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**PHYSICO - CHEMICAL PROPERTIES OF
CONVENTIONAL FUELS MIXTURES WITH
BIOFUELS**

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A special place in renewable sources is played by the biofuels, for which, due to the recent global energy crisis and the oscillation of the crude oil prices, the international scientific community has sought new methods of production. Because of the fluctuations of the oil prices, the need to ensure energy security, and the worries about climate changes, biofuels have come to the forefront of technical and fundamental research.

Similarly, there are concerns around the world about emissions into the atmosphere from the burning of fossil fuels. Dangerous emissions produce the effect of global warming with potentially catastrophic consequences, including climate changes, rising sea levels and excessive heat.

One of the ways to solve these problems is the use of renewable energy sources in which biomass occupies an important place. Biomass is the biodegradable part of products, waste and residues resulting from nature or human activity. From it you can get biodiesel, bio-alcohols, biogas.

For traditional fuels diesel and gasoline, alternative fuels such as biodiesel and bio-alcohols have been added primarily from food sources, then from non-food, biomass, and other sources, respectively.

Thus, it is frequently practiced, regulated at the government's level, the use of blends of gasoline with bio-alcohols and diesel with biodiesel. Other components are added to basic blends to improve combustion and reduce the toxicity.

In order to use the biofuels, a lot of research are carried out, done to test technical performance, but the amount of experimental data is still low and the domain faces a lack of a fundamental-scientific approach to fuels blends physicochemical properties. The experimental data available are limited and not always sufficiently accurate determined.

The study of the literature shows that a large amount of research has been invested in biofuel production technologies, engine performance research, and noxious content, less for the fuel blends properties.

The Reid vapor pressure, distillation range, density, viscosity, and octane rating represent the group of properties that characterizes a fuel. The first ones are reflecting the efficiency of the combustion process, density is a fuel property that directly affects the atomisation process, thus

the engine performance and emission characteristics. Viscosity has effects on the quality of atomization, fuel droplet size, fuel flow characteristics and filtering qualities, thus on the quality of the combustion.

For blends with biofuels, standards are continuously completed and refined. Calculation and correlation models are also still under accumulation. There are used borrowed equations from the field of petroleum products, from the classical thermodynamics of molecular solutions, or there are equations proposed for biofuel blends.

In this field, there is a vast potential for both technical and theoretical research, to deepen the study of the properties of biofuels, their mixtures, influence of composition, temperature and other factors.

In this context is the subject of this present work, the study of some physicochemical properties of conventional fuels mixtures with biofuels. It was developed the direction of the two major traditional fuels for automotive field: gasoline and diesel fuel and some of their blends of interest in the actual research. Experimental data were obtained for the properties of (pseudo) binary and (pseudo) ternary blends of gasoline with bio alcohol and diesel fuel with biodiesel and benzene for which there are no experimental data accurately determined by large scale of composition and temperature, useful for testing some equations and patterns for properties correlation and prediction.

The research objectives are:

- presentation of the methods for prediction and correlation of properties for fuel blends applicable to biofuels used until now in research and practice;
- characterization of gasoline by determining the composition, average molar mass and main physico-chemical characteristics: Reid vapor pressure, distillation range, octane number.
- the study of the influence of alcohols addition: ethanol, i-propanol and n-butanol to gasoline on the physico-chemical characteristics of gasoline;
- obtaining high-precision experimental data on broad composition and temperature ranges for gasoline with alcohols: ethanol, i-propanol and n-butanol and diesel fuel blends with biodiesel and benzene, applying correlation and prediction models, supplementing the data bases;
- testing equations and patterns correlation and prediction for blends of the traditional fuels with biofuel: gasoline with alcohols, diesel fuel with biodiesel.
- obtaining equations for representation property - composition, property - temperature and complex dependence property - composition - temperature useful in practice;
- making correlations between properties that are useful to the practice and contributing to the understanding of the thermodynamic behavior of the analyzed systems, the basis for future theoretical and practical applications.

The study is structured in two main parts: the literature study and the original contributions, followed by the general conclusions and the bibliography.

The literature study includes two chapters.

CHAPTER1 include general considerations regarding biofuels use, namely bio-diesel and bio-alcohols, with the development of the bio-alcohols: a short history, the bio-alcohols proposed to be used, the advantages and disadvantages of use.

CHAPTER 2 defines the important physico-chemical properties of biofuels in the combustion process. The properties as density, viscosity, volatility with Reid vapor pressure and distillation range, octane number and lead, sulfur, oxygen and water content were analyzed. A

special focus has been put on density and viscosity, volumetric and transport important properties for liquids, depending on their structure, especially in the range of studied temperatures. Viscosity and density affects fuel atomization by injection into the combustion chamber and may contribute to the formation of deposits in the engine. Corelative and predictive calculation models were identified from literature for biofuel systems.

For these mixtures relatively recently introduced in current practice, researchers and users use mostly empirical equations specifically proposed for biofuels, borrowed equations from the petroleum products, but also semi-empirical equations borrowed from the thermodynamics of molecular solutions extended in this area. An overview of methods of correlation and predictive calculation of the properties of pure components and mixtures is presented

The original contributions are presented in Chapters 3-7.

CHAPTER 3 describes the substances, measurement *equipment* , experimental procedures and operating.

CHAPTER 4 contains experimental data concerning the physico - chemical characteristics of gasoline and gasoline – bioalcohols blends. Gasoline chemical composition was determined chromatographically and medium molar mass was calculated through cryoscopic and cromatographic metods. Diesel and biodiesel medium molar masses were determined by cryoscopic metod. The volatility of gasoline and gasoline mixtures with (bio) alcohols (ethanol, i-propanol, n-butanol) was determined by Reid vapor pressure and distillation curves. Octane number was also determined. Thereby, a basis for the comparison of the results with the data in literature was realized.

CHAPTER 5 presents experimental data for physico- chemical properties (density, viscosity, refractive index) of gasoline – alcohol blends: gasoline +etanol, gasoline +i-propanol and gasoline +n-butanol over a wide range of composition and temperature for which data are not given or limited in the literature. The ethanol is the alcohol that is currently used, but other alcohols such as n-butanol are in atention, with new benefits.

Experimental data were used for predictive and corelative calculation of mixtures physico-chemical properties. Obtaining new experimental data is the opportunity to test different methods and their ability to represent the properties of complex, relatively recently proposed and used systems as those studied in the present study. Predictive calculation methods for binary and ternary mixtures were tested: for density, viscosity, and refractive index. Predictive equations and correlative equations for property-composition, property-temperature and property-composition-temperature were tested. It has also been attempted to establish correlations between properties such as viscosity-refractive index, density-refractive index.

To predict the mixture density, equations and models were used as Kay blending method and other equations used in petroleum products área, and for corelation, Alptekin equation was used and also the equation proposed by Ramirez-Verduzco.

For viscosity, empiric, semiempiric or predictive equations were used, especially corelative and predictive equations. From the molecular thermodynamics area, the Grunberg-Nissan, Wielke and McAllister equations were used. From the petroleum products área, the Orbey and Sandler equation and empirical equations were used. In order to correlate the experimental data with temperature, the Andrade equation extended by Tat and Van Gerpen was used. The equation proposed by Krisnangkura was used to correlate viscosity by temperature and composition. For the refractive index the well-known equations Lorentz-Lorenz, Eykman, Gladstone-Dale, Newton and Arago Biot were used.

In petroleum mixture area, the relationship between properties is used in practice. For example, empirical equations to calculate density, viscosity, or other properties are commonly used based on refractive index values that are easier to approach experimentally. In this respect, empirical equations for calculating the density and viscosity of mixtures from refractive indices have been attempted in this study.

CHAPTER 6 approach the study of other combustible fuels mixtures, ternary systems of diesel fuel with biodiesel and benzene. In addition to diesel fuel + biodiesel binary systems, the interest in ternary mixtures has increased in recent years. This chapter presents the results of the study of diesel fuel blends with bio-diesel and benzene of practical interest to obtain mixtures with improved properties and theoretical interest for better understanding the behavior of blends with biodiesel. Experimental density, viscosity and refractive index data were obtained that were used to verify the correlation-prediction capability of the various equations proposed in the thermodynamics of molecular solutions or in the field of petroleum products, extended in the field of blends with biofuels. Correlation equations with composition and temperature were used. Generally, the equations used to model data for binary systems extended to three-component systems.

CHAPTER 7 contains general conclusions of the research.

Experimental data in this work were in the Petrolier Products laboratory, „Rompetrol Quality Control“ (RQC) from Rafinaria Petromidia Navodari, Physico-chemical properties laboratory from Chemical Engineering Department, “Ovidius” University Constanța and National Research and Development Institute for Chemistry and Petrochemistry in Bucharest (chromatographic analyzes).

The work contains approx. 200 pages and over 180 bibliographic references.

The results of the research are partly published or communicated in scientific journals and scientific events in the country and abroad: 3 published ISI papers (REV CHIM BUCHAREST, Energy Procedia and Sci. Bull U.P.B, 2017), 1 paper in press (Fuel), 1 papers in Scientific UPB Bulletin (BDI indexed, 2012), 2 papers in Ovidius University Annals of Chemistry (B+) and several international scientific communications abroad and in the country (CHISA-Prague, RICCCE-Romania, New trends in Oil, gas and Petrochem., Ind.-Constanta, Internat. Workshop Challenges in Food Chemistry-Romania-Constanta, and New Trends in Applied Chemistry-Romania).

4. PHYSICO-CHEMICAL CHARACTERISTICS OF GASOLINE AND GASOLINE – ALCOHOL BLENDS

Gasoline is a complex liquid mixture, derived from petroleum, containing liquid hydrocarbons with boiling temperatures between 40-200°C. Gasoline can contain up to 500 hydrocarbons containing between five and more than twelve carbon atoms in the molecule and the additives which improve its fuel properties.

In this work, for precise chemical characterization, a catalytic reformer gasoline was used, without additives, with high octane number.

Gasoline, being a mixture of hydrocarbons, a characterization as a pseudocomponent in blends with studied alcohols it's necessary. For this purpose, the main physico-chemical or technological characteristics were determined experimentally [125, 128]: chemical composition, medium molar mass, volatility (distillation curve and Reid vapor pressure) and octane number.

Also, the same properties were determined for blends of gasoline and the (bio) alcohols: ethanol, i-propanol and n-butanol, in order to assess the influence of alcohol in gasoline. The

alcohols proposed to be studied are ethanol, already used in practice, i-propanol and n-butanol which are soluble in the gasoline. n-Butanol may be considered an alternative to ethanol because of its high density compared to gasoline. i-Propanol, can also be considered as an alternative to ethanol, using as an additive in the preparation of high octane gasoline.

4.1. GASOLINE CHEMICAL COMPOSITION

Gasoline chemical composition was determined by gas chromatography. The studied gasoline contain: 25.33% (v/v) paraffins, 1.05% (v/v) oleffins, 1% (v/v) naphthenic and 72.63% (v/v) aromatics. Gasoline composition used in present study is according with standard SR EN ISO 3170:2004/ASTM D 4057-11 regarding hydrocarbons content [183].

4.2. MEDIUM MOLAR MASS

Gasoline medium molar mass can be determined by various methods. In this study, the gasoline molar mass was experimentally determined by the cryoscopic method and calculated from the chemical composition resulting from the chromatographic analysis: $105.1 \text{ g}\cdot\text{mol}^{-1}$. Also the molar mass of diesel fuel was determined: $213.9 \text{ g}\cdot\text{mol}^{-1}$ and of biodiesel: $289.28 \text{ g}\cdot\text{mol}^{-1}$.

