determine the properties and phase behavior of water-in-diesel MFs, stabilized by the Neonol AF 9-6−2-ethylhexanol system, with the main focus on the influence of the microemulsion composition on their behavior under varying temperatures.

2. EXPERIMENTAL METHODS

2.1. Materials. The following components were used to prepare MF: diesel fuel (EURO, class 3, type I−III (winter) according to the RF state standard GOST R 52368-2005); distilled water with the specific conductivity of no more than 5 μS/cm; surfactant—Neonol AF 9-6, isononylphenol poly(ethylene glycol)ether (PEG-6), $C_9H_{19}C_6H_4O(C_2H_4O)_6H$ (commercial, TU 2483-077-05766801-98, PJSC "Nizhnekamskneftekhim", Russia); cosurfactant—2-ethylhexanol (commercial, GOST 26624-2016, AO "Sibur-Khimprom", Russia). Table 1 presents the properties of diesel fuel.

Table 1. Properties of Diesel Fuel

parameter	values
(1) density at 25 °C, kg/m^3	830
(2) kinematic viscosity, m^2/s·10^6, at temperature	
25 °C	2.780
40 °C	2.065
60 °C	1.515
80 °C	1.160
(3) flash temperature in the closed crucible, °C	60
(4) cloud point, °C	−21

2.2. Phase Diagram. In this study, we used the volume ratios of the components. To plot a phase diagram, we used a visual titration method,[28,29] in which the samples of the diesel fuel−water mixture of a known volume and with a fixed component ratio were titrated with an emulsifier. In the paper, by "emulsifier" we always mean the Neonol AF 9-6−2-ethylhexanol mixture with a volume ratio of 9:1. The terms "surfactant" and "cosurfactant" are used exclusively for Neonol AF 9-6 and 2-ethylhexanol, respectively. The diesel fuel−water ratios (DF/W) were varied as follows: 98:2, 95:5, 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, and 10:90. The emulsifier concentration was from 0 to 50 vol %. All of the experiments were conducted at 25 ± 0.5 °C. The reagents and laboratory glassware were preliminarily equilibrated in a thermostated air bath to 25 ± 0.5 °C. The sample temperature was measured using an LT-300 electronic laboratory thermometer with a measurement range of −50···+300 °C and an accuracy of ±0.05 °C.

In this paper, the concept of "water-in-diesel microemulsion" or simply "microemulsion" implies homogeneous (on the macrolevel) optically clear systems composed of water, diesel fuel, and emulsifier, irrespective of their structures on the microlevel.

2.3. Viscosity. The kinematic viscosity was determined in accordance with GOST 33768-2015, using a capillary Ubbelohde-type viscometer with capillaries of diameters of 1.16 and 1.31 mm. The relative error of estimation was ±1.0%. A Termex KRIO-VIS-T-06-01 thermostat was used for temperature control.

2.4. Density. The density of microemulsions was measured at a temperature of 25 ± 0.1 °C by a pycnometer using bidistilled deionized water as a standard.

2.5. Size of Particles. The size of particles was analyzed using the dynamic light scattering technique and a Zetasizer Nano ZS particle size analyzer (Malvern Instruments Ltd., Great Britain). Before preparing the samples for particle size measurement, diesel fuel was preliminarily filtered using a Swinny steel filter holder (Millipore Corp.) through a poly(vinylidene fluoride) membrane with pores of a size of 0.22 μm (Millipore Corp.). The measurements were conducted at 28 °C.

2.6. Fish-Cut Diagram Plotting and Heat Stability. By "temperature stability of a microemulsion" or just "stability of a microemulsion" we mean the ability of a fuel composition to exist as a single-phase clear liquid under medium temperature variation.

