**ACADEMIA ROMÂNĂ**
**ŞCOALA DE STUDII AVANSATE A ACADEMIEI ROMÂNE**
**DEPARTAMENTUL DE ŞTIINȚE EXACTE**

**INSTITUTUL DE CHIMIE – FIZICĂ „ILIE MURGULESCU”**

**PhD THESIS SUMMARY**

# MICROEMULSIONS AS ALTERNATIVE FUELS FOR INTERNAL COMBUSTION ENGINES BASED ON DIESEL AND DIESEL-VEGETABLE OIL

**SCIENTIFIC COORDINATOR,**
Dr. Dan-Florin ANGHEL
DAnghel

**PhD STUDENT,**
URICANU (MIHĂILESCU)
Florentina-Cristina

Bucharest
2019

# TABLE OF CONTENTS

**Note:** In this **TABLE OF CONTENTS**, the numbering of pages is that in the thesis.

## Part I

## Theoretical considerations

## Part II

## Original contributions

**investigations**

**Key words:** microemulsion, alternative fuel, energy from fossil fuels, fuel microemulsion, amphiphile*⁾, anionic surfactant, extended surfactant, nonionic surfactant, cosurfactant, phase transition, interfacial tension, solubilization parametru, phase equilibrium, rapeseed oil, diesel fuel, ternary diagram, pseudo-ternary diagram.

*) Amphiphile – Any organic compound composed of hydrophilic and hydrophobic portions (https://www.dictionary.com/browse/amphiphile).

# 1. Introduction

One of the most challenging problems confronting the humankind today is the one of energy. The majority part of the energy comes from natural sources like crude oil, gas, coal etc. At present, crude oil is the most important energy source at our disposal, which is processed to gasoline, diesel, kerosene and other products for locomotion and heating [1]. The increased demand for fuel, the indiscriminate extraction and depletion of crude oil reservoirs entailed shortages in supply and fluctuant prices on the market [2].

Due to the crude oil reservoirs' depletion, and the noxious exhaust of the internal combustion engines, especially of the diesel engine, the interest in alternative fuels is very high nowadays. Reservoirs' depletion and the environment pollution are putting a real strong stress on companies and governments to improve the situation. From this point of view, commutation from fossil to the alternative fuels is a big challenge of our times, and its accomplishment can be done only by corroborating and putting together the efforts and achievements of all the people which are working on.

Among the alternative fuels, the vegetable oils are a viable option because they are renewable, and have similar properties with the diesel fuel. Vegetable oils like those of sunflower, rape and cotton seeds etc., contain triglycerides (about 98%), small amounts of mono- and diglycerides and free fatty acids. They have a high amount of oxygen, but no sulfur and aromatics, which are the main advantages over the fossil fuels. Moreover, vegetable oils are renewable, biodegradable, and have less noxious exhaust than the fossil fuels [3]. Among the vegetable oils, rapeseed oil is important because it can be processed to biodiesel [4], mixed with diesel [5] or directly injected into engine [6].

However, low volatility and high viscosity of vegetable oils are disadvantages that limit their use as diesel substitutes. The viscosity of vegetable oils can be reduced by: transesterification (with short-chain alcohols), pyrolysis (thermal cracking), dilution with less viscous liquid fuels (diesel or ethanol) and emulsification (microemulsification) with surfactants [7]. Among the listed methods, the most advantageous is microemulsification because:

- Replaces in part or totally the diesel with vegetable oils [8],
- Introduces water into fuel [9],
- Improves fuel atomization and burning [9],
- Reduces noxious emissions of $NO_x$, particulate matter and soot from the exhaust gases [9].

Microemulsions are macroscopically homogeneous systems of oil, water and surfactant (sometime with cosurfactant), which at microscopic level consist of individual areas of oil and water separated by a surfactant monolayer [10]. Microemulsions are spontaneously formed by hand agitation and are thermodynamically stable. In addition to thermodynamic stability, they have unique properties, such as extremely low interfacial tension ($\gamma_{ow}$ <0.1 mN/m), high oil and water solubilization capacity, and nanometric dispersion (<100 nm). The size and distribution of droplets can predict the stability of such systems. This depends on the quantity and types of surfactants used, the nature of the interfacial layer formed and the mutual solubilities of the two oil and water phases [11].

Due to the complex structure of triglycerides [12], the combustible microemulsions with vegetable oils are more difficult to be obtained than those from petroleum products. This is due to the low solubilization of triglycerides by conventional surfactants, which are unable to develop low interfacial tension without addition of cosurfactants, expanded surfactants or binding agents [13].

The purpose of this Ph.D. thesis is to obtain a/u microemulsions with diesel and diesel-rapeseed oil blend as an oil phase using non-ionic surfactants, anionic surfactants and a cosurfactant. To determine the water solubilization capacity in microemulsions, the phase diagrams were used. For a ternary oil/water/surfactant (OWS) or a pseudo-ternary oil/water/ surfactant-cosurfactant (OWSC) system, the phase diagram is a vertical Gibbs triangle prism as the base and the ordinate as the temperature [14].

The reciprocal solubility of these compounds was estimated through the single-phase region on the pseudo-ternary diagrams and the phase behavior of the OWSC systems in the multiphase areas. To clarify the co-solubilization of oil and water in microemulsion, the phase behavior was investigated according to the surfactant and electrolyte concentration. The results of the phase transitions were correlated with the oil/water interfacial tension ($\gamma_{ow}$), the droplet size of the dispersed phase, and the solubilization of water and oil in the microemulsion.

The main goal of the doctoral thesis was obtaining "Microemulsions as alternative fuels for internal combustion engines based on diesel and diesel-vegetable oil". It was achieved by means of the following specific objectives:
- Obtaining microemulsions with diesel and diesel-rapeseed oil as the oil phase;
- Using for this purpose surfactants (AOT, Brij 30) and a cosurfactant (*i*-butanol);
- Use of biodegradable extended surfactants (Synperonic A9C);
- Increase the number of nonionic surfactants (Brij 30, Igepal 520, Tween 65 and Tween 85);
- Utilize of inorganic (NaCl) and organic ($CH_3COONa$) electrolytes;
- Determination of the monophasic and polyphasic areas in the pseudo-ternary diagrams;
- Estimation of co-solubilization of oil and water in microemulsion as a function of the nature and concentration of surfactant and the electrolyte;
- Correlation of oil/water interfacial tension ($\gamma_{ow}$) with the particle size of the dispersed phase and the solubilization of oil and water in the microemulsion;
- Investigation of relevant properties of diesel and diesel-rapeseed oil blend microemulsion fuels.

This doctoral thesis consists of two parts and ten chapters. The first part has two chapters. In **Chapter 1** the theoretical considerations regarding the necessity to obtain and use alternative fuel microemulsions with diesel and diesel-vegetable oil as the oil phase are presented. Microemulsions are stable oil/water or water/oil dispersion systems, isotropic, optically transparent, stabilized by surfactants or mixed amphiphile surfactants and cosurfactants. The microemulsions form spontaneously and are thermodynamic stable because the variation of the Gibbs free energy of formation ($\Delta G_f$) is negative [15]. In this chapter, the specific purpose and objectives of the thesis are also stated. In **Chapter 2** the materials, their provenance and the experimental methods are described.