4.3. VOLATILITY

The volatility of a gasoline is expressed by Reid vapor pressure (RVP), distillation curve and vapor / liquid ratio (also expressed as Vapor Lock Index) or the driveability Index (DI). From the data provided by the distillation curve, the Driveability Index (*Indice d'efficacité de carburation*) is calculated.

Reid Vapor Pressure (RVP) is an indicator of the volatility of the light fraction of gasoline, and the distillation curve shows information on gasoline volatility through the distillation range.

The vapor / liquid ratio is the property that correlates best with vapor blocking and other fuel handling issues (difficult starting or non-spinning, poor acceleration response). It is expressed by the temperature at which the gasoline contains a mixture of vapors and liquid in a proportion of 20 to 1 ($V / L = 20$). The normal values range from 35°C to 60°C . Frequently, the vapor lock index is calculated for the same purpose. The Vapor Lock Index (VLI) depends both on the Reid vapor pressure (RVP) and the distillate percentage collected until the temperature of 70°C is reached in the distillation process (E70).

$$\text{VLI} = 10 \cdot \text{RVP} + 7 \cdot \text{E70} \quad (4.5)$$

Manevrabilitatea (*Driveability*) inseamna pornire, ardere si rulare. Intregul profil al curbei de distilare a benzinei reflecta ceea ce motorul trebuie să distribuie, vaporizeze și sa arda. Pentru a descrie manevrabilitatea pornirii la rece sau la cald a benzinei, a fost introdus un index de manevrabilitate (*Driveability Index*, DI) utilizand temperaturile la care se culeg 10 %, 50 % si respectiv 90 % (v/v) distilat in procesul de distilare a benzinei, respectiv T10, T50 si T90. Indexul de manevrabilitate (DI) se calculeaza conform standardului american de calitate pentru benzine (ASTM 4814) cu relatia:

Driveability means start, burn and run. The full profile of the gasoline distillation curve reflects what the engine needs to distribute, vaporize and burn. To describe the handling of cold or hot start gasoline, a Driveability Index (DI) was used using the 10%, 50% and 90% (v / v) distilled temperatures, T10, T50 and T90, respectively. The Driveability Index (DI) is calculated according

to the American Standard for Gasoline (ASTM 4814) with the following relations[83]:

$$DI = 1.5 (T_{10}) + 3.0 (T_{50}) + 1.0 (T_{90}) \quad (4.6)$$

or

$$DI = 1.5 \cdot T_{10} + 3.0 \cdot T_{50} + 1.0 \cdot T_{90} + 1.33 \cdot (\text{percent of ethanol, \% v/v}) \quad (4.6')$$

4.3.1. Reid pressure vapor

Reid Vapor Pressure (RVP) is the vapor pressure of the fuel in kPa, measured at 37.8°C. For gasoline it is a quality parameter with standard recommended values.

In the present study the Reid vapor pressure (RVP) was determined according to the American standard ASTM-D-323 [131]. The results are shown in Figure 4.1 for gasoline and gasoline blends with alcohols, potential bioalcohols.

In the domain of reduced alcohol concentrations in gasoline (0-10% v/v alcohol), significant increases in RVP for gasoline blends with ethanol and i-propanol are observed and very low in the case of the mixture with n-butanol. As the concentration of alcohol in the mixture continues to increase, RVP remains approximately constant across the investigated concentration range (up to 40% v/v), with values up to 22.5 kPa for ethanol.

In the case of i-propanol, the maximum RVP is recorded for the 20% concentration, after which there is a slight decrease in the further increase of the alcohol concentration in the gasoline. For gasoline blends with n-butanol there is only a slight increase in RVP up to 5% alcohol concentrations, after which the vapor pressure drops slightly below the RVP of gasoline at 40%. A similar variation has also been obtained in the literature for different types of gasoline with alcohols [8]. In contrast to ethanol, the addition of n-butanol in gasoline reduces vapor pressure [8,105,107], but at the same time butanol reduces the evaporation losses.

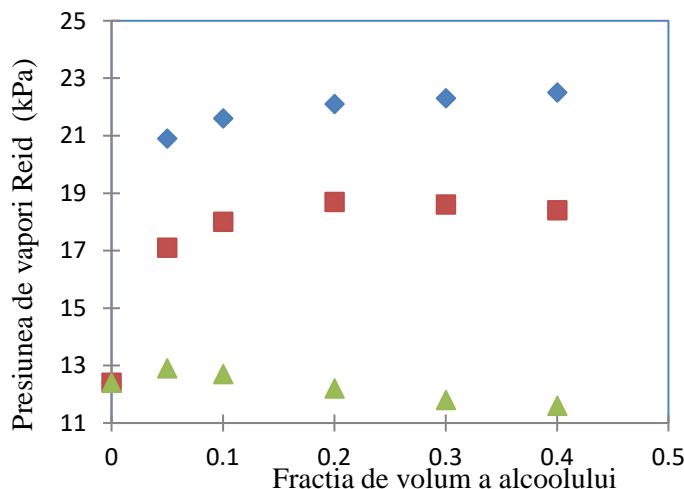


Fig.4.1. Reid vapor pressure *versus* alcohol concentration for gasoline blends with
 ◆ ethanol, ■ i-propanol and ▲ n-butanol.

4.3.2. Distillation curves

The results for distillation curves are presented in fig. 4.3-5.

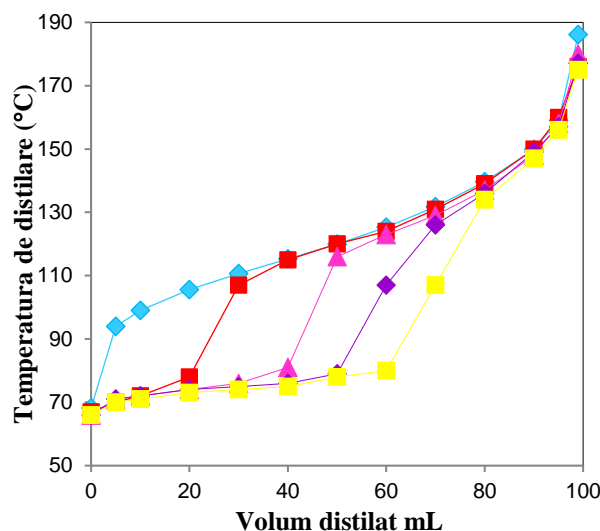


Fig. 4.3. Distillation curves for gasoline and gasoline blends with ethanol in different percents: 10%, 20%, 30% si 40%.

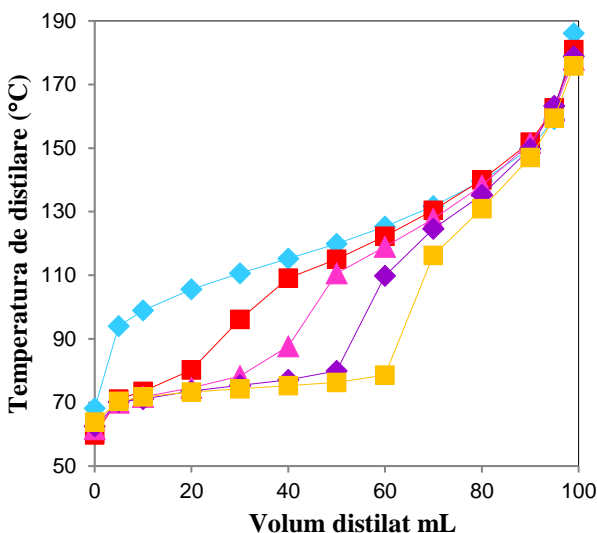


Fig. 4.4. Distillation curves for gasoline and gasoline blends with i-propanol in different percents: 10%, 20%, 30% si 40%.

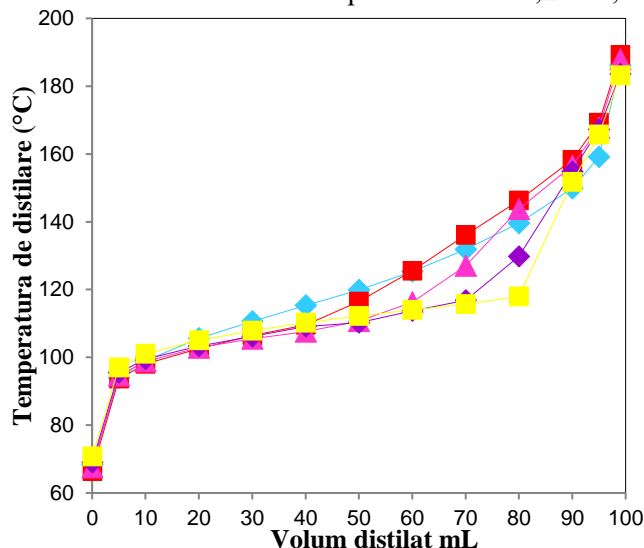


Fig. 4.5. Distillation curves for gasoline and gasoline blends with n-buthanol in different percents: 10%, 20%, 30% si 40%

Addition of alcohols in gasoline slightly alters the shape of the distillation curve, the differences in the distillation curves depending on the nature and amount of alcohol in the mixture. The higher the concentration of alcohol in the mixture, the deviation of the distillation curve of the mixture from the gasoline distillation curve is higher, except in the case of butanol. In the case of gasoline blends with ethanol (Figure 4.3) or i-propanol (Figure 4.4), the deviation of the mixture distillation curve from the basic gasoline distillation curve is explained by the formation of alcohol-hydrocarbon azeotrope which reduce the boiling point and increase the vapor pressure of the mixture.

The distillation curve can be schematically represented by three points, namely T10, T50 and T90, representing the temperature at which 10%, 50% and 90% of 100mL are obtained in the distillation process of the gasoline. These temperatures characterize the volatility of the light, medium or heavy fractions of the fuel that affect the operating mode of the engine. The addition of alcohols: ethanol, i-propanol, n -butanol in gasoline changes the value of these parameters.

Generally, all parameters decrease with the addition of alcohol, more for light and medium fractions (T10 and T50), very little for heavy duty fractions (T90), so adding alcohol increases gasoline volatility, more for light and medium fractions. In this respect, increasing the concentration of ethanol does not bring significant variations in volatility; T10, once low, remains practically constant with increasing the percentage of alcohol in the mixture. For T50, increasing the alcohol concentration brings about a decrease in this parameter at concentrations higher than 30% for ethanol and i-propanol.

Using the experimental data, the VLI (eq. 4.6) and DI (eq. 4.6) were calculated for the three gasoline-alcohol blends. The addition of ethanol or i-propanol decreases DI; Butanol less influences the DI values.

4.4. OCTANE NUMBER

The detonation process is related to the fuel self-ignition resistance that is quantified by the octane number expressed by RON (Research Octane Number) and MON (Motor Octane Number). The octane number reflects the quality of gasoline. Higher octane gasoline is a good gasoline, allowing the engine to perform better. Often low-octane distillation gasoline is converted by thermal or catalytic reforming into gasoline with the highest octane number [138]. The octane number varies with the fractional gasoline composition depending on the boiling range of gasoline [138]. The combustion process depends heavily on the chemical structure of the components that make up the gasoline.

In the present work, RON was determined on the equipment recommended by EN ISO 5164. The results obtained for gasoline blends with alcohols are shown in Figure 4.11. The variation of the alcoholic octane number for the catalytic reforming gasoline blends with the three types of alcohols: ethanol, i-propanol, n-butanol is shown. It is noted that the octane value increases linearly with the amount of added alcohol. For n-butanol blending, increasing alcohol concentration does not bring significant changes. Similar results there are in literature [10], the most studied being the blends with ethanol.