Fish-cut diagrams were plotted using the method of long-term conditioning of microemulsion samples at constant temperatures. Five sets of microemulsion samples were prepared with a fixed DT/W ratio (98:2, 95:5, 90:10, 80:20, and 70/30) and a different content of emulsifier in each set. The samples were placed into glass test tubes that were submerged into the thermostat bath and kept at a certain temperature for no more than 5 days with an accuracy of temperature control of ±0.1 °C. The condition of the samples was visually determined after each experiment. The results for each of the sets were marked as points on a graph in the emulsifier concentration−temperature coordinates. We obtained a map consisting of a number of points, reflecting the phase condition of microemulsions and forming regions with one, two, or three phases, accordingly. The obtained regions were separated by the resulting curves. The research was conducted in the temperature range from −21 to 80 °C. A low-temperature, liquid Termex KRIO-VIS-T-06-01 thermostat was used for temperature control (with a mixture of propylene glycol with water at a 50:50 ratio as an operating liquid).

3. RESULTS AND DISCUSSION

3.1. Phase Diagram and Properties. The phase behavior of water−oil−surfactant system is commonly presented as ternary-phase diagrams. In our case, a "pseudoternary" diagram is used. It has water, diesel, and a mixture of a surfactant (Neonol AF 9-6) with a cosurfactant (2-ethylhexanol) at a constant ratio in its angles. Experimentally, we determine the single-phase and multiphase regions of the system condition and the transition boundary between them, marked as a solid line in the diagram.

The phase diagram is a typical example of a system formed by a hydrophobic surfactant at a temperature different from that of a hydrophilic−lipophilic balance. Such systems are characterized by an elongated two-phase region (emulsion), dilating from the angle of oil. This is a laminating Winsor II type microemulsion, in which the water and hydrocarbon phases coexist, the latter containing microdroplets (swollen micelles) of water.[6]

In the study of MFs, a single-phase region rich in oil (diesel fuel in our case) is of the most considerable interest. The fraction of water in such compositions should normally be about 20−30%,[12] while the fraction of surfactants (emulsifier), as the most costly component, should be minimal. Thus, in this study, we research a region limited by the maximum fraction of water (30−35%) and emulsifier (about 40%); the maximum DF/W ratio is 98:2. In the lower part of the diagram, the above region borders the phase separation curve. In Figure 2, the region under study is shown with dashed lines. It is clear from the diagram that stable single-phase microemulsions in the region rich in DF can only be formed at low emulsifier concentrations (8−15%), which is a definite advantage of the surfactant−cosurfactant system, as compared to other suggested systems.[7,8,12]

Viscosity is an important performance characteristic of any liquid fuel. It determined its pumpability and has a significant influence on atomization in combustion chambers. In this study, we have determined the kinematic viscosity of water-in-diesel microemulsions for different compositions within the region under study. The obtained results are presented as a gradient field on the ternary-phase diagram (Figure 3a). It has been shown that the viscosity of MFs in the region under study is slightly influenced by the emulsifier concentration and is primarily determined by the fraction of the water phase in them, which is proved by the viscosity gradient that is parallel to the constant emulsifier concentration lines. Numerically, kinematic viscosity rises from 6−10 mm²/s (for microemulsions with a DF/W ratio = 98:2) to 150−160 mm²/s (DF/W = 50:50).