The second part contains the original contributions of the thesis and has four chapters. **Chapter 3** shows innovative contributions to the preparation and characterization of microemulsions obtained with diesel and/or diesel-rapeseed oil as the oil phase, AOT and Brij 30 as surfactants and cosurfactant *i*-butanol. The solubilization data obtained from the phase diagrams are in agreement with those of the phase behavior and recommends the use of the mixture of anionic and nonionic surfactants and of the diesel and vegetable oil for the production of combustible microemulsions. For a given OWSC system, increasing the electrolyte concentration produces the phase transition WI → WIII → WII, and increasing the amphiphile concentration allows the single-phase WIV system to be obtained. WIII systems in the phase transition have the lowest values for the $\gamma_{ow}$, the highest quantities of water and the solubilized oil, and the largest sizes for dispersed particles.

**Chapter 4** contains the obtained results for fuel microemulsions made with less aggressive surfactants towards the environment. The ionic surfactant used was an extended one, namely SA9C, and in addition to Brij 30 other nonionic surfactants like ICO 520, Tween 65 and Tween 85 were used. Such water/oil microemulsions are spontaneously formed and the capacity of water solubilization depends mainly on the structural and hydrophilic-lipophilic properties of the surfactants. The solubilization capacity increases with the use of anionic-nonionic-cosurfactant surfactant mixtures, but decreases in the presence of electrolytes. The dispersed particle size for both the oil/water (u/a) (WI) or water/oil (a/u) (WII) microemulsions as well as for microemulsions from the sequence WI → WIII → WII and those of type WIV was in the microemulsion range, *i.e.* below 70 nm. These results are particularly valuable contributing to the advancement and development of knowledge in liquid-liquid dispersion as they are a means of obtaining efficient and environmentally friendly microemulsions.

**Chapter 5** continues the research on microemulsions described in the previous chapter of Ph.D. thesis with the investigation of other relevant fuel characteristics such as: time and temperature stability, flowing in a large temperature range, the cloud point and the pour point, and the heating power. The good stability of the microemulsions, their rheological behavior over a high temperature range, flow characteristics and calorific values, as well as their harmless environmental impact, recommend them as alternative fuels for the diesel engine.

The final conclusions from the studies undertaken into this PhD thesis are contained in **Chapter 6**.

**Chapter 7** contains the original contributions made in these studies, **Chapter 8** highlights future prospects, **Chapter 9** includes dissemination of the results of the studies carried out, and **Chapter 10** presents the selective bibliography on the content of the Abstract of this doctoral thesis.

# Part II

# Original Contributions

## 3. Alternative fuels: Diesel and diesel-rapeseed microemulsions with AOT and Brij 30

**The results of this chapter were published in Fuel 117 (2014) 251-258.**

Diesel and diesel-rapeseed oil mixture can solubilize water in the presence of surfactants to form w/o microemulsions. Fig. 1 shows the pseudo-ternary phase diagram of the oil/water/surfactant-cosurfactant (OWSC) system containing diesel fuel, the ionic surfactant (AOT) and/or the nonionic surfactant (Brij 30), and i-butanol as a co-surfactant. The mutual solubility of these compounds was estimated by the single-phase region on the pseudo-ternary diagrams.

When AOT is mixed with Brij 30 or with *i*-butanol, one-phase microemulsion areas are well defined on the phase diagram, unlike Brij 30-*i*-butanol blend that produces microemulsions only in the area of high surfactant concentrations. It is evident that the W/O microemulsion area for the AOT-Brij 30-i-butanol mixture is the highest among the studied systems. The microemulsion area increases in the case of the surfactant mixture and in the presence of co-surfactant, but decreases with the hydrophobicity of the surfactant or by adding electrolyte (0.5% NaCl). The area does not vary significantly if half the amount of diesel is replaced by rapeseed oil. The results obtained show that by careful selection of the mixture of surfactants, the oil phase and the electrolyte concentration, the stability of the interfacial film can be optimized, resulting in the solubilization of a large amount of water in the reverse microemulsions.

To clarify the co-solubilization of oil and water in the microemulsion, the phase behavior was investigated according to the surfactant and electrolyte concentration.

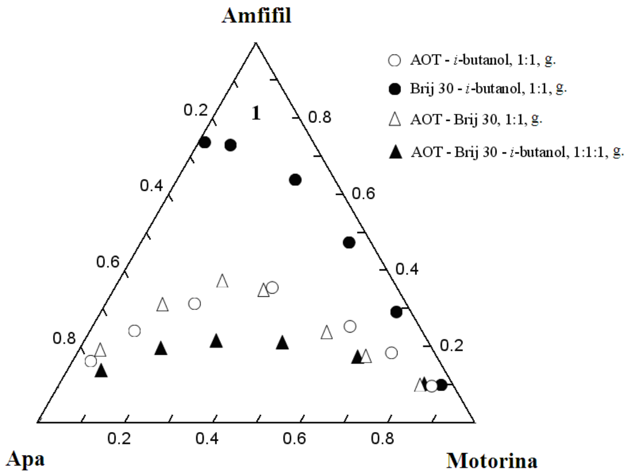

Fig. 1. Pseudo-ternary phase diagrams of diesel, water and surfactants. One-phase microemulsion is marked with 1.

The phase behavior of the diesel/water/AOT-Brij30-*i*-butanol system (1: 1: 1) as a function of the amphiphile concentration is shown in Fig. 4. Considering only the Brij 30 non-ionic surfactant, the phase behavior of the system is in good agreement with the modification of the hydrophilic-lipophilic properties of the Brij 30 oligomers separated in the oil and aqueous phases of the system. Due to their different hydrophilic-lipophilic properties, the ethoxymers are selectively separated depending on the affinity each has for the two immiscible phases. By using the anionic-nonionic surfactant mixture, the phase transition is much more complex than of the Brij 30. When the amphiphile content in the system is less than 10% (vials 1-5), biphasic systems appear in which the continuous phase is cloudy irrespective of whether it is water (vials 1-3, WI) or oil (vials 4 and 5, WII ) (see Figure 4). At 10% amphiphile (vial 6, WIII) three phases appear with a small volume of the middle phase. At a concentration of 15% amphiphile, two microemulsion phases are formed as a lower phase (WI) (vial 7). The lower phase volume increases with amphiphile concentration and at a concentration higher than 18% amphiphile (vials 8 and 9), the system becomes one-phase (WIV). This sequence is similar to the one in the isothermal section at 30 °C in the water/*n*-decane/AOT-$C_4E_1$ pseudo-ternary system [16]. In that study, the WI system became WIV at a much higher amphiphile concentration (*i.e.*, of about 35%), which is attributable to $C_4E_1$.

**Fig. 5** illustrates the effect of NaCl on the phase behavior of the diesel-rapeseed oil/water (NaCl)/AOT–Brij 30 (1: 1) system. The phase transition sequence WI → WIII → WII is evident. It is noted that by increasing the NaCl concentration in the aqueous phase, a medium phase microemulsion containing approximately equal volumes of oil and water is formed (see vial 3). It occurs at 0.5% NaCl, and this corresponds to the optimum salinity (S *). Similar phase transitions were obtained for diesel/water (NaCl)/AOT–Brij 30 (1: 1), diesel/water (NaCl)/AOT–Brij 30 and diesel-rapeseed oil/water (NaCl)/AOT–Brij 30-*i*-butanol (1: 1: 1) systems.

The results of the phase transitions were correlated with the oil/water interface ($\gamma_{ow}$), the droplet size of the dispersed phase and the solubilization of water and oil in the microemulsion.

The variation of the oil/water interfacial tension versus the electrolyte concentration for the OWS systems with diesel as a oil phase and AOT–Brij30 (1:1) mixture as amphiphile, in the absence and presence of *i*-butanol, is illustrated in **Fig. 6**.