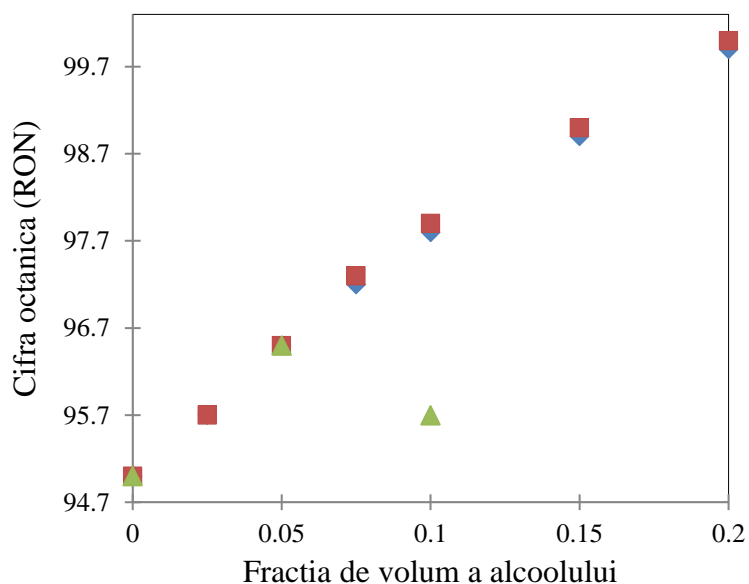


Figure 4.11. Octane number RON *versus* alcohol concentration for gasoline blends with : ■ ethanol, ■ i-propanol, ▲ n-butanol.

5. PHYSICO-CHEMICAL PROPERTIES OF GASOLINE BLENDS WITH ETHANOL, i-PROPANOL OR n-BUTHANOL

The physico-chemical properties of gasoline-alcohol combustible mixtures, especially the volumetric and viscosity properties that influence the ignition system and pipeline transport, are less studied on broad range of concentration and temperature. In the literature, there are limited density and viscosity studies, generally at the temperature required by the property standards, possibly to set some variation limits for them to avoid damaging the engine performance and emission characteristics [70,100].

In order to provide data for mixtures of traditional fuels with biofuels, density, viscosity and refractive index measurements were made for gasoline blends with alcohol covering the entire compositional domain on the temperature range of 293.15 K and 323.15K. Experimental determinations of refractive indices, easier to obtain experimentally, are useful for characterization of mixtures and for estimation of other properties like density and viscosity.

Experimental data were used to test predictive and correlation methods for the physico-chemical properties of mixtures. Predictive equations and property-composition, property-temperature and property-composition-temperature correlations were tested. It has also been attempted to establish correlations between properties such as viscosity-refractive index, density-refractive index.

5.1. EXPERIMENTAL DATA

5.1.1. Density

The gasoline(1) + ethanol(2), gasoline(1) + i-propanol (2) and gasoline(1) + n-buthanol(2) systems, on a temperature range between 293.15-323.15K, using catalytic reforming gasoline, have been studied. Density values for these systems are shown in figures 5.1-3. To highlight the influence of temperature on the density of the studied systems, the curves in Figures 5.4-6 were represented.

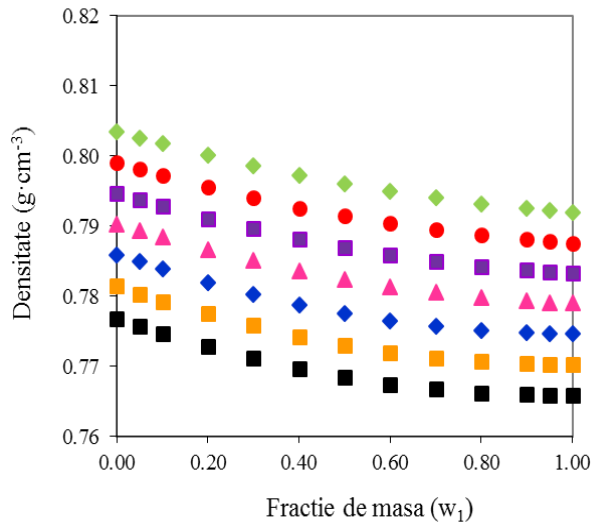


Fig. 5.1. Density variation with composition for gasoline(1) + ethanol(2) blends at different temperatures: \blacklozenge 293.15 K, \bullet 298.15 K, \blacksquare 303.15 K, \blacktriangle 308.15 K, \blacklozenge 313.15 K, \blacksquare 318.15 K, \bullet 323.15 K.

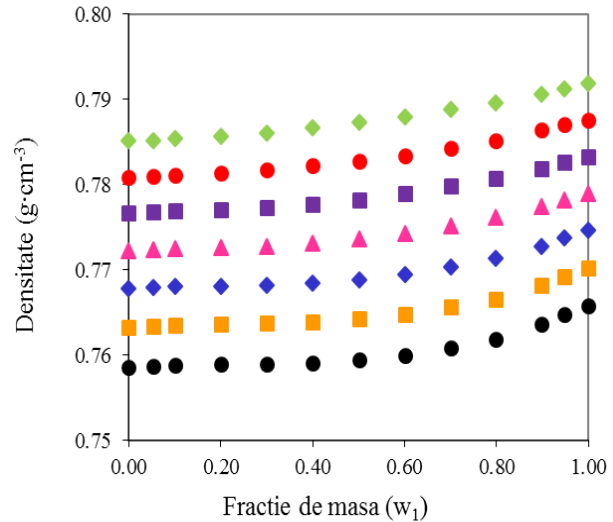


Fig. 5.2. Density variation with composition for gasoline(1) + i-propanol(2) blends at different temperatures: \blacklozenge 293.15 K, \bullet 298.15 K, \blacksquare 303.15 K, \blacktriangle 308.15 K, \blacklozenge 313.15 K, \blacksquare 318.15 K, \bullet 323.15 K.

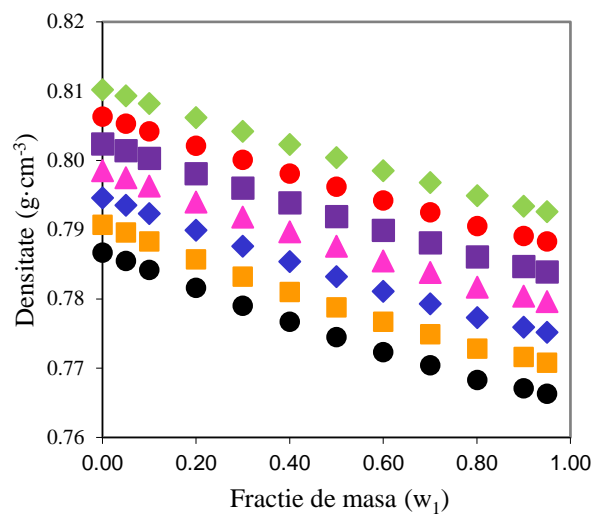


Fig. 5.3. Density variation with composition for gasoline(1)+n-buthanol(2) blends at different temperatures: \blacklozenge 293.15 K, \bullet 298.15 K, \blacksquare 303.15 K, \blacksquare 313.15 K, \bullet 323.15 K.

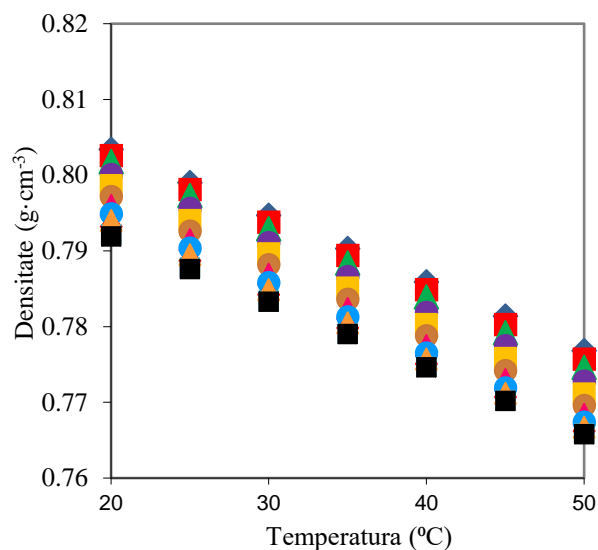


Fig. 5.4. Density variation with temperature for gasoline(1) + ethanol(2) blends at different concentrations, w_1 \blacklozenge 0, \blacksquare 0.05, \blacktriangle 0.1, \bullet 0.2, \blacksquare 0.3, \bullet 0.4, \blacktriangle 0.5, \blacksquare 0.6, \blacklozenge 0.7, \blacklozenge 0.8, \blacksquare 0.9, \blacklozenge 0.95, \bullet 1.

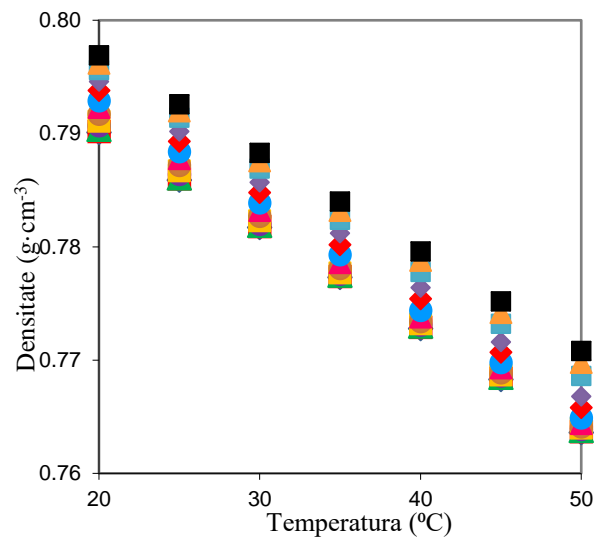


Fig. 5.5. Density variation with temperature for gasoline(1)+i-propanol(2) blends at different concentrations, w_1 \blacklozenge 0, \blacksquare 0.05, \blacktriangle 0.1, \bullet 0.2, \blacksquare 0.3, \bullet 0.4, \blacktriangle 0.5, \blacksquare 0.6, \blacklozenge 0.7, \blacklozenge 0.8, \blacksquare 0.9, \blacklozenge 0.95, \bullet 1.

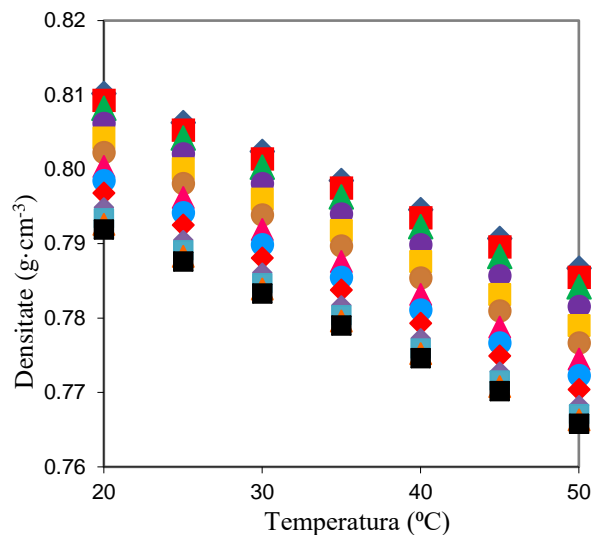


Fig. 5.6. Density variation with temperature for gasoline(1) + n-butanol(2) blends at different concentrations, w1: 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0

For all studied systems a monotonous variation of density with the alcohol composition is found, without extreme points, the variation depending on the values of the pure components.