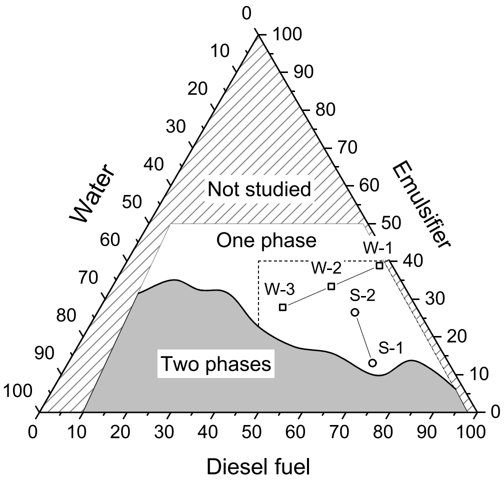
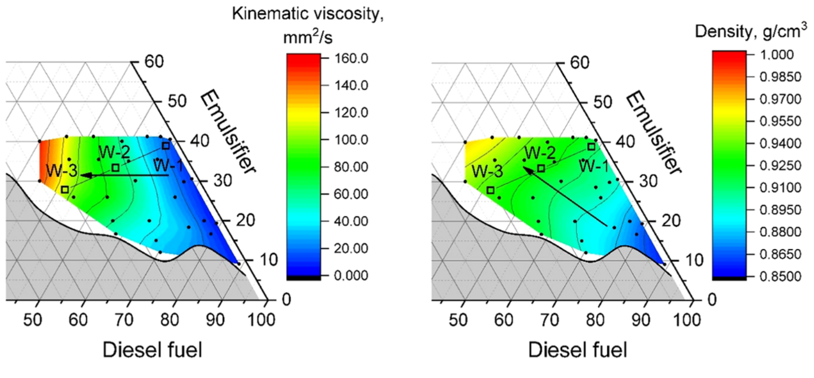


Figure 2. Pseudoternary diagram of water−diesel−Neonol AF 9-6/2-ethylhexanol (9:1) at 25 °C.

In a similar way, the density of water-in-diesel microemulsions was presented as a function of their composition (Figure 3b). In this case, the density gradient is parallel to the line, corresponding to the constant water/emulsifier ratio, i.e., the density of microemulsions increases with an increase in the content of both water and emulsifier. This result is quite logical as it reflects an increasing contribution of components with the highest density to the overall density of the microemulsion system.

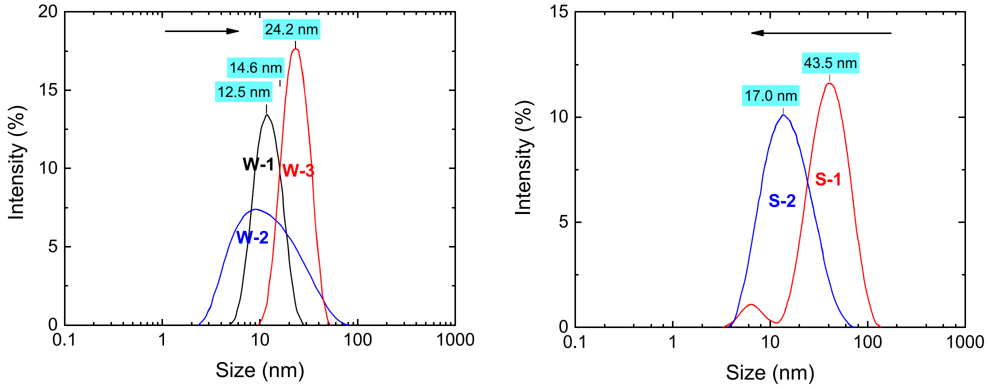
Using the dynamic light scattering technique, we determined the size of particles for two sets of microemulsion compositions. The first set of samples ("W-1", "W-2", and "W-3") had a constant DF/surfactant ratio = 60:40, the water fraction of water in them was 2.9, 16.7, and 30.6%, respectively. The DF/surfactant ratio in the second set of samples ("S-1" and "S-2") was constant at 80:20; the samples contained 13.0 and 26.5% of emulsifier, respectively. The actual compositions of the described microemulsions are marked with the corresponding points in Figure 2. The distribution of particles by size and the average hydrodynamic radii are presented in Figure 4.

The results in Figure 4a indicate that the average hydrodynamic radius of particles almost doubled at a higher content of water in the microemulsions. Thus, the increase in viscosity, as described above (Figure 3a), is explained by the bigger size of micelles, as well as the higher fraction of the dispersed (water) phase. For the set of "S" samples (Figure 4b), a higher concentration of the emulsifier resulted in a decrease in the average particle size. The composition S-1, located near the boundary, separating a single-phase region from a two-phase one (Figure 2), has the biggest size of droplets. This is because it contains the lowest amount of the emulsifier; thus, the size of micelles is closest to "critical". The



(a) (b)

Figure 3. Kinematic viscosity (a) and density (b) of MF (at 25 °C): gradients are shown with arrows.