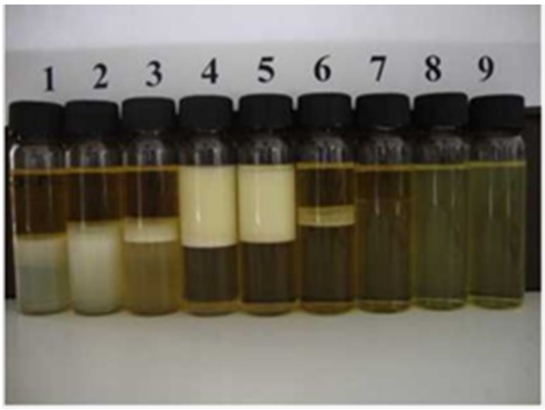

**Fig. 4.** Phase behavior of diesel/water/amphiphile [AOT–Brij 30-*i*-butanol (1: 1: 1)] system based on amphiphile concentration. The amphiphile concentration in the 1-9 vials was: 2%, 4%, 5%, 6%, 7%, 10%, 15%, 18% and 20%

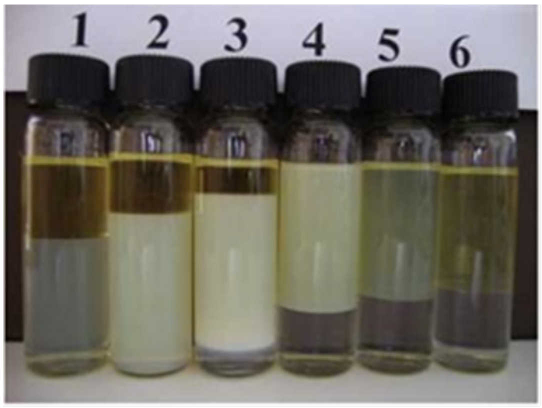

**Fig. 5**. Phase behavior of diesel-rapeseed oil/water (NaCl)/AOT–Brij 30 systems as a function of salt concentration in water. The NaCl concentration in vials 1-6 was: 0.25%, 0.4%, 0.5%, 0.6%, 0.7% and 0.8%.

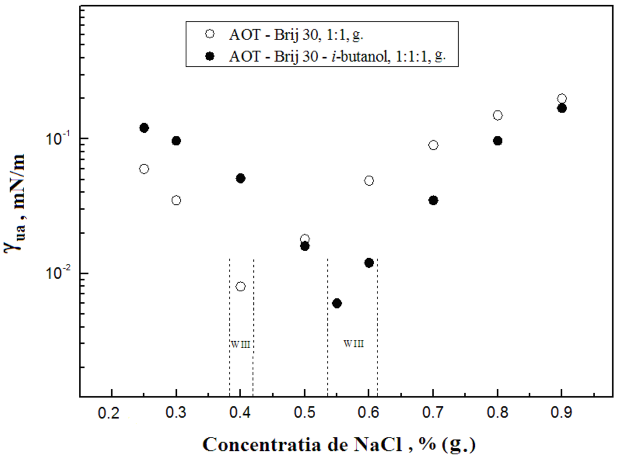

**Fig. 6**. Variation of oil/water interfacial tension ($\gamma_{ow}$) of the diesel/water/AOT-Brij 30 system versus the NaCl concentration in the absence (○) and in the presence of *i*-butanol(●).

The value of $\gamma_{ow}$ between diesel oil and water is of 16 mN/m. The data in **Fig. 6** show that the AOT–Brij 30 mixture, at a low NaCl concentration, namely in the WI system, has a two orders of magnitude lower interfacial tension. By increasing the electrolyte concentration, three phases (WIII) appear and the $\gamma_{ow}$ reaches the smallest value ($8 \times 10^{-3}$ mN/m) at 0.4% NaCl. For the WII systems that occur at a high concentration of NaCl, the $\gamma_{ow}$ increases and tends to reach about $2 \times 10^{-1}$ mN/m at 0.9% NaCl.

In the presence of *i*-butanol, the $\gamma_{ow}$ has a minimum at $6 \times 10^{-3}$ mN/m that corresponds to a NaCl concentration of 0.55%. The same tendency of the $\gamma_{ow}$ was recorded in all the other systems studied in this doctoral thesis. The results are similar to those described in the literature, where the $\gamma_{ow}$ changes regardless of the parameter that governs the system [17]. It should be noted that the minimum value of the $\gamma_{ow}$ in this case is slightly less than that obtained without *i*-butanol. When *i*-butanol is present in the system, it has a high affinity for the oil/water interface where it co-adsorbs together with the surfactant and provides a larger space between the surfactant molecules, so decreasing the cohesion and rigidity of the film. At the same time, the co-surfactant molecules entering the interfacial film reduce the curvature of the film, allowing the appearance of the middle-phase microemulsion that solubilizes big amounts of oil and water.

The oil/water interfacial tension data are closely related to the microemulsion structure. Increasing the microdomain of the dispersed phase into microemulsions is associated with the decrease of the interfacial tension o/w. Thus, the particle size of the middle phase microemulsion is higher than o/w or w/o microemulsions for all investigated systems. In the Winsor III diesel/water (NaCl)/AOT-Brij 30 system, the optimum salinity is at 0.4% NaCl where the interfacial tension has a minimum value of 8 x $10^{-3}$ mN/m, and the radius of the dispersed water particles is of 67 nm (standard deviation = 0.2192). In the presence of *i*-butanol, in the three-phase system, the $\gamma_{ow}$ minimum is at 6 x $10^{-3}$ mN/m at a concentration of 0.55% NaCl, and the dispersed particles have a radius of 61 nm (standard deviation = 0.2370).

The correlation between the $\gamma_{ow}$ and the microemulsion structure also applies to the diesel/water (NaCl)/AOT–*i*-butanol system. The particle size in the middle phase microemulsion, obtained at 0.5% NaCl, was 21 nm (standard deviation = 0.1980) and the minimum $\gamma_{ow}$ value was of 2 x $10^{-2}$ mN/m. The much lower $\gamma_{ow}$ value for systems with anionic-nonionic surfactant blends as well as the larger size of the microemulsion particles of these systems compared to nonionic surfactants indicates that the ethoxylated surfactant favors the decrease of $\gamma_{ow}$ and improves the solubilization.

In the investigated OWSC systems, the microemulsions have particle sizes from 20 to 70 nanometers. They are formulated very easy, without high energy input and have a good stability in time.

Solubilization of oil and water in the middle phase defines the quality of a microemulsion. The results obtained in this PhD thesis show that microemulsions with mixtures of anionic and nonionic surfactants, without cosurfactant, but with diesel-RSO blends, have the highest oil and water solubilizations. In the above case, the results show that 1 gram of surfactant is able to solubilize 8.0 grams of water and oil. Using diesel as an oily phase, the same system has solubilization parameters $SP_o$ and $SP_w$ slightly lower, *i.e.* of 7.3 grams. In the system containing diesel and *i*-butanol as a cosurfactant, the $SP_o$ and $SP_w$ for microemulsion WIII are even smaller (6 grams). These results indicate a decrease in oil and water solubilization in the system when a part of surfactant is substituted with cosurfactant. These results indicate a decrease in oil and water solubilization in the system when a part of the surfactant is substituted with cosurfactant. However, the values of the optimal solubilization parameters, SP*, for the investigated system are high and explains the turbidity shown by some of the microemulsions [18]. Comparing the solubilization data with those of interfacial tension and particle size, it results that the maximum solubilization of oil and water in the middle phase microemulsion corresponds to the maximum size of the dispersed particles and the lowest oil/water interfacial tension.