Regarding the influence of temperature on the density of the pure components, the influence is similar, the density-composition curves in fig. 5.1-3 at different temperatures being practically parallel in the temperature range studied. Gasoline density decreases from 0.7919 to 0.7658, for ethanol from 0.8034 to 0.7768, for i-propanol from 0.7851 to 0.7586 and for n-butanol from 0.8102 to 0.7867 g·cm⁻³.

The knowledge of density variation with composition and temperature is of practical interest to users of the studied mixtures. Density variations with temperature are not high, so the density values remain in the range recommended by European standards EN 228 for catalytic reforming gasoline, with a maximum value of 0.830 g·cm⁻³. In this way it can be said that the blend of gasoline with alcohols is useful as a fuel mixture. Density variation with composition and temperature was represented in ternary diagrams for all the studied mixtures. Figure 5.7 shows, for example, the gasoline-ethanol system diagram.

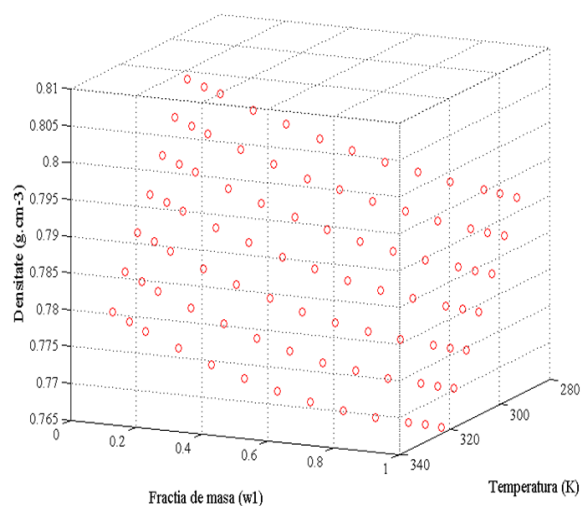


Fig. 5.7. Density variation with composition and temperature for gasoline (1) + ethanol(2) blends.

5.1.2. Viscosity

The viscosity variation with composition or temperature for binary systems in Figures 5.12-14 and figures 5.15-17, respectively, are shown.

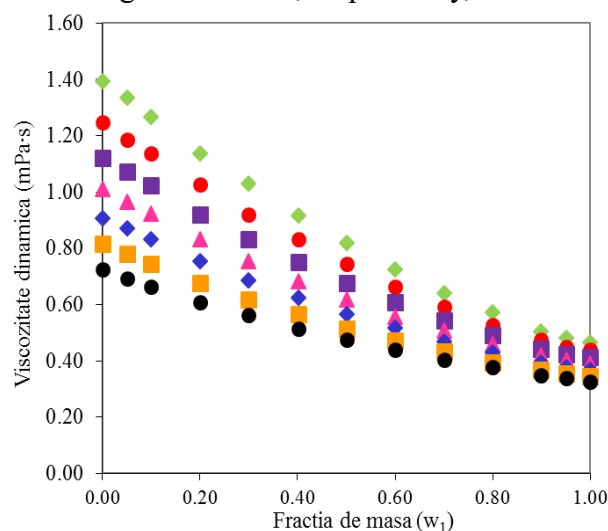


Fig. 5.12. Viscosity variation with composition for gasoline(1) + ethanol (2) blends at different temperatures: \blacklozenge 293.15 K, \bullet 298.15 K, \blacksquare 303.15 K, \blacktriangle 308.15 K, \blacklozenge 313.15 K, \blacksquare 318.15 K, \bullet 323.15 K.

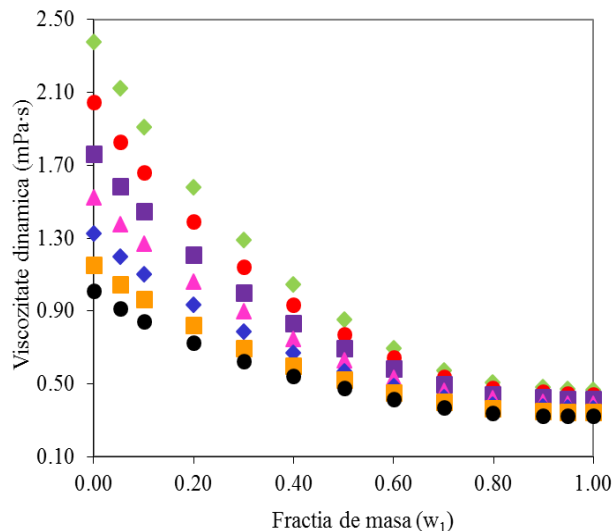


Fig. 5.13. Viscosity variation with composition for gasoline(1) + i-propanol (2) blends at different temperatures: \blacklozenge 293.15 K, \bullet 298.15 K, \blacksquare 303.15 K, \blacktriangle 308.15 K, \blacklozenge 313.15 K, \blacksquare 318.15 K, \bullet 323.15 K.

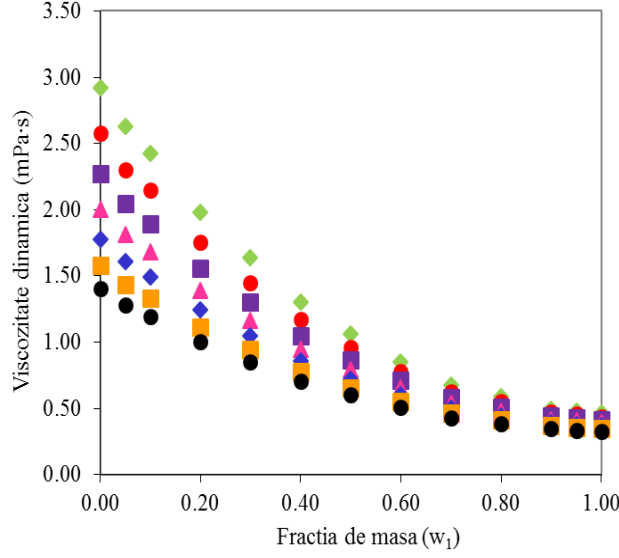


Fig. 5.14. Viscosity variation with composition for gasoline(1)+n-butanol(2) blends at different temperatures: \blacklozenge 293.15 K, \bullet 298.15 K, \blacksquare 303.15 K, \blacktriangle 308.15 K, \blacklozenge 313.15 K, \blacksquare 318.15 K, \bullet 323.15 K.

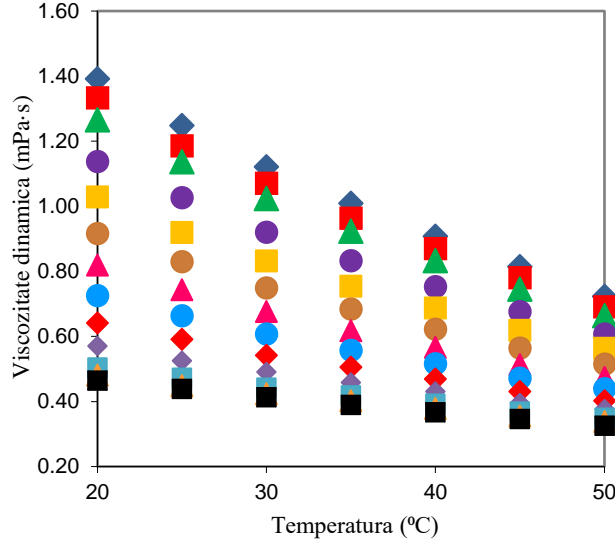


Fig. 5.15. Viscosity variation with temperature for gasoline(1) + ethanol(2) blends at different concentrations, w_1 : \blacklozenge 0, \blacksquare 0.05, \blacktriangle 0.1, \bullet 0.2, \blacksquare 0.3, \bullet 0.4, \blacktriangle 0.5, \blacksquare 0.6, \bullet 0.7, \blacklozenge 0.8, \blacksquare 0.9, \blacktriangle 0.95, \bullet 1.

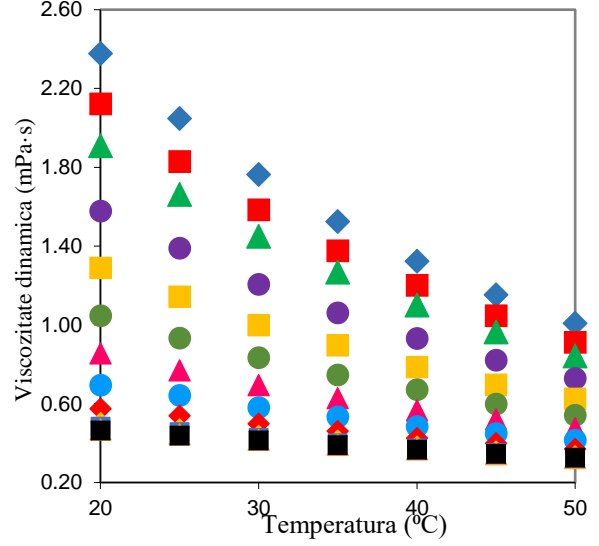


Fig. 5.16. Viscosity variation with temperature for gasoline(1) + i-propanol(2) blends at different concentrations, w_1 : \blacklozenge 0, \blacksquare 0.05, \blacktriangle 0.1, \bullet 0.2, \blacksquare 0.3, \bullet 0.4, \blacktriangle 0.5, \blacksquare 0.6, \bullet 0.7, \blacklozenge 0.8, \blacksquare 0.9, \blacktriangle 0.95, \bullet 1.

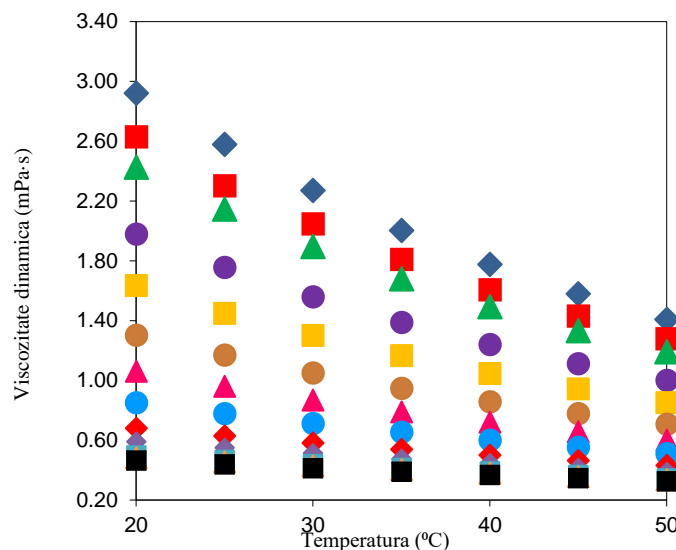


Fig. 5.17. Viscosity variation with temperature for gasoline(1) + n-butanol(2) at different concentrations, w_1 :

◆ 0, ■ 0.05, ▲ 0.1, ● 0.2, ■ 0.3, ● 0.4, ▲ 0.5, ◆ 0.6, ◆ 0.7, ◆ 0.8, ◆ 0.9, ▲ 0.95, ■ 1.

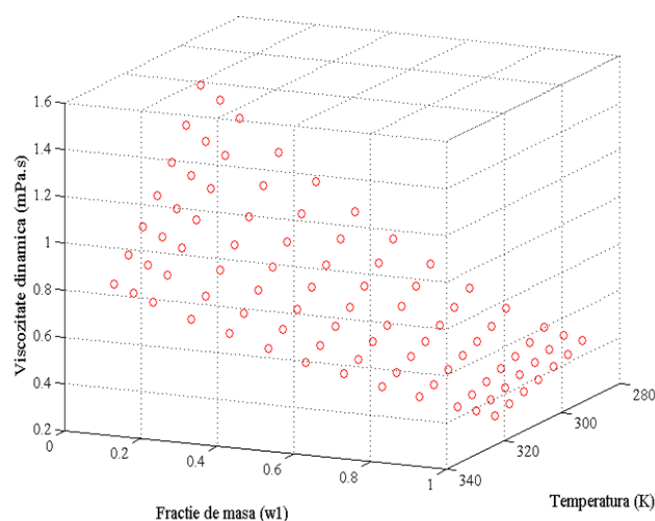


Fig. 5.18. Viscosity variation with composition and temperature for gasoline (1) + ethanol (2) blends.