(a) (b)

Figure 4. Distribution of microemulsion droplets by size (25 °C): the arrows demonstrate the increment in water (a) and emulsifier (b) contents.

differences in the appearance of the S-1 and S-2 samples demonstrate it, as well. The above effect stems from the balance between the number of surfactant and water molecules in the system. The smaller the size of the dispersed-phase droplets, the larger the specific surface area of the interface, and, consequently, a large amount of the surfactant is required for an adsorption layer to form and for the efficient stabilization of the dispersion system. Thus, a higher surfactant-to-water ratio contributes to the formation of smaller globules.

The obtained results suggest that the region under study is chiefly presented by a reverse micellar phase L_2, in which water is in the micelle centers, surrounded by a shell of surfactant molecules.

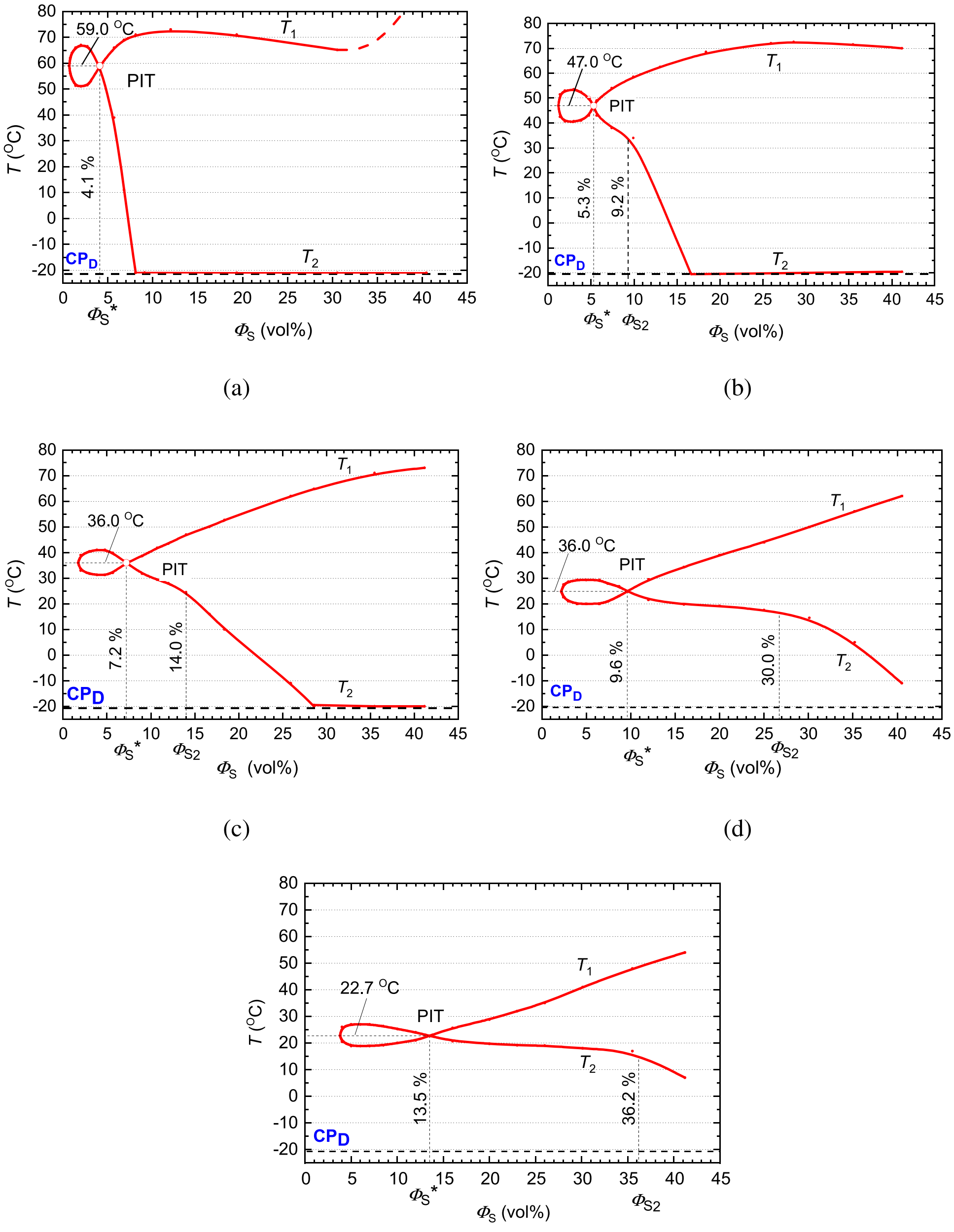
3.2. Temperature Stability: Fish-Cut Diagrams. We plotted fish-cut diagrams for the MFs under study, in which we defined the upper (T_1) and lower (T_2) cloud points, limiting the temperature range of their existence, vs the emulsifier content. The results are presented in Figure 5 as a set of diagrams with a constant DF/W ratio. We researched five fixed DF/W ratios: 98:2, 95:5, 90:10, 80:20, and 70:30.