## 4. Combustible microemulsions from renewable products: phase diagrams, interfacial tensions, solubilization parameters and structural investigations

**The results of the research in this chapter of the PhD thesis are the subject of the paper: "Combustible microemulsions with diesel and diesel admixed with rapeseed oil" by F.C. Mihăilescu, M. Balcan, M.E. Maxim, D.F. Anghel. The work is accepted and will appear in Rev. Chim. (Bucharest), vol. 70 no. 9/2019, according to the certificate no. 05/05/06.2019.**

In this chapter, combustible microemulsions with diesel and/or diesel-rapeseed oil (RSO) were obtained in which AOT was replaced by an expanded surfactant, namely, Synperonic A9CNa (SA9C). The number of nonionic surfactants was increased, so that in addition to Brij 30, Igepal CO520 (ICO520), Tween 65 (T65) and Tween 85 (T85) were used, and sodium chloride was replaced with sodium acetate (NaAc). The replacement was necessary because AOT is environmentally harmful and NaCl damages the engine.

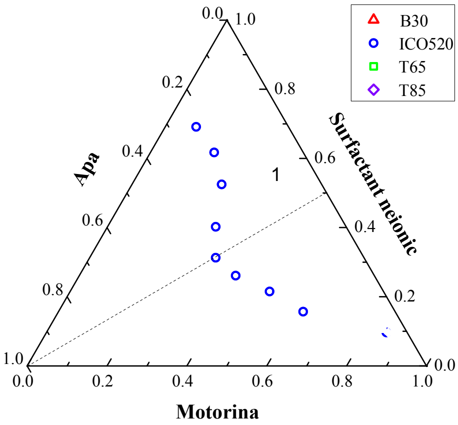

**Fig. 8.** Ternary phase diagram of systems containing diesel, distilled water, Brij 30 (B30), Igepal CO-520 (ICO520), Tween 65 (T65) and Tween 85 (T85). One-phase microemulsion is marked with 1.

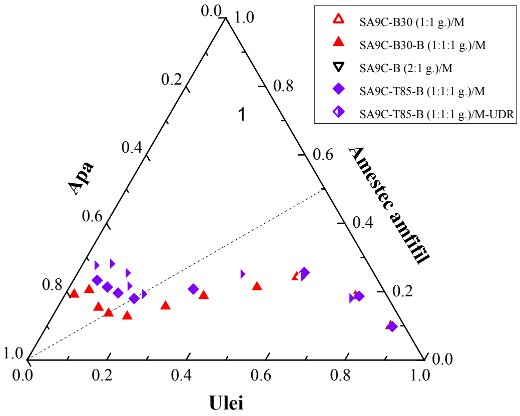

**Fig. 9.** Pseudo-ternary oil/amphiphile/water diagram. The oil is diesel (M) or diesel-rapeseed oil mixture. Amphiphile mixtures are: SA9C-B30, SA9C-B30-B, SA9C-B and SA9C-T85-B. In the case of the last mixture, half of the amount of diesel was replaced by UDR. One-phase microemulsion is marked with 1.

Attempting to obtain monophasic microemulsions with SA9C alone did not give the desired results. Instead, the single-phase areas obtained for single non-ionic surfactants are well delimited on the ternary phase diagrams as shown in **Fig. 8**. In the monophasic microemulsion, on the dotted line corresponding to the unity surfactant/oil weight ratio, the volume of water embedded in the microemulsion, $W_m$, is 43.2% for B30, 37.1% for ICO520, 17.8% for T65 and 20.4% for T85. This data indicates a different affinity of the interfacial film for water. It is the highest for B30 and the lowest for Tween surfactants, with a small difference between T65 and T85.

By mixing SA9C with non-ionic surfactants or with *i*-butanol, such microemulsions can be obtained very ease. **Fig. 9** shows the phase diagrams obtained by mixing SA9C with nonionic surfactants in the absence and presence of *i*-butanol. The results show that the SA9C-B30 mixture forms reverse microemulsions, but the single-phase area is much smaller than that of B30 in **Fig. 8**. The $W_m$ value obtained is of 18.9% and is 2.3 times smaller than with B30 alone. Similar results have also been obtained for other nonionic surfactants in admixture with SA9C. They can be explained by assuming that the POE chains of B30 do instert at the u/a interface between the SA9C carboxylate heads, lowering the electrostatic repulsion between them. The phenomenon lowers o/w interfacial tension to extremely low values.

Addition of *i*-butanol into the SA9C-B30 mixture increases very much the monophase area of the systems, indicating a high water solubilzation capacity of the microemulsions. The maximum amount of solubilized water, $W_m$, is 72.7%, being much higher than for the system without *i*-butanol (18.9%). **Fig. 9** also shows that monophasic a/u microemulsions can be obtained by adding *i*-butanol to SA9C, but $W_m$ is only equal to 46.1%. The result is due to cosurfactant that significantly alters the interactions in the interfacial film between surfactant, oil and water [19]. In the presence of vegetable oil, $W_m$ is 61.0%, being practically equal to

$W_m$ for diesel (61.2%). In both cases, the areas of single-phase microemulsions are very large, proving that vegetable oil changes very little the phase diagram in the area of interest. **Fig. 9** shows that any of the amphiphile mixtures used can solubilize more than 10% water on the amphiphile/oil dilution line of 3:7 without any phase separation.

The presence of an electrolyte, such as NaAc, in such a system leads to changes in the amphiphile interactions at the oil-water interface and consequently to changes in the phase behavior of the system. The phase transitions of the diesel/water (NaAc)/SA9C-ICO520-B system versus the electrolyte concentration are given in **Fig. 11**.

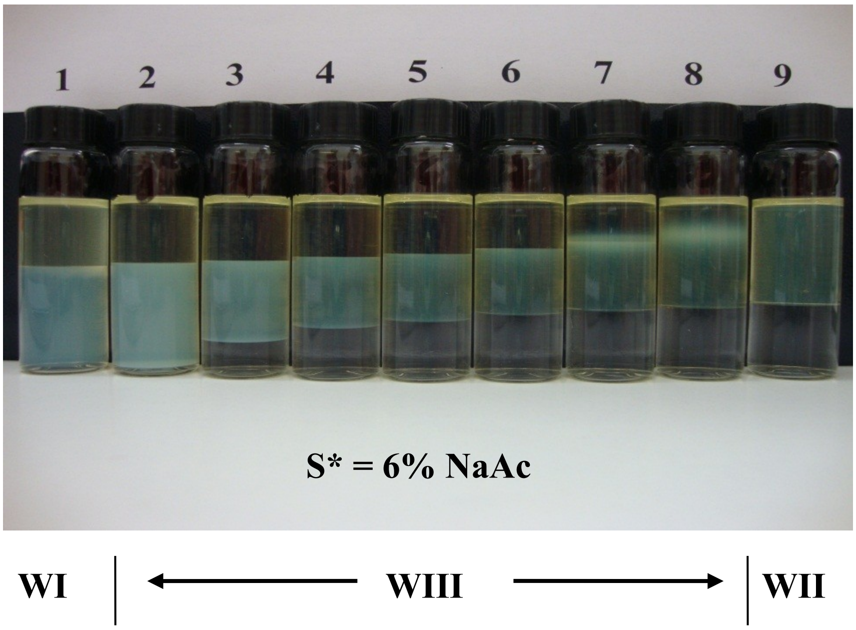

**Fig. 11.** Winsor diagram of the system: diesel/water + NaAc/(ICO520-SA9C-B) versus the sodium acetate (NaAc) concentration in water. The concentration of NaAc in the vials changes from 2 to 10% in steps of 1%. The optimum salinity (S*) is 6% NaAc in vial # 5.