The viscosity of the mixtures increases with increasing alcohol concentration in the mixture. Influence is more important in the field of higher concentrations of alcohol (alcoholic mass fraction, w_2 with values of 0.6-1). For the pure components, from figures 5.12-14 (y-axis), it can be seen that the viscosity of the catalytic reforming gasoline varies with the temperature between 293.15 and 323.15K, in the range of 0.4644-0.3256 mPa s, the variation being lower than in the case of alcohols: for ethanol ranges from 1.3923 to 0.7233, for i-propanol from 2.3785 to 1.0080 and for n-butanol from 2.9215 to 1.4071 mPa s. The influence of temperature is more important for i-propanol and n-butanol.

For binary mixtures of gasoline with ethanol, i-propanol and n-butanol, a normal decrease in viscosity with a rise in temperature was noted. As the concentration of blended gasoline increases, the decrease in viscosity with temperature is less important, the viscosity - temperature curves is less inclined (Figure 5.15-17).

In Figure 5, the viscosity variation with concentration and temperature on the same diagram in three-dimensional representation for gasoline-ethanol blends is shown.

5.1.3. Refractive index

The refractive index is a relatively easy experimentally obtained property, compared to other properties such as density, viscosity, being experimentally determined by a precise method using small amounts of sample. It can be correlated with other properties through different equations. Because of this, refractive index data is required and used to calculate other properties.

Refractive index values versus composition for gasoline mixtures with ethanol, i-propanol and n-butanol are shown in figures 5.21-23. The figures show a significant variation of the refractive index with the composition, so that the index-composition dependence curves can be used as calibration curves to determine the composition of mixtures from refractive indices readily to determine experimentally and for correlations with other properties.

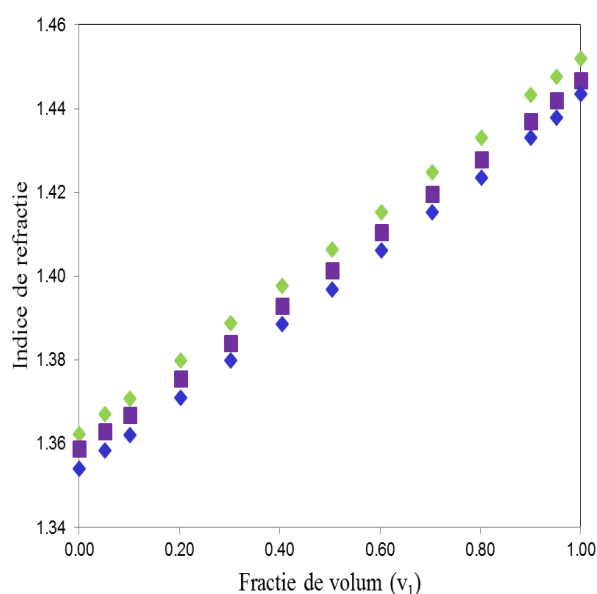


Fig.5.21. Refractive index variation with composition for gasoline(1) + ethanol(2) blends at different temperatures: ◆ 293.15 K, ■ 303.15 K, ◆ 313.15K.

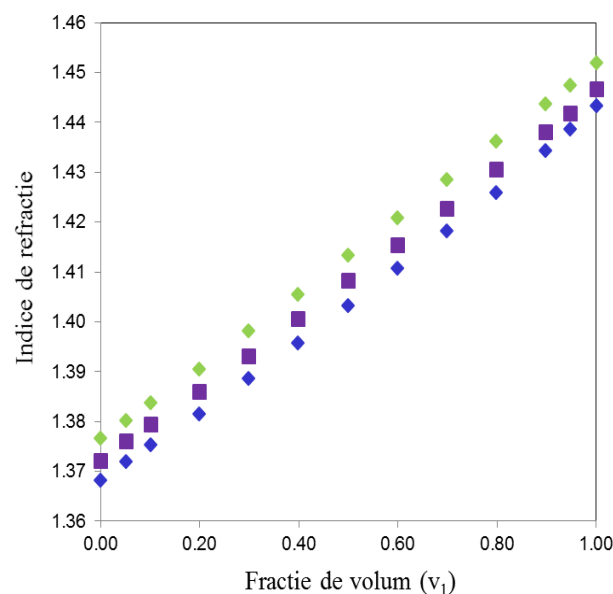


Fig.5.22. Refractive index variation with composition for gasoline (1)+i-propanol(2) blends at different temperatures: ◆ 293.15 K, ■ 303.15 K, ◆ 313.15K.

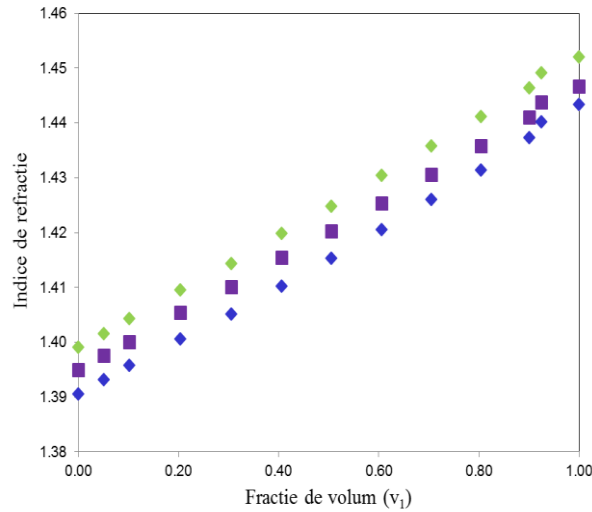


Fig.5.23. Refractive index variation with composition for gasoline (1) +n-butanol(2) blends at different temperatures: ◆ 293.15 K, ■ 303.15 K, ◆ 313.15K.

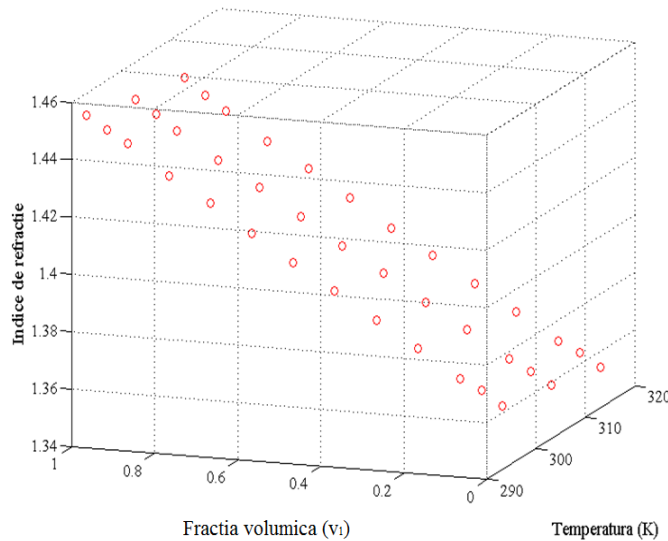


Fig. 5.27. Refractive index variation of gasoline mixtures with ethanol composition (v_1) and temperature

The variation of the refractive indices of the gasoline blend with ethanol with the composition and temperature are shown in fig.5.27 in three-dimensional representation.

5.2. CORRELATION AND PREDICTION OF THE PROPERTIES

5.2.1. Modeling data on the density

Experimental density data were modeled with prediction and correlation equations: the density depending on composition or temperature and complex equations, density depending on composition and temperature.

The prediction of blends density was achieved with equations 5.1 and 5.2. Equation 5.1 is Kay's blending rule for petroleum products that is commonly used in the literature to predict the density of blends with biofuels [5,20,29,39,162]. Equation 5.2 is an equation taken from the domain of petroleum products which predicts the density of mixtures according to the densities of pure components and their molecular masses [161].

$$\rho = w_1\rho_1 + w_2\rho_2 \quad (5.1)$$

$$\rho = \frac{x_1M_1 + x_2M_2}{\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}} \quad (5.2)$$

$$\rho = aw_1^2 + bw_1 + c \quad (5.3)$$

$$\rho = a \cdot T + b \quad (5.4)$$

$$\rho = a \cdot w_1 + b \cdot T + c \quad (5.5)$$

For density function of temperature, equation 5.4 was used [169,179]. More complex equation is the equation proposed by Ramirez-Verduzco [137] to express the density of mixtures depending on temperature and composition(ec.5.5).

The accuracy of the equations was evaluated by the mean relative percentage deviation (RPMD), relative percentage deviation (RPD) or correlation coefficient (R^2):

$$RPMD = \frac{100}{N} \sum_{i=1}^N \left| \frac{Y_{cal,i} - Y_{exp,i}}{Y_{exp,i}} \right| \quad (5.6)$$

$$RPD = \frac{Y_{cal,i} - Y_{exp,i}}{Y_{exp,i}} \cdot 100 \quad (5.7)$$

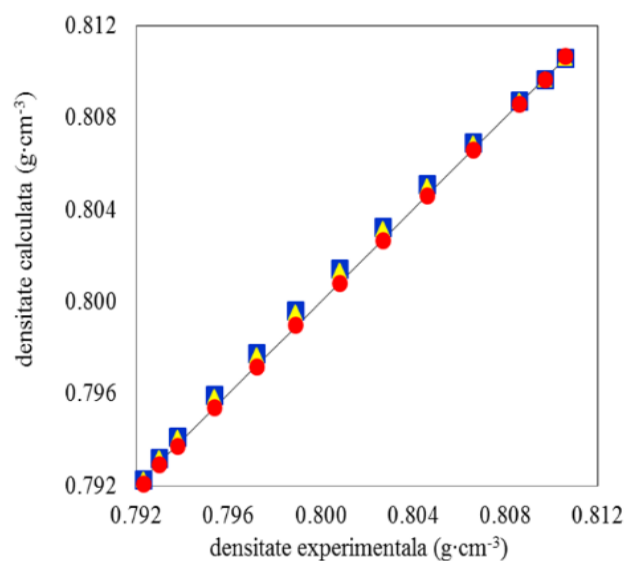
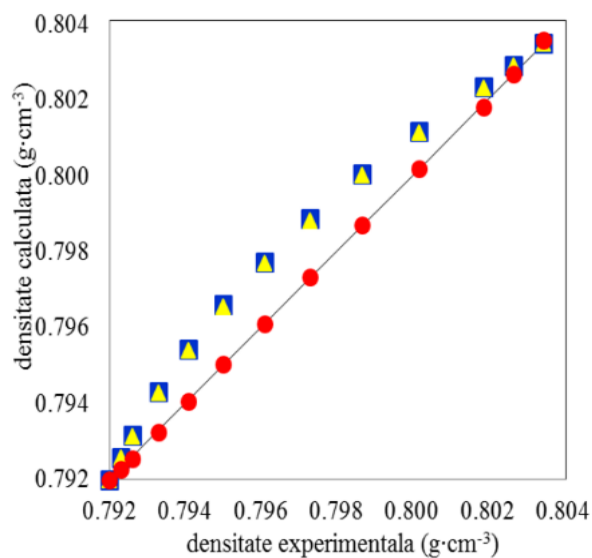
ρ is the density of mixture, ρ_1 și ρ_2 , M_1 și M_2 – the densities and molar masses, respectively, of components, w_1 și w_2 , x_1 și x_2 – mass fractions and molar fractions, respectively; a , b , c - parameters; Y_{cal} is the calculated value, Y_{exp} , the experimental value, N is the number of experimental determinations.