The results make it possible to draw a few conclusions about the appearance and position of T_1 and T_2 curves on the diagrams. A common trend is a gradual narrowing of the temperature range of MF stability with an increase in the water-to-diesel fuel ratio in them. The widest range of stability (under 90 °C) is demonstrated by microemulsions with the lowest relative fraction of water (DF/W = 98:2, Figure 5a). The stability range of samples with the maximum content of water (DF/W = 70:30, Figure 5e) in the region under study does not exceed 50 °C.

The minimum recorded temperature, at which a fuel microemulsion exists as a homogeneous system, corresponds to the cloud point of the winter DF, used in the research (Table 1). Below this limit, it seems impossible to produce a stable single-phase microemulsion (CP_D line in Figure 5). We have not established the nature of this new emerging phase; therefore, turbidity can be caused by the destruction of the microemulsion and formation of a new liquid phase (emulsion formation), as well as by the crystallization of paraffins in the diesel fuel as a solid phase (slurry formation). The second version is more probable. In any case, the results indicate that the temperature stability of a fuel microemulsion as a single-phase system is also determined by the properties of DF, as its main component.

Another important point is the asymmetry of T_1 and T_2 curves relative to PIT, which is especially true for microemulsions with a low relative fraction of water. In this case, the PIT is much closer to the T_1 curve than to T_2. A further decrease in the DF/W ratio results in a gradual decrease of the PIT and the T_1 curve, as well as a simultaneous fast evolution of the T_2 curve, making the microemulsion stability region more symmetrical.

Interestingly, the maxima of the upper cloud point curves tend to shift to higher emulsifier concentrations as the relative fraction of water in the microemulsions increases. In the emulsifier concentration range under study, these maxima can



(a) (b)

(c) (d)

(e)

Figure 5. Fish-cut diagrams of water-in-diesel microemulsions at different DF/W ratios: (a) 98:2; (b) 95:5; (c) 90:10; (d) 80:20; and (e) 70:30. PIT, phase inversion temperature; T_1 and T_2, upper and lower cloud points, respectively; CP$_D$, cloud point of the basic DF; Φ_S*, emulsifier concentration in the phase inversion point; and Φ_{S2}, emulsifier concentration in the region of sharp fall in T_2.