In WI → WIII → WII phase transitions, at low electrolyte concentrations, the amphiphilie interaction with water is stronger than with oil. The system formed is of the WI type, *i.e.*, an amphiphile-rich microemulsion, in equilibrium with an upper oil phase. By increasing the NaAc concentration, the salt ions compete with the carboxylate group of the surfactant for hydration water and gradually form a meddle phase rich in surfactant incorporating oil and water. At a certain concentration of NaAc (6%), the microemulsion solubilizes almost equal volumes of oil and water. This is considered the optimum salinity, denoted by S*. In such a system, the interactions of the surfactant at the oil/water interface are balanced, and the oil and water are solubilized as elongated domains, separated by amphiphile film, forming a bicontinuous microemulsion [13]. At higher salinity, interactions of the surfactant with the oil are stronger than those with water and the microemulsion is in balance with excess water, being a WII system.

For all the systems investigated in this PhD thesis, the phase transitions obtained were similar to the phase transition WI → WIII → WII presented above. **Table 5** shows five three-phase microemulsions with their characteristic properties: the salinity range, $\gamma_{ow}$*, SP* and r*. All microemulsions contain different non-ionic surfactants, extended anionic surfactant, cosurfactant and diesel oil in the amphiphile mixture. One of the microemulsions (# 3) has the oil-RSO blend as the oil phase. Using the same amphiphile mixture (SA9C-ICO520-*i*-

butanol), but with diesel-RSO as an oily phase, three phases appear in the same salinity range, but S* increases to 7% NaAc.

**Table 5.** Salinity range of three-phase microemulsions (WIII), oil/water interfacial tension ($\gamma_{ow}$*), optimal solubilization parameter (SP*) and radius of dispersed phase particles (r*)

| Sample No. | System components | Salinity range of WIII phase (% NaAc) | $\gamma_{ow}$* (mN/m) | SP* (mL/g amfifil) | r* (nm) |
|---|---|---|---|---|---|
| #1 | B30-SA9C-B/M | 6 - 10 | 9 x $10^{-2}$ | 2.67 | 32 |
| #2 | ICO520-SA9C-B/M | 3 - 9 | 11 x $10^{-2}$ | 2.65 | 36 |
| #3 | ICO520-SA9C-B/(M-UDR) | 3 - 9 | 7 x $10^{-2}$ | 3.10 | 73 |
| #4 | T65-SA9C-B/M | 7 - 11 | 9 x $10^{-2}$ | 2.68 | 43 |
| #5 | T85-SA9C-B/M | 6 - 10 | 8 x $10^{-2}$ | 3.31 | 63 |

* Denote the optimal values of those parameters.

Such microemulsion characteristics are important criteria useful for choosing the optimal microemulsion. With respect to the effect of the nonionic surfactant it can be stated that microemulsions containing the same anionic surfactant, cosurfactant and diesel, but different nonionic surfactants (e.g., B30 and T85 respectively, for microemulsions # 1 and # 5) have the same salinity range of phase WIII (6% -10% NaAc). However, the other parameters are different. For microemulsion # 1, $\gamma_{ow}$* is equal to 9 x $10^{-2}$ mN/m, SP* = 2.67 mL/g and r* = 32 nm (standard deviation = 0.245 nm), while for microemulsion # 5, the $\gamma_{ow}$* is equal to 8 x $10^{-2}$ mN/m, SP* = 3.31 mL/g and r* = 63 nm (standard deviation = 0.406 nm). As can be seen from these data, lower values of $\gamma_{ow}$* and higher SP* produce microemulsions with larger dispersed particles. Thus, it is observed that of the two investigated systems, microemulsion # 5 has the largest particles.

By comparing microemulsion # 4 with microemulsion # 5, we find out that salinity of the WIII phase extends over substantially equal ranges (7 - 11% NaAc) and 6 - 10% NaAc respectively. For the first microemulsion, PS* is equal to 2.68 mL/g, and for the second it is of 3.31 mL/g. The solubility data are also in agreement with r* which is 43 nm (standard deviation = 0.294 nm) for T65 and 63 nm respectively (standard deviation = 0.406 nm) for T85. These data can be explained by the fact that although the two nonionic surfactants have similar structures, T85 has a double bond in the molecule, resulting in lower interfacial tensions, higher solubilization parameters and, implicitly, larger particles of the microemulsion dispersed phase.

Regarding the influence of the nature of the oil, microemulsions # 2 and # 3 contain both ICO520 in the amphiphile mixture, but in sample # 3, half of the diesel is replaced by UDR. Samples have the highest salinity range of WIII phase (3 - 9% NaAc), but the other parameters are different. Thus, microemulsion # 2 has $\gamma_{ow}$* equal to 11 x $10^{-2}$ mN/m, and microemulsion # 3 has $\gamma_{ow}$* equal to 7 x $10^{-2}$ mN/m, which is the lowest has $\gamma_{ow}$ value for the five microemulsions. On the other hand, PS* is 2.65 mL/g for microemulsion # 2 and 3.10 mL/g for microemulsion # 3. These values are consistent with the radius of the dispersed particles (r*) in the microemulsion, which is 36 nm (standard deviation = 0.385 nm) for diesel and 73 nm (standard deviation = 0.428 nm) for the diesel-RSO mixture. The obtained results show that replacing half of diesel oil with rapeseed oil (*i.e.*, microemulsion # 3) is beneficial on the process of formulating combustible microemulsions. This assertion is supported by the broadest salinity range in which the three-phase microemulsion, the smallest interfacial tension o/w, the high solubilization parameter, and the largest droplets of the dispersed phase do exist.

## 5. Combustible microemulsions: structure, stability, viscosity, cloud point and pour point, heat of combustion

In this chapter of the doctoral thesis I investigated the relevant characteristics of fuel microemulsions prepared with diesel and diesel-rapeseed oil blend. The study was focused on structural changes, stability and viscosity in relation to temperature and time, flow at low temperature (cloud point - CP and pour point - PP) and heat of combustion. The properties of microemulsions were compared with those of diesel or rapeseed oil.

The results on the one-year test of the microemulsions dropplet radius prepared with diesel and diesel-RSO and the amphiphile T65-SA9C-B system at 25 ± 1 ° C and 10 % water are shown in **Fig. 15**. For diesel oil microemulsions, the particle size of the dispersed phase increases from 16.4 nm to 17.6 nm for the first 22 days, then they stabilize around an average radius of 17.7 nm. With regard to diesel-RSO microemulsions, the data in the same figure shows that the droplet sizes vary randomly in the first two weeks, but the trend is increasing from ~ 17 nm to ~ 18 nm. The size of the dispersed particles then drops to ~ 16.5 nm, and remained at this value with low fluctuations for one year.