Table 5.5 presents the results of the predictive calculations, RPMD values obtained by applying the equations 5.1 and 5.2 to different temperatures for the three binary systems.

To assess the quality of the various calculations (eq. 5.1-3), in Figure 5.30 are plotted the calculated *versus* experimental density at 298.15K for gasoline blends with ethanol, i-propanol and n-butanol.

Table 5.5. RPMD (%) errors value of predictive density calculation based on composition mixtures

Eq.	Temperature (K)						
	293.15	298.15	303.15	308.15	313.15	318.15	323.15
Gasoline+ethanol							
$\rho = w_1\rho_1 + w_2\rho_2$	0.106	0.123	0.140	0.153	0.184	0.191	0.198
$\rho = \frac{x_1M_1 + x_2M_2}{\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}}$	0.103	0.120	0.137	0.150	0.181	0.189	0.196
Gasoline+i-propanol							
$\rho = w_1\rho_1 + w_2\rho_2$	0.088	0.100	0.120	0.138	0.160	0.174	0.196
$\rho = \frac{x_1M_1 + x_2M_2}{\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}}$	0.087	0.099	0.119	0.137	0.159	0.173	0.195
Gasoline+n-butanol							
$\rho = w_1\rho_1 + w_2\rho_2$	0.044	0.054	0.066	0.078	0.094	0.111	0.124
$\rho = \frac{x_1M_1 + x_2M_2}{\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}}$	0.039	0.048	0.060	0.073	0.088	0.104	0.117



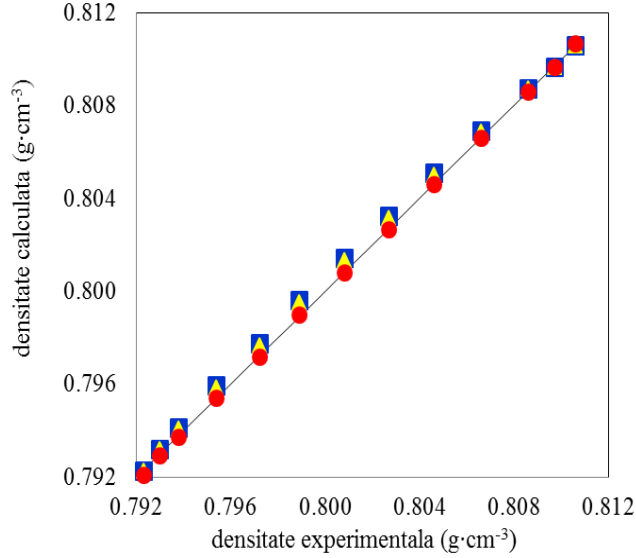


Fig. 5.30. Calculated density with different equations *versus* experimental density at 298.15K for gasoline blends with ethanol (a), i-propanol (b), n-butanol (c); ■ eq.5.1; ▲ eq.5.2; ● eq. 5.3.

Table 5.5 shows that predictive equations (5.1 and 5.2) give very good results for all systems, especially for the gasoline + n-butanol system. For the correlation of density with temperature, the linear equation 5.4 correlates very well all alcohol-based gasoline systems with values for R^2 of 0.9997-1. The equations can be used practically in the calculation of the density, in the studied field of temperature.

For the simultaneous correlation of density with composition and temperature, equation 5.5 was used. The obtained (p - v - T) dependence equations, valid for the all composition range and for temperatures ranging from 293.15 to 323.15K give satisfactory results

5.2.2. Modeling data on the viscosity

Corelation with composition(η - w_1)

Experimental viscosity data were modeled with viscosity depending on composition or temperature derived from thermodynamics of molecular solutions, petroleum blends or from biofuels domain. From the field of molecular thermodynamics, the Grunberg-Nissan, Wielke and McAllister equations were used. From the petroleum products area, the Orbey and Sandler equation and empirical equations were used.

A generalized equation for the viscosity of mixtures, originally proposed by Arrhenius and described by Grunberg and Nissan [60] was used to predict the viscosity of gasoline blends [136,140], being commonly used for biofuels [164][51]:

$$\ln \eta = \sum_{i=1}^n x_i \ln \eta_i + \sum_{i=1}^n \sum_{j=i, j \neq i} x_i x_j G_{ij} \quad (5.9)$$

This equation was used in the simple form without parameters (ec. 5.10.) and with a parameter (ec. 5.11):

$$\ln \eta = w_1 \ln \eta_1 + w_2 \ln \eta_2 \quad (5.10)$$

$$\ln \eta = w_1 \ln \eta_1 + w_2 \ln \eta_2 + w_1 w_2 G_{12} \quad (5.11)$$

Another commonly used equation in correlating viscosity data is the McAllister equation, semiempiric equation resulting from the theory of the activated complex applied to the viscous flow

[136].

$$\ln \eta = x_1^3 \ln \eta_1 + x_2^3 \ln \eta_2 + 3x_1^2 x_2 \ln \eta_{12} + 3x_2^2 x_1 \ln \eta_{21} + x_1^3 \ln M_1 + x_2^3 \ln M_2 - \ln(x_1 M_1 + x_2 M_2) + 3x_1^2 x_2 \ln M_{12}$$

$$M_{12} = (2M_1 + M_2)/3 \quad M_{21} = (M_1 + 2M_2)/3 \quad (5.12)$$

For estimating viscosity by predictive calculation, the Wielke, Orbey and Sandler equations were used. The Wielke equation estimates the viscosity of the blends according to the properties of the pure components:

$$\eta = \frac{x_1 \eta_1}{x_1 + x_2 \theta_{12}} + \frac{x_2 \eta_2}{x_2 + x_1 \theta_{21}} \quad (5.13)$$

$$\theta_{12} = \frac{[1 + (\eta_1/\eta_2)^{1/2} (M_2/M_1)^{1/2}]^2}{\{8[1 + (M_1/M_2)]\}^{1/2}} \quad \theta_{21} = \theta_{12} \frac{\eta_2}{\eta_1} \frac{M_1}{M_2}$$

The equation of Orbey and Sandler (1993) taken from Kendall-Monroe [120], originally proposed for liquid alkane mixtures, was applied for petroleum products and extended to blends with biodiesel:

$$\eta = (w_1 \eta_1^{1/3} + w_2 \eta_2^{1/3})^3 \quad (5.14)$$

Other equations encountered in chemical engineering which can be used in the predictive calculation of the viscosity of binary mixtures[5]:

$$\eta = \frac{(x_1 M_1) + (x_2 M_2)}{\frac{x_1 M_1}{\eta_1} + \frac{x_2 M_2}{\eta_2}} \quad (5.15)$$

$$\eta = a w_1^2 + b w_1 + c \quad (5.16)$$

In equations η is viscosity, G_{ij} , η_{ij} -, the models parameters, the other terms having the same meaning as used above.

Corelation with temperature (η - T)

Correlation of viscosity of mixtures with temperature was achieved with the Andrade[92] and Tat and Van Gerpen[167] equations, eqs. 5.17-18, respectively.

$$\ln \eta = a + \frac{b}{T} \quad (5.17)$$

$$\ln \eta = a + \frac{b}{T} + \frac{c}{T^2} \quad (5.18)$$

Corelation with composition and temperature (η - w_1 - T)

Using experimental data, more complex dependence equations, such as viscosity-composition-temperature, have been attempted. For the correlation of viscosity by temperature and composition, the Krisnangkura equation [92] was used:

$$\ln \eta = a + b w_1 + \frac{c}{T} + \frac{d w_1}{T} \quad (5.19)$$

Corelation of viscosity with composition (η -w)

The study present the results of viscosity data modeling: predictive calculations, viscosity correlation with composition, viscosity correlation with temperature, and complex viscosity correlation with composition and temperature. Here are some examples.

Table 5.10 shows the results of the viscosity correlation with the composition at different temperatures. Parameter values of Grunberg-Nissan (equation 5.10), McAllister (equation 5.12) and polynomial (equation 5.16) equations with the corresponding errors for gasoline (1) + alcohol (2) are presented. In Figure 5.32 are the results of the calculation with predictive and correlative equations. The figures show the calculated viscosity versus experimental values at 298.15K for 5.10, 5.13-5.15 predictive equations and 5.11, 12, 16 correlative equations. The correlative equations give better results.

The polinomial empirical equation with three-parameter gives very good results in the viscosity representation, the two-parameter Grunberg-Nissan and McAllister equations with a theoretical basis also show good and acceptable results.

Tabelul 5.10. Corellation of viscosity (mPa*s) with composition for gasoline blends with alcohols at different temperatures

Equation		Temperature (K)						
		293.15	298.15	303.15	308.15	313.15	318.15	323.15
Gasoline+ethanol								
Grunberg–Nissan	G_{12}	0.045	-0.012	-0.055	-0.072	-0.077	-0.131	-0.085
	RPMD (%)	1.240	1.256	1.168	0.865	0.668	0.690	0.248
McAllister	Π_{12}	0.522	0.484	0.457	0.438	0.415	0.386	0.376
	Π_{21}	0.739	0.668	0.601	0.544	0.500	0.451	0.417
	RPMD (%)	0.232	0.307	0.322	0.193	0.266	0.270	0.221
(5.16)	a	0.439	0.393	0.367	0.327	0.283	0.263	0.198
	b	- 1.382	- 1.214	- 1.084	- 0.951	- 0.827	- 0.733	- 0.592
	c	1.398	1.251	1.125	1.011	0.910	0.815	0.721
	R^2	0.999	0.999	0.999	0.999	0.999	0.999	0.999
	RPMD (%)	0.503	0.551	0.416	0.244	0.197	0.244	0.288
Gasoline+i-propanol								
Grunberg–Nissan	G_{12}	-0.933	-0.896	-0.898	-0.866	-0.877	-0.847	-0.826
	RPMD (%)	4.167	3.629	3.404	3.204	3.004	2.460	2.312
McAllister	Π_{12}	0.434	0.416	0.393	0.371	0.348	0.335	0.312
	Π_{21}	0.749	0.677	0.602	0.549	0.491	0.442	0.407
	RPMD (%)	1.075	0.894	0.723	0.564	0.595	0.418	0.620
(5.16)	a	2.266	1.872	1.575	1.306	1.108	0.924	0.763
	b	- 4.112	- 3.428	- 2.884	- 2.416	- 2.040	- 1.708	- 1.425
	c	2.334	2.013	1.737	1.506	1.307	1.136	0.990
	R^2	0.999	0.999	0.999	0.999	0.999	0.999	0.999
	RPMD (%)	1.745	1.434	1.319	0.972	0.911	1.080	0.811
Gasoline+n-butanol								
Grunberg–Nissan	G_{12}	-0.465	-0.495	-0.504	-0.510	-0.515	-0.518	-0.514
	RPMD (%)	3.708	3.305	3.147	2.907	2.639	2.481	2.261
McAllister	Π_{12}	0.495	0.474	0.447	0.424	0.402	0.379	0.358

	η_{21}	0.762	0.682	0.621	0.566	0.516	0.474	0.435
	RPMD (%)	0.753	0.745	0.680	0.638	0.610	0.564	0.536
(5.16)	a	2.525	2.180	1.882	1.619	1.400	1.213	1.052
	b	-4.930	-4.264	-3.696	-3.196	-2.776	-2.418	-2.109
	c	2.889	2.541	2.243	1.980	1.755	1.560	1.391
	R ²	0.999	0.999	0.999	0.999	0.999	0.999	0.999
	RPMD (%)	1.308	1.421	1.209	1.130	1.085	0.992	0.936