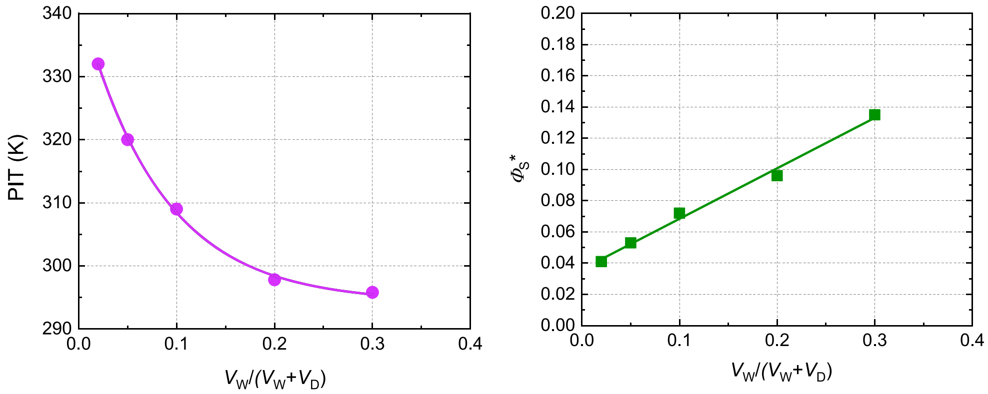
be explicitly observed in samples with DF/W ratios 98:2 and 95:5 (Figure 5a,b).

For further analysis, in the diagrams, we have distinguished characteristic regions and points, in which there is a critical change of microemulsion properties.

3.2.1. PIT Point and the Corresponding Emulsifier Concentration (Φ_S).* The significance of this point is clear from the diagrams. It shows the lower limit of the emulsifier concentration (compositions containing a surfactant and a cosurfactant at a given ratio), required to obtain a single-phase microemulsion (W IV). The results presented in Figure 5 show that a decrease in the DF/W ratio shifts the phase inversion point in the diagram toward a lower temperature and a higher corresponding Φ_S*; thus, when changing the DF/W ratio from 98:2 to 70:30, the PIT decreases by almost 35 °C (from 59.0 to 22.7 °C), whereas Φ_S* rises from 4.1 to 13.5%.

Then, we plotted the PIT and Φ_S* curves vs $V_W/(V_W + V_D)$, where V_W and V_D are the volumes of water and diesel fuel, respectively (Figure 6). This ratio does not take into account the emulsifier concentration and shows the fraction of water relative only to the total amount of water and hydrocarbons. Therefore, the curves obtained characterize the influence of the DF/W ratio on the position of the PIT in the phase diagram.

The analysis of the curves obtained shows that, in the system under study, an increase in the relative fraction of water results in a nonlinear decrease in the PIT (expressed in K, Figure 6a). This function is very close to exponential decay, like



(a) (b)

Figure 6. PIT (a) and Φ_S* (b) vs $V_W/(V_W + V_D)$.

$$\mathrm{PIT} = \mathrm{PIT}_0 + ab^{(V_W/V_W+V_D)} \tag{1}$$

where PIT_0 is a threshold phase inversion point, to which the value of this equation approaches at $V_W/(V_W + V_D) \to 1$; a and b are coefficients, whose values are probably determined by the nature and ratio of the surfactant and cosurfactant, as well as by the properties of the basic diesel fuel. In our case, we determined $\mathrm{PIT}_0 = 294.2$ K; $a = 48.1$; $b = 4.3 \times 10^{-6}$ (adj. $R^2 = 0.99793$).

Φ_S* vs $V_W/(V_W + V_D)$ ratio is an increasing linear function (Figure 6b), which, in the concentration range under study, can be described by the following equation

$$\Phi_S^* = c + d\left(\frac{V_W}{V_W + V_D}\right) \tag{2}$$

where c and d are the coefficients also determined by the value and ratio of the surfactant and cosurfactant, as well as by the properties of the diesel fuel. It was determined that $c = 0.036$ and $d = 0.323$ (adj. $R^2 = 0.98998$).