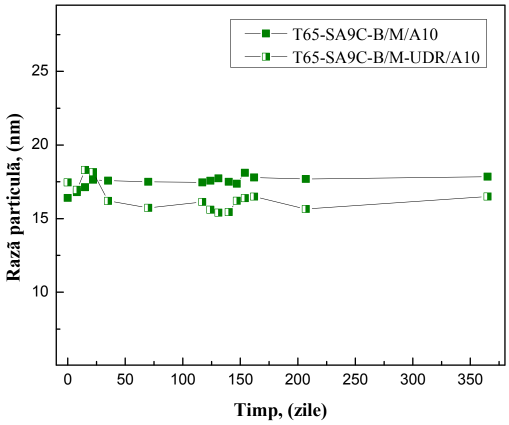

**Fig. 15.** Change in the mean size of water droplets in the microemulsion with T65-SA9C-B mixture, with 10% water, in the absence and in the presence of rapeseed oil, over a year at 25 ºC.

As for the viscosity variation with the temperature of the water/oil microemulsions, a similar behavior to the oil was observed, but the values obtained are higher. The fitting of the viscosity curves with the temperature was done using the Andrade equation ($\ln \eta = A + B/T$) [20, 21], where $\eta$ (mPa·s) is the dynamic viscosity of the liquid at temperature T (K), A the intercept, B the slope, $R^2$ the correlation coefficient and SD the standard deviation. The resulting parameters for stabilized microemulsions with mixtures of B30 and T65 non-ionic surfactants as well as for diesel, RSO and diesel-RSO mixture are given in **Table 8**.

Correlation coefficient values obtained ($R^2 > 0.9985$) show Newtonian behavior of the studied microemulsions. According to the Andrade equation, slope B represents the ratio $E_a/R$, where R is the universal gas constant and E is the energy of activation of the viscous flow which is considered a measure of the potential energy barrier corresponding to the elementary molecular motion step. The results in **Table 8** show that microemulsions have higher $E_a$ values than diesel oil, rapeseed oil, diesel-RSO mixture. This means that, unlike oils, microemulsions are more strongly affected by temperature. However, based on the results obtained, I can say that viscosity variation with temperature is similar for all microemulsions studied, and the small differences observed are due to the structural changes induced by the composition.

**Table 8.** Parameters of Andrade equation (A and B), correlation coefficient ($R^2$), standard deviation (SD), and the activation energy ($E_a$) of viscosity of the oils and microemulsions containing B30 and T65 as nonionic surfactants in the amphiphile mixtures (anionic surfactant-nonionic surfactant-cosurfactant (1:1:1) and water between 6 and 10%.

| System* | A | B | $R^2$ | SD | $E_a$ (kJ/mol) |
|---|---|---|---|---|---|
| Diesel fuel (D) | -6.17 | 2.11 | 0.9986 | 0.02 | 17.50 |
| Rapeseed oil (RSO) | -6.46 | 2.40 | 0.9988 | 0.02 | 19.97 |
| Diesel-RSO | -6.21 | 2.20 | 0.9985 | 0.02 | 18.31 |
| B30-SA9C-B/D/W6 | -7.42 | 2.72 | 0.9999 | 0.01 | 22.58 |
| B30-SA9C-B/D/W8 | -7.82 | 2.88 | 0.9999 | 0.01 | 23.97 |
| B30-SA9C-B/D/W10 | -8.61 | 3.17 | 0.9998 | 0.01 | 26.34 |
| B30-SA9C-B/D-RSO/W6 | -7.50 | 2.81 | 0.9999 | 0.01 | 23.34 |
| B30-SA9C-B/ D-RSO/W8 | -7.92 | 2.98 | 0.9999 | 0.01 | 24.78 |
| B30-SA9C-B/ D-RSO/W10 | -8.80 | 3.30 | 0.9999 | 0.01 | 27.40 |
| T65-SA9C-B/D/W6 | -8.05 | 3.00 | 0.9997 | 0.01 | 24.90 |
| T65-SA9C-B/D/W8 | -8.48 | 3.18 | 0.9991 | 0.02 | 26.41 |
| T65-SA9C-B/D/W10 | -9.77 | 3.63 | 0.9993 | 0.02 | 30.14 |
| T65-SA9C-B/ D-RSO/W8 | -8.79 | 3.33 | 0.9994 | 0.02 | 27.65 |
| T65-SA9C-B/ D-RSO/W10 | -9.67 | 3.67 | 0.9999 | 0.01 | 30.54 |

***Note:** B in the **System** item stands for *i*-Butanol; The figure(s) after W indicate the water percent in the microemulsion. For example, W6 means that microemulsion has 6% water, etc.

During rheological measurements, by raising the temperature, the systems containing B30 or ICO520 become cloudy above the temperature of 55 °C. For all systems containing the more hydrophilic nonionic surfactant T65, except for diesel-RSO and 10% water, the cloudiness does not occur at 60 °C. These observations allow us to assert that systems containing T65 have a better temperature stability than the other systems investigated in this thesis.

To study the effect of temperature on the structure of such a system, the microemulsion samples prepared with amphiphile T65-SA9C-*i*-B mixture, 10% water, and diesel fuel or diesel-RSO mixture, were measured by DLS at different temperatures. **Fig. 17** illustrates the variation of the main distribution of water particle size by temperature for those microemulsions. It can be noticed that the water particles in the diesel system are slightly smaller than those in the diesel fuel - rapeseed oil mixture and this is kept on the entire temperature scale. By increasing the temperature, the size of the water drops decreases and around 50 °C, the particles have a minimum. Then, the size increases until the occurence of phase separation, whici is at 62 °C for the system with diesel, and at 58 °C for that with diesel-RSO, being consistent with the rheological data.

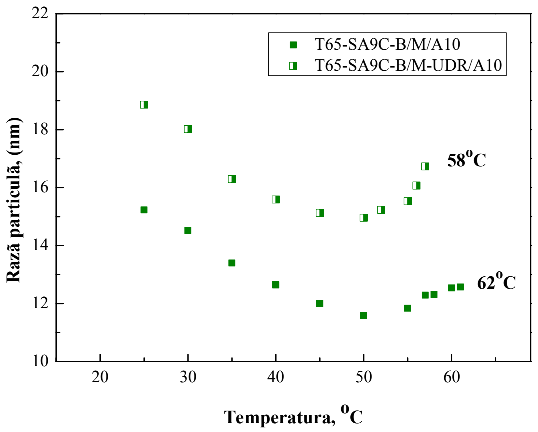

**Fig. 17.** The effect of tenperature on the particle size of water nano-dropplets dispersed in the microemulsions containing T65-SA9C-B and 10% water, in the absence and in the presence of rapeseed oil.

In order to explain the high temperature stability of the microemulsions obtained in this PhD thesis, the temperature sensitivity of the interfacial curvature of the monolayer formed by the ionic and nonionic surfactants must be taken into account. The temperature-dependent dependence of the two surfactants is well known [16]. Therefore, such surfactant mixtures should be used to obtain insensitive microemulsions at temperature [22].

The values of cloud and pour points of the a/u microemulsions with 10% water, as well as those for diesel oil, rapeseed oil and diese oil-rapeseed oil mixture, are shown in **Table 10**. Values obtained for diesel or rapeseed oil are quite close to those in the literature [23]. In the case of diesel oil-rapeseed oil mixture, the PP and CP values are intermediate to those of the single oils.