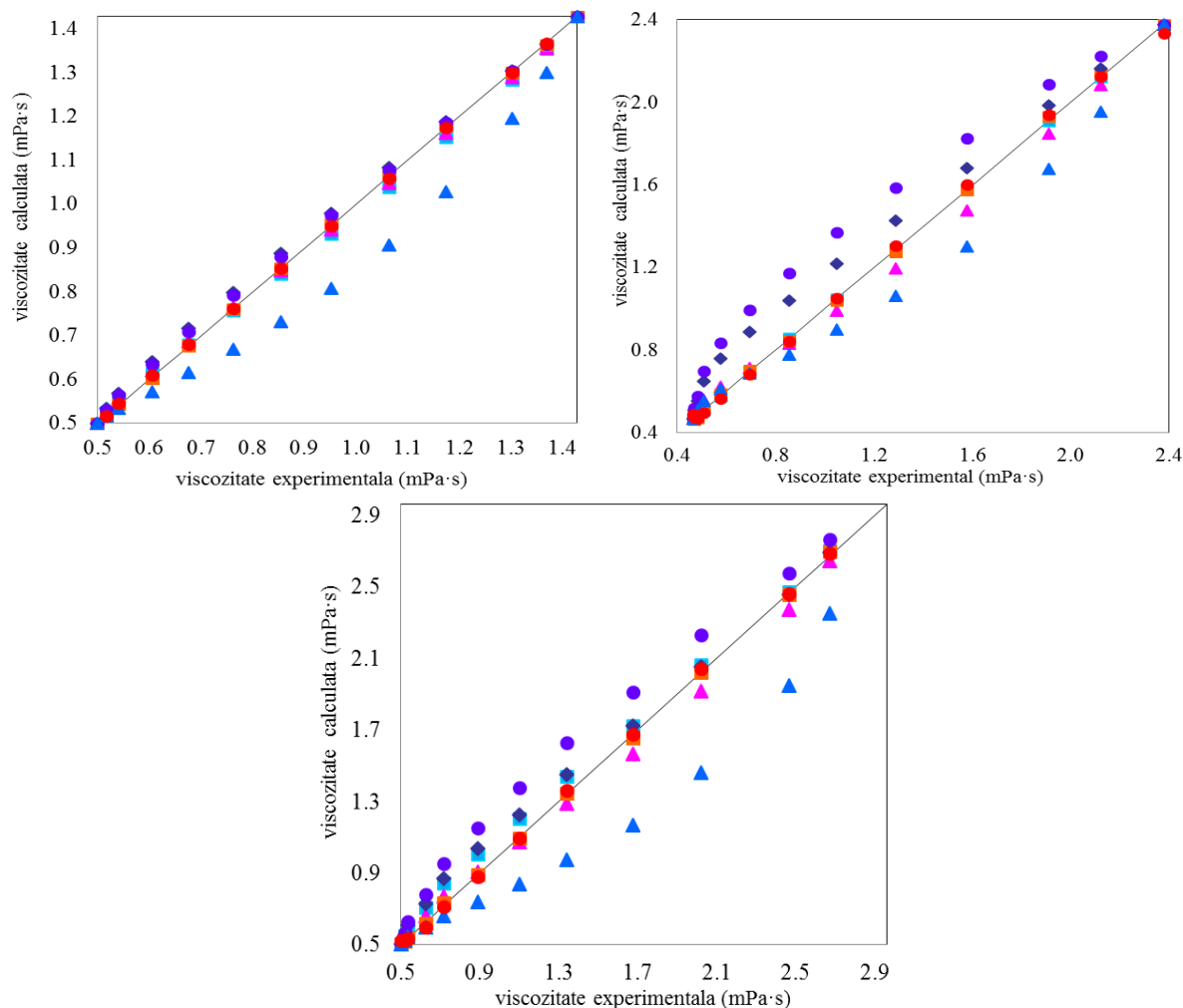


Fig.5.32. Viscosity calculated with different equations *versus* experimental viscosity at 298.15K for gasoline blends with ethanol (a), i-propanol (b), n-butanol (c);

■ eq.(5.10), ▲ eq.(5.11), ■ eq.(5.12), ◆ eq.(5.13), ● eq.(5.14), ▲ eq.(5.15), ● eq.(5.16)

From a practical point of view, the simpler polynomial equation can be used to calculate the viscosity of the mixtures. From a theoretical point of view, it is noteworthy that it can represent the viscosity of pseudo-binary systems with complex equations such as Grunberg-Nissan and McAllister. The viscosity correlation equations with the composition are very useful in practice for estimating the viscosity of various blends with gasoline.

Corelation of viscosity with temperature (η - T)

The Andrade equation correlates well the temperature viscosity data for all (pseudo)binary systems: gasoline – ethanol, gasoline - i-propanol and gasoline - n-butanol at all studied

compositions. The viscosity can be calculated with these equations with errors of approximately 0.2-0.8% over the temperature range 293.15-323.15K for the gasoline-ethanol system, 0.2-0.5 for the gasoline- i-propanol system and with 0.1-0.3 for the gasoline-n- butanol system. Andrade extended three-parameter equation does not bring a higher precision than the Andrade equation with two parameters with errors of 0.1-1.9%.

For **correlation of viscosity with composition and temperature** ($\eta-w_1-T$) the Krisnangkura proposed equation (equation 5.19) was used [92]. The parameters a, b, c, d and the corresponding equations were obtained with RPMD of 0.7-3.9%.

5.2.3. Modeling data on the refractive index

Based on experimental data, refractive index - composition equations ($n_D - v_1$) were obtained which can be used to determine the amount of gasoline blended with alcohol from experimental refractive index determinations:

$$n_D = av_1^2 + bv_1 + c \quad (5.20)$$

The prediction of the values of mixture refractive indices from refractive indices of the pure components of the mixture can be realised using different mixing rules taken from the thermodynamics of the molecular solutions applied to the gasoline systems: Lorentz-Lorenz, Gladstone-Dale, Eykman, Newton and the Arago Biot, equations known in the literature [66].

By similarity to the equations used for density and viscosity (Krisnangkura equation), the following equation of refractive index-composition-temperature was proposed:

$$\ln n_D = a + bv_1 + \frac{c}{T} + \frac{dv_1}{T} \quad (5.26)$$

In equations, n_D is the refractive index, v_1 is the volume fraction, a, b and c are regression coefficients.

Figures 5.34 (a) show as exemple the calculated values *versus* the experimental values of refractive index at 298.15K for gasoline blends with ethanol which give the best results having RPMD values of approximately 0.02%. For other systems, errors are about 0.02-0.04%. A similar behavior of the three gasoline blends with alcohols was observed. Both correlative and predictive equations give very good results.

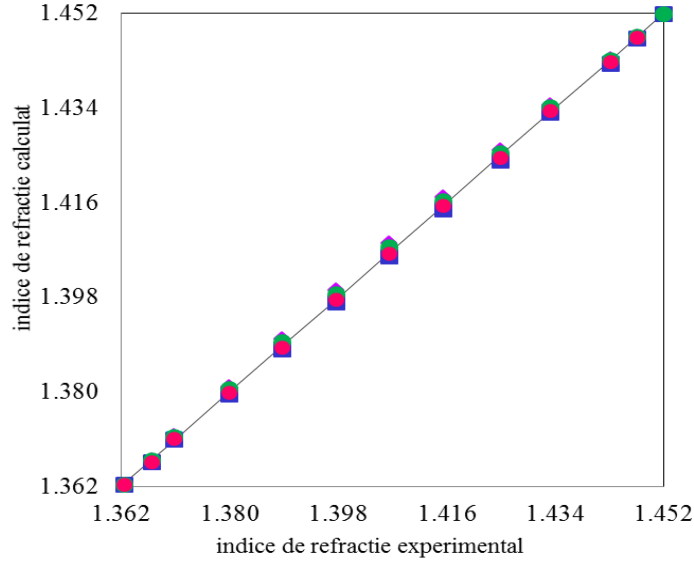


Fig.5.34. Refractive index calculated with different equations *versus* experimental refractive index at 298.15K for gasoline blends with ethanol;

■ eq.(5.20), ▲ eq.Lorenz- Lorenz ■ eq.Gladstone-Dale ◆ eq.Eykman, ● eq.Newton, ▲ eq. (5.22), ● eq. (5.23)

Equation 5.26 of the complex dependence refraction index-composition-temperature can be used to estimate the refractive index for all three alcohol blends with RPMD values between 0.02% and 0.05%.

5.3. PROPERTY-PROPERTY CORRELATIONS

Relations linking properties can be used in practice in order to avoid experimental effort. Empirical equations to calculate density, viscosity, or other properties from refractive index values easier to determine experimentally, are used. The calculation is most frequently used in the petroleum products and fuels area.

The equations are the result of experimental findings regarding the correlations between properties

The equations used to estimate the density from refractive index are equations 5.27-28.

$$\rho = a \cdot M^b \cdot \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right)^c \quad (5.27)$$

$$\rho = an_D^2 + bn_D + c \quad (5.28)$$

The equations used to estimate viscosity from index data are eqs. (5.29-32) which was used to estimate the viscosity of hydrocarbons and petroleum fractions at different temperatures. Equation (5.29) is proposed by Riazi and Alo-Otaibi [141]. Equations 5.31 and 5.32 are the result of experimental findings regarding the dependence of the two properties, viscosity and refractive index.

$$\frac{1}{\eta} = a + \frac{b}{n_D} \quad (5.29)$$

$$\eta = a + \sqrt{T}(b - c\sqrt{M}) + dM \quad (5.30)$$

$$\eta = an_D^2 + bn_D + c \quad (5.31)$$

$$n_D = a\eta^b \quad (5.32)$$

These equations were tested over the entire range of concentrations and temperatures studied. The quality of the correlation was evaluated by calculating the mean relative percentage deviation (RPMĐ) and the correlation coefficient (R^2).

5.3.1. Density - refractive index correlation

The equation 5.27 gives a good prediction of density from refractive index and molar mass for all studied systems with a relative percentage mean deviation (RPMĐ) between 0.020 and 0.023%. Polynomial equation 5.28 also correlates well the density with the refractive index, with correlation coefficients above 0.99. This is reflected in Figures 5.36 and 37.

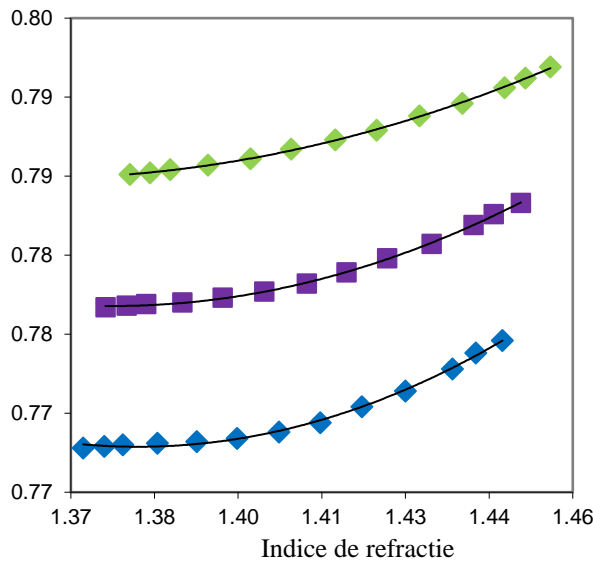


Fig. 5.36. Density versus refractive index For gasoline mixture with ethanol at \blacklozenge 293.15K, \blacklozenge 303.15K, \blacklozenge 313.15K correlation with eq. 5.28.