The obtained eqs 1 and 2 can be used to predict PIT and Φ_S* in the water−DF−oxyethylated nonylphenol system, provided that we know the coefficients in these equations. The practical importance of the phase inversion point in microemulsion fuel compositions is that stable microemulsions with a minimal content of emulsifier are only possible in the region of the angle, limited by the PIT, T_1, and T_2 curves.

3.2.2. Region of Sharp Drop in T_2. This region corresponds to the emulsifier concentrations above which the lower cloud point of the microemulsions under study falls sharply. This effect is clearly seen in the fish-cut diagrams (Figure 5), where the slope of most of the T_2 curves changes markedly with a higher content of the emulsifier. The emulsifier concentration, Φ_{S2}, corresponding to such transition, can, in most cases, be determined quite accurately, e.g., by an abrupt change of the $\partial T_2/\partial \Phi_S$ differential. Curves of a similar appearance can be seen in some studies, e.g., refs 31−33, 35. They investigate the phase behavior of water−oil−nonionic surfactant systems vs temperature. However, we have been unable to find any explanation of this effect. At the same time, microemulsion systems were described in which such effects were not observed.[11,34,36] Building on Kahlweit's research,[31−33] we can assume that in the region of Φ_{S2} concentrations, there is a transition from the micellar phase L_2 to the lamellar phase L_α, often observed in such cases. According to Kahlweit, for certain microemulsion compositions, this phase can border the T_2 curve. It is known that the phase transformations in microemulsions are accompanied by a sharp change in the intensive system parameters, e.g., viscosity, specific conductivity, etc. Turning to the data we obtained for the viscosity of microemulsions (Figure 3a), it is clear that such transformations are likely to occur. Moving along the lines, connecting the microemulsion compositions with a constant DF/W ratio, toward a higher emulsifier concentration, we can see an interval with a nonlinearly rising viscosity, like it is in the case of the samples with the DF/W ratio = 90:10 or 80:20. Also, the position of these intervals on the scale of emulsifier concentrations roughly coincides with the Φ_{S2} values obtained. This may suggest that a new liquid crystal phase emerges. Although the physical and chemical mechanisms of the discussed phenomena are not completely clear, it is highly interesting in terms of practical applications when producing MF. This interest is explained by the fact that, above the Φ_{S2} limit, it is possible to obtain microemulsions with the widest range of thermal stability.

The analysis of the diagrams in Figure 5 shows that the Φ_{S2} concentration, above which the temperature range of microemulsion stability is significantly wider, depends largely on the DF/W ratio. The microemulsions, containing the minimum relative fraction of water (DF/W = 98:2), have no distinct region of a sharp fall in T_2. It is clear from Figure 5a that, in this case, the lower cloud point decreases rapidly right after the phase inversion point. In all of the other cases, we can see a proportional growth of Φ_{S1} with an increase in the relative fraction of water in microemulsions.

Then, we analyzed the results in terms of the composition and structure of micelles. For that, a dimensionless parameter η was introduced, which numerically equals the ratio of the number of H_2O moles (n_W) to that of surfactant moles (n_S)

$$\eta = \frac{n_W}{n_S} \tag{3}$$

The η parameters were calculated for the microemulsion compositions in the characteristic regions and points specified above: η*, for the phase inversion point; η_2, for the region of a sharp drop in the lower cloud point. The η parameter indirectly characterizes the critical degree of micelle swelling, at which certain phase or structural transformations occur in microemulsions. Figure 7 presents η vs $V_W/(V_W + V_D)$.