**Table 10.** Cluod points and pour points of diesel fuel, rapeseed oil, and diesel fuel-rapeseed oil mixture and of fuel microemulsions containing 10% water.

| **Amphiphile*/ulei** | **Cloud Point (°C)** | **Pour Point (°C)** |
|---|---|---|
| Diesel fuel (D) | -15 | -23 |
| Rapeseed oil (RSO) | -10 | -11 |
| D-RSO (1:1) | -12 | -18 |
| B30-SA9C-B/D | -15 | -20 |
| B30-SA9C-B/D-RSO | -4 | -6 |
| ICO520-SA9C-B/D | -15 | -20 |
| ICO520-SA9C-B/D-RSO | -13 | -18 |
| T65-SA9C-B/D | -5 | -10 |
| T65-SA9C-B/D-RSO | -1 | -3 |

***Note:** B in **Amphiphile** stands for *i*-Butanol

There are some obvious observations regarding the w/o microemulsions. For most systems, CP and PP values are not very different from those found in previous studies [24] and are comparable to those of diesel. For microemulsions containing the diesel fuel – RSO mixture UDR, CP and PP are slightly higher than those of diesel fuel. When the nonionic surfactants have low ethoxylation rates, 4 for B30 and 5 for ICO520, PP and CP are low. Instead, these values are higher for the system stabilized with T65 because the surfactant is more hydrophilic. This suggests different structural changes induced in the systems by water and temperature changes that depend on the surfactant used.

The calorific values determined for Diesel, RSO, Diesel-RSO mixture and for microemulsions containing 10% water are shown in **Fig. 19**. During the measurements, there was no evidence of soot formation in the calorimetric bomb.

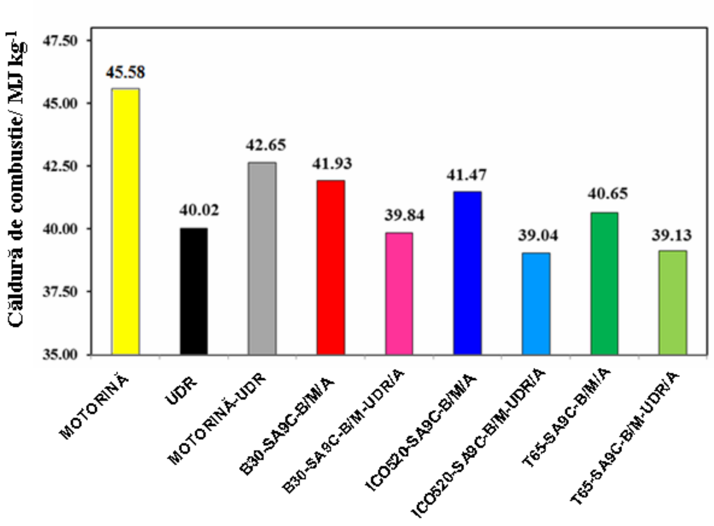

**Fig. 19.** The heat power values for diesel oil, rapeseed oil, diesel oil – rapeseed oil (1: 1 by weight) and for microemulsions prepared with SA9C anionic surfactant and B30, ICO520 and T65 as nonionic surfactants containing 10% water in the absence and presence of vegetable oil.

It should also be noted that for microemulsions with the same oily phase but containing different nonionic surfactants, those with T65 have the lowest calorific value. To explain this, we determined the caloric values of nonionic surfactants. The values obtained are 56.14 ± 0.35 MJ/Kg for B30, 67.02 ± 0.25 MJ/Kg for ICO520 and 32.47 ± 0.50 MJ/Kg for T65. These data reflect the carbon content of the components. The heat of combustion of our microemulsions is similar to that shown in literature for w/o microemulsions [25] and recommends them as diesel fuels.

The results obtained in this chapter of the PhD thesis lead to the following conclusions:

1. The freshly prepared microemulsions contain a very large number of nanometric water droplets and a very small one of micrometric drops.
2. This composition does not change over time and at constant temperature.
3. The fluidity of the w/o microemulsions is lower than of the oil phases used in their preparation.
4. The microemulsion fluidity decreases by: increasing the amount of water, replacing half of the diesel fuel with rapeseed oil, and by increasing the molecular weight of the nonionic surfactant, whereas the viscosity-activating energy has a reverse trend.
5. Depending on the nature of the components, the microemulsions are thermally stable in the temperature range from 10 to 55/60 ° C.
6. By heating, the size and proportion of nanometer water particles decreases in favor of the micrometric ones.
7. The most stable microemulsion contains SA9C, T65, *i*-butanol, diesel fuel and 10% water.
8. The cloud point, the pour point and the caloric power of the microemulsions are close to those of the diesel fuel.

The good thermal stability, the rheological behavior over a large temperature range, the flow characteristics and heats of combustion, as well as the harmless environmental impact, recommend these microemulsions as alternative fuels for the diesel engine.

## 6. Final conclusions

The study carried out in this PhD thesis aimed to elucidate some less known or even unknown aspects regarding the formulation of combustible microemulsions. It highlights relationships between the microemulsion phase transitions, oil/water interfacial tension, water and oil solubilization parameters and the droplet size of the dispersed phase. The final conclusions of this work are as follows:

1) The binary diesel-RSO system can be mixed with water to produce microemulsions in the presence of Brij 30 and/or AOT as surfactants and *i*-butanol as cosurfactant.

2) The microemulsion area increases in mixtures of anionic and nonionic surfactants and cosurfactant.

3) The microemulsion area decreases with the hydrophobicity of the surfactant and in the presence of the electrolyte.

4) The microemulsions made with distilled water form more easily than those whith salt (NaCl).

5) In the oil/water/surfactant/cosurfactant system, the increase in electrolyte concentration leads to phase transitions of type W1 → WIII → WII.

6) The single-phase WIV system is obtained at high amphiphile concentrations.

7) In WIII systems, $\gamma_{ow}$ has a minimum value as a fubction of salinity. The salinity corresponding to the minimum $\gamma_{ow}$ coincides with the maximum oil and water solubilization, and with the highest area of microemulsion.

8) The solubilization data obtained from phase behavior and phase diagrams are in good agreement and recommends the use of diesel fuel-rapeseed oil mixture to produce combustible microemulsions.

9) Since AOT contains sulfur, it has been replaced with an ecofriendly extended SA9C anionic surfactant.

10) The SA9C surfactant does not form alone combustible microemulsions.

11) Combustible microemulsions can be obtained by mixing SA9C with various ethoxylated nonionic surfactants (*i.e.*, B30, ICO520, T65 and T85) with HLB ranging from 9.7 to 11.

12) Mixing nonionic surfactants with *i*-butanol (cosurfactant) leads to good amphiphile products for the formulation of diesel fuel or diesel fuel-rapeseed oil blend microemulsions.

13) The nonionic surfactants used in this doctoral thesis form single monophasic microemulsions, but the size of the microemulsion area in the ternary phase diagrams depends on their HLB.

14) The ternary extended anionic surfactant-nonionic surfactant-cosurfactant mixture forms large single-phase microemulsion areas capable of solubilizing large amounts of water without phase separation.

15) Solubilization of water in the microemulsion decreases by the addition of sodium acetate.

16) By replacing half the amount of diesel oil with rapeseed oil, the pseudo-ternary pattern does not change significantly in the single-zone area.

17) The three-phase microemulsion has the widest salinity range, the smallest interfacial tension o/w and the highest values of the solubilization parameters and of the droplets of the dispersed phase.

18) During the phase transition WI → WIII → WII, resulted from increasing the organic electrolyte concentration, the phase behavior of the oil-water-amphiphile systems correlates well with the interfacial tension, oil and water solubility and the size of the dispersed droplets.

19) In Winsor III systems, at optimum salinity, interfacial tension is minimal, the oil and water solubility parameters are maximal, and the particles of the dispersed phase have the largest dimension.

20) The diesel-rapeseed oil microemulsions have the $\gamma_{ow}$*, SP* and r* parameters superior to those prepared with diesel fuel, and recommends vegetable oils for combustible microemulsions.