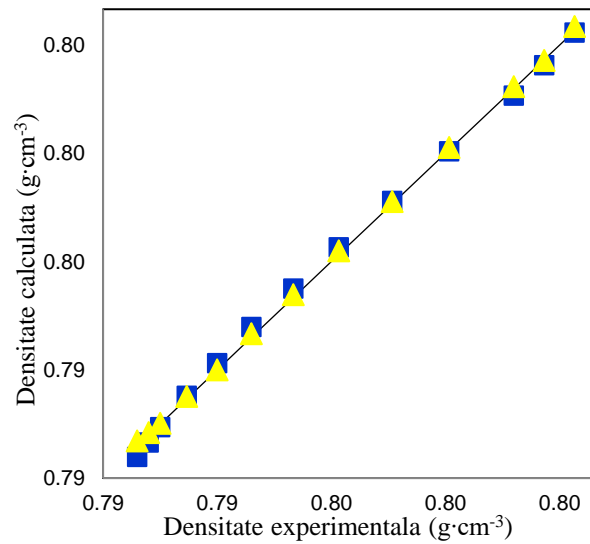


Fig.5.37. Density calculated with different equation versus experimental density for gasoline mixture with ethanol \blacksquare ec.(5.27); \blacktriangle ec.(5.28);

5.3.2. Viscosity - refractive index correlation

Equation 5.29 allows a satisfactory viscosity prediction for the ethanol gasoline system with errors (RPMĐ) between 3 and 7%, for the other systems the results are weaker. The equation 5.30 gives good results, allowing for the calculation of the viscosity with errors (RPMĐ) of 0.3-2.8%, which suggest the practical use of the equation.

The performance of eq.5.32 is shown in figures 5.37 (a), (b), (c). It can be noticed that equation 5.32 can represent the viscosity-refractive index dependence with very good results with a correlation coefficient of 0.9988 for the gasoline system with i-propanol [115]. Equation 5.31 is less useful.

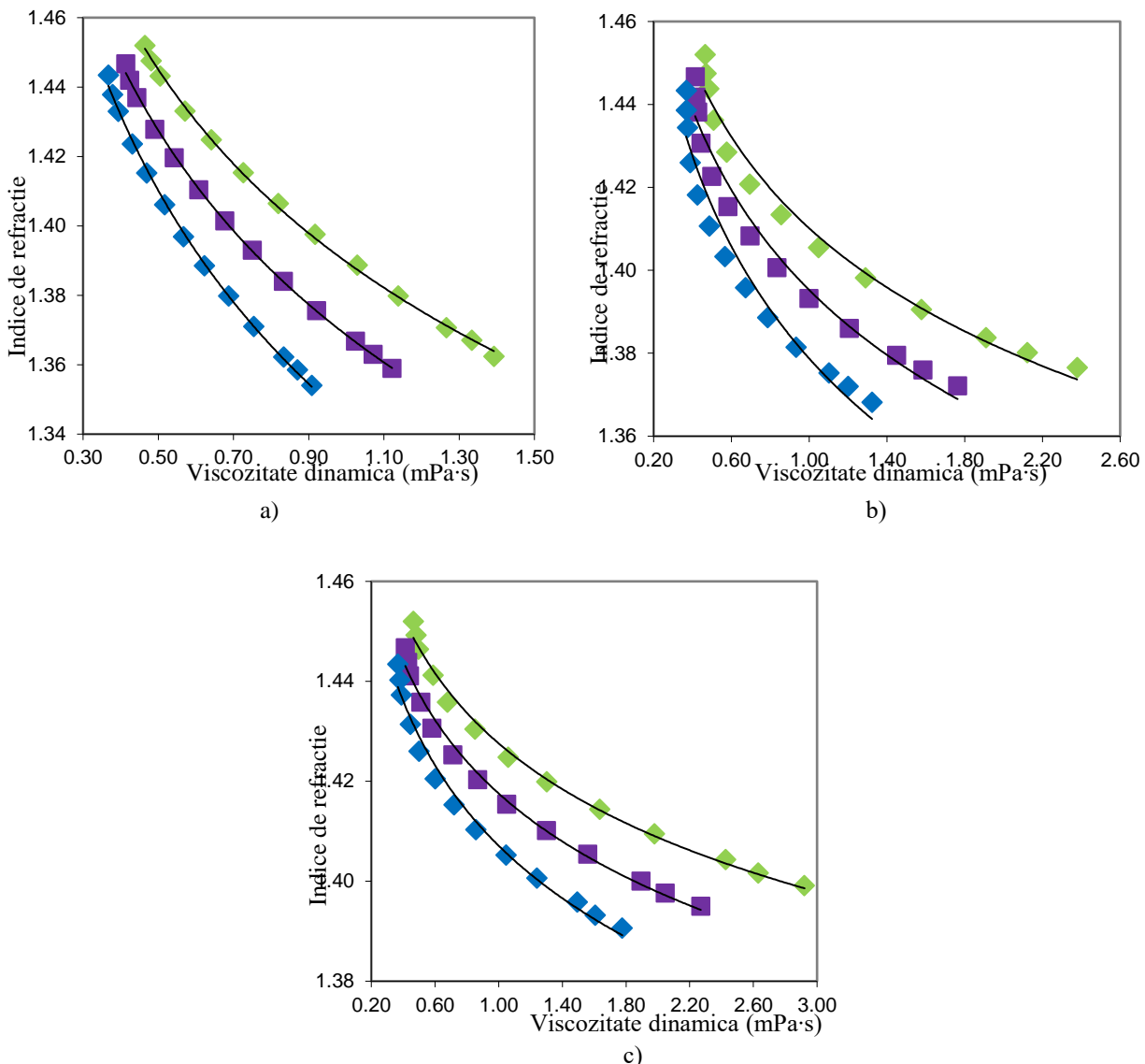


Fig. 5.38. Dependence of refractive index-viscosity for gasoline mixtures with ethanol (a), i-propanol (b) and n-butanol (c) at: \blacklozenge 293.15K, \blacklozenge 303.15K, \blacklozenge 313.15K, —correlation with eq. 5.32.

6. PHYSICO-CHEMICAL PROPERTIES OF DIESEL FUEL BLENDS WITH BIODIESEL AND BENZENE

The most popular fuel is diesel +biodiesel blend. For this, it has been found that, when biodiesel is added, the viscosity of the mixture increases and is higher than diesel fuel and influences the combustion properties of the mixture. In order to reduce the fuel viscosity, it has been proposed the addition of a third component, alcohol or hydrocarbon [17, 111, 120].

The present work studies the behavior of diesel fuel+biodiesel + benzene ternary mixture, for which no data were found in the literature. The results obtained from the study of the properties of ternary mixtures and their variation with composition and temperature are presented. That

allows the better understanding of the behavior of combustible mixtures as theoretical interest [113,114].

6.1. EXPERIMENTAL DATA

6.1.1. Density

Experimental data for biodiesel (1) + diesel (2) + benzene (3) on temperature range 293.15-323.15K are presented. A total of 32 mixtures were studied to uniformly cover the entire range of ternary compositions in order to obtain relevant results on the dependence of the property on the composition of the mixtures, and temperature. To better illustrate the density variation with the composition, the diagrams in Figure 6.1 are plotted. The 3D diagram presented in figure 6.1a and the iso-property curves in the Gibbs-Roozeboom ternary diagram, figure 6.1b, were highlighted by different colors representing different value domains of property.

Similarly, dynamic viscosity and refractive index data were obtained and represented.

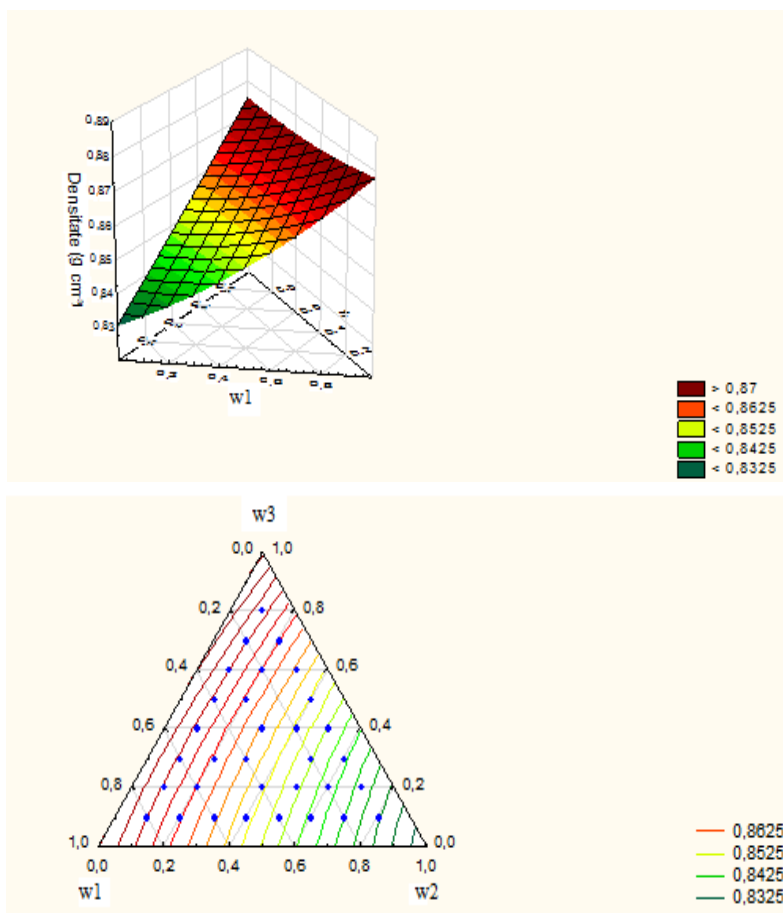


Fig. 6.1. Variation of density of ternary blends biodiesel(1)+diesel(2)+benzene(3) with composition at temperatures of 298.15K, a) 3D representation, b) curves for the ternary system

- Experimental data; (—) and correlated with ec. 6.3.

6.1.1. Viscosity

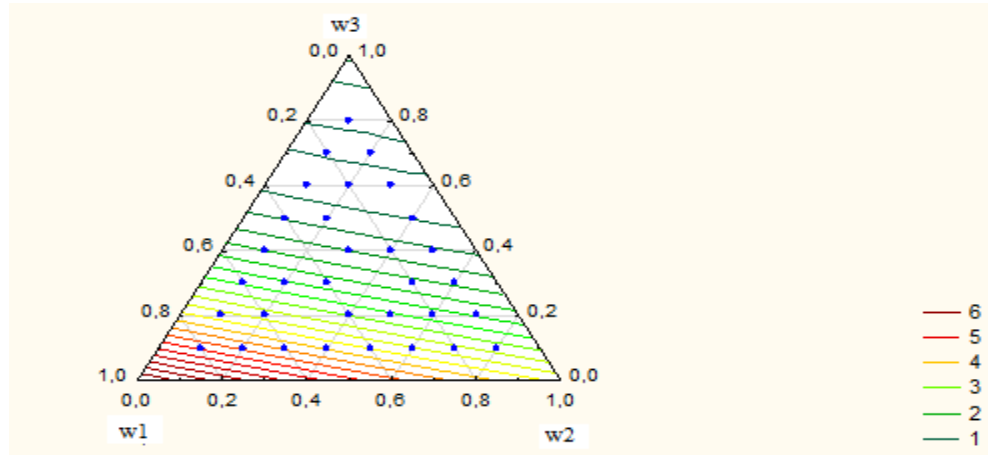