The data shows that the correlation is strong for the phase inversion point. As the relative fraction of water increases, η

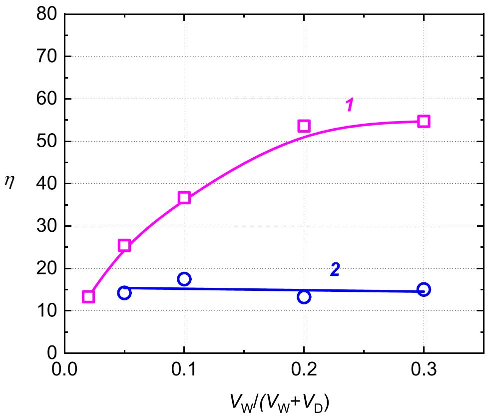


Figure 7. η vs $V_W/(V_W + V_D)$: 1, for the phase inversion point; 2, for the region of sharp fall in T_2.

changes from approximately 15 to 55 water molecules per surfactant molecule. Also, η grows significantly only at the initial curve interval, at a relatively low content of water in microemulsions. Then, the curve approaches a plateau, and η no longer correlates with the relative fraction of water. The analysis of η as a function of DF/W for the region of a sharp drop in the lower cloud point reveals interesting results. According to Figure 7, the obtained correlation can be described by a straight line, almost parallel to the X-axis. This signifies that the said effect does not influence the DF/W ratio and can be observed in all of the cases, when there are about 15 H_2O moles on average per surfactant mole, or about 2.5 H_2O molecules per oxyethyl unit of the surfactant molecule, providing that one molecule of Neonol AF 9-6 contains six such units on average. It is safe to assume that this pattern is a property of oxyethylated surfactants.

Thus, the obtained curves and empirical equations can be used to predict the properties of MF, prepared using nonionized surfactants.

4. CONCLUSIONS

The novelty and, consequently, the contribution of the study to the energy and fuel technologies lies in exploring the phase behavior of the water−diesel fuel−Neonol AF 9-6/2-ethylhexanol system, which is regarded as a promising microemulsion fuel, in a wide range of temperatures, including low negative temperatures, up to −20 °C. A pseudoternary diagram was plotted for this system, and the boundaries of single-phase (microemulsion) and multiphase regions were defined. In the single-phase region, a microemulsion area was distinguished, which is of great interest for the practical application of alternative fuels. This area is limited by the range of the diesel fuel/water ratio from 98:2 to 50:50 and the emulsifier concentration of 8−40 vol %. It was shown that, in the region under study, the kinematic viscosity gradient of microemulsions is along the lines of the constant emulsifier concentration, whereas the density gradient is parallel to the line of the constant water/emulsifier ratio. We assume that, in the microemulsion region under study, a reverse micellar phase L_2 exists predominantly and the growth of viscosity is caused by an increase in the fraction of the dispersed phase and micelle size. Fish-cut diagrams have been obtained for a number of diesel fuel/water (DF/W) ratios in the emulsifier concentration−temperature coordinates. Using them, we analyzed the temperature ranges of microemulsion stability vs the content of the emulsifier it contains. It has been shown that an increase in the relative fraction of water in microemulsions significantly narrows the range of their stability and reduces the PIT. On the fish-cut diagrams, we have identified characteristic regions and points, corresponding to the critical changes of microemulsion properties (phase inversion point and sharp fall in T_2). This study shows that the curves of the PIT vs the relative fraction of water in microemulsions $(V_W/(V_W + V_D))$ are described by the exponential law and the curve of the emulsifier concentration in the phase inversion point is described by the linear law. Also, we analyzed the results in terms of the composition and structure of micelles. It was shown that for the phase inversion point, the η parameter, characterizing the critical degree of micelle "swelling", grows nonlinearly with an increase in the $V_W/(V_W + V_D)$ ratio. For the region of a sharp fall in T_2, η does not depend on the relative fraction of the water phase and is in the range from 13 to 17 H_2O moles per surfactant mole. The results can be useful when developing water-in-diesel MFs. It is important to note that the selection of diesel or hydrocarbon as a base fluid will strongly affect the phase diagrams. The use of other types of base fluids to produce microemulsions will require implementing the full cycle of the typical experiments.

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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