21) The structure of freshly prepared microemulsions consists of a majority population of nanometric droplets of water $D_1$ accompanied by a small secondary micrometric population $D_2$. This structure does not change over time at constant temperature.

22) The viscosities of w/o microemulsions are slightly higher than those of diesel and increase with the water content, molecular weight of the surfactant and by replacing half the amount of diesel with rapeseed oil, but decrease with temperature in the range 10-60 ° C.

23) The microemulsions have slightly lower $E_a$ values than those of diesel and RSO and they increase with the proportion of water in the system, with the molecular weight of the nonionic surfactant and by replacing half the amount of diesel with RSO

24) The microemulsions have good stability over a wide range of temperatures ranging from 10 ° C to 60 ° C.

25) Temperature causes important structural changes to microemulsions. The main population of dispersed nanometric particles as well as their average area decrease due to the appearance of larger particles. The microemulsion containing T65, diesel and 10% water has the highest stability.

26) The flow properties at low temperature, the cloud and the pour point, as well as the caloric power of the microemulsions are close to those of diesel, and recommend using these systems as substitutes for diesel fuel.

27) The results obtained in this doctoral thesis contribute to the advancement of knowledge in the field of liquid-liquid dispersions by providing a fast and efficient method of obtaining combustible microemulsions based on ecological compounds.

## 7. Original contributions

In this doctoral thesis titled: ‘Microemulsions as alternative fuels for internal combustion engines based on diesel and diesel-vegetable oil’, the research was carried out and original results were achieved in:

- Obtaining microemulsions with diesel and diesel-rapeseed oil mixture as the oil phase;
- Use of surfactants and co-surfactants (AOT, Brij 30 and i-butanol);
- Use of biodegradable extended surfactants (Synperonic A9C);
- Increasing the number of nonionic surfactants (Brij 30, Igepal 520, Tween 65 and Tween 85);
- Use of inorganic electrolytes (NaCl) and organic ones (CH3COONa);
- Determination of the monophasic and polyphasic areas in the pseudo-ternary diagrams;
- Estimation of co-solubilization of oil and water in microemulsion as a function of concentration and type of surfactant and electrolyte;
- Correlation of oil/water interfacial tension, with the particle size of dispersed phase and the solubilization of oil and water in microemulsion.

## 8. Perspectives of the future

The depletion of crude oil reservoirs deposits and the degradation of the environment are major challenges today that require the shift from fossil fuels to alternative fuels.

The results obtained in this doctoral thesis provide valuable information on the formulation and stability of environmentally friendly microemulsions.

They also show how formulators can avoid situations of ‚needle-searching in the haystack’, saving time, materials and energy.

The microemulsions obtained open the way for the use of vegetable oils in the process of formulating alternative fuels, friendly to the environment, to animals and human beings on the Earth.

A first step already done towards a cleaner planet is replacing half of the diesel fuel in the formulated microemulsions with rapeseed oil.

In the future, research will continue with the preparation of alternative fuels using a wide range of vegetable oils, surfactants and cosurfactants. From this perspective, switching from fossil fuels to alternative ones is a great challenge to our time, and its realization can not be done without sound scientific research in this area.

## 9. Dissemination of results

The results obtained in this doctoral dissertation were disseminated by:

1) Publication of a paper: Balcan M, **Mihăilescu FC**, Anghel DF, Văcăreşteanu IC, Aricov L, Vasilescu EL. "Microemulsion systems containing diesel and colza oil as alternative fuels: Phase studies, interfacial tension and solubilization" in Fuel 2014; 117: 251-258 [Impact Factor (FI 2014) = 3,520];

2) A work entitled: "Combustible microemulsions with diesel and diesel admixed with rapeseed oil", authors: F.C. Mihăilescu, M. Balcan, M.E. Maxim, D.F. Anghel. The work is accepted for publication and will appear in the REVISTA DE CHIMIE (Bucharest), vol. 70 no. 9/2019, according to the certificate no. 51/05/ 06.2019, [Impact Factor (FI 2014) = 1.605].

At the same time, the results were presented at 8 international scientific meetings. One paper obtained the second prize for the best poster.

## 10. Selective bibliography

1. Temple J. At this rate it’s going to take nearly 400 years to transform the energy system, MIT Technology Review, Sustainable Energy, 14 martie 2018; https://www.technologyreview.com/s/610457/at-this-rate-its-going-to-take-nearly-400-years-to-transform-the-energy-system/.
2. https://www.eia.gov/forecasts/steo/report/prices.cfm. US Energy Information Agency, 12 februarie 2019.
3. Schwab AW, Bagby MO, Freedman B. Fuel 1987;66:1372-1378.
4. Singh SP, Singh D. Renew Sust Energy Rev 2010;14:200-216.
5. Labecki L, Ganippa LC. Fuel 2012;98:15-28.
6. Russo D, Dassisti M, Lawlor V, Olabi AG. Renew Sust Energ Rev 2012;16:4056-4070.
7. Neuma de Castro Dantas T, da Silva AC, Neto AAD. Fuel 2001;80:75-81.
8. Acharya B, Guru PS, Dash S. Fuel 2016;171:87-93.
9. Ochoterena R, Lif A, Nyden M, Andersson S, Denbratt I. Fuel 2010;89:122-132.
10. Holmberg K, Jonsson B, Kronberg B, Lindman B. Surfactants and polymers in aqueous solutions. John Wiley & Sons; 2002. p. 139-155.

11. Delmas T, Piraux H, Couffin AC, Texier I., Vinet F, Poulin P, Cates ME, Bibette J. Langmuir 2011;27:1683-1692.
12. Phan TT, Harwell JH, Sabatini DA. J Surfactants Deterg 2010;13:189-194.
13. Do LD, Withayapayanon A, Harwell JH, Sabatini DA. J Surfactants Deterg 2009;12:91-99.
14. Balcan M, Mihailescu FC, Anghel DF, Vacaresteanu IC, Aricov L, Vasilescu EL. Fuel 2014;117:251-258.
15. Kahlweit M, Strey R, Busse G. J Phys Chem 1990;94:3881-3894.
16. Kahlweit M, Strey R, Schomacker R, Haase D. Langmuir 1989;5:305-315.
17. Anghel DF. Progr Colloid Polym Sci, 1990;83:188-195.
18. Salager JL, Anton RE, Sabatini DA, Harwell JH, Acosta EJ, Tolosa LI. J Surfactants Deterg 2005;8:3-21.
19. Kahlweit M, Strey R, Busse G. J Phys Chem 1991;95:5344-5352.
20. Noor El-Din MR, El-Gamal IM, El-Hamouly SH, Mohamed HM, Mishrif MR, Ragab AM. Colloid Surf A 2013;436:318-324.
21. Al-Hamamre Z, Al-Salaymeh A, Physical properties of (jojoba oil+biodiesel), (jojoba oil+diesel) and (biodiesel+diesel) blends, Fuel 2014;123:175-88.
22. Binks BP, Fletcher PDI, Taylor DJF, Langmuir 1997;13:7030-7038.
23. Neuma de Castro Dantas T, Da Silva AC, Neto AAD. Fuel 2001;80:75-81.
24. Sivaramakrishnan K, Ravikumar P. Int J Eng Sci Technol (IJEST) 2011;3(11):7981-7987.
25. Nguyen T, Abraham J, Ramallo M, Wagner D, McLennan J. J Am Oil Chem Soc 2012;89:1905-1912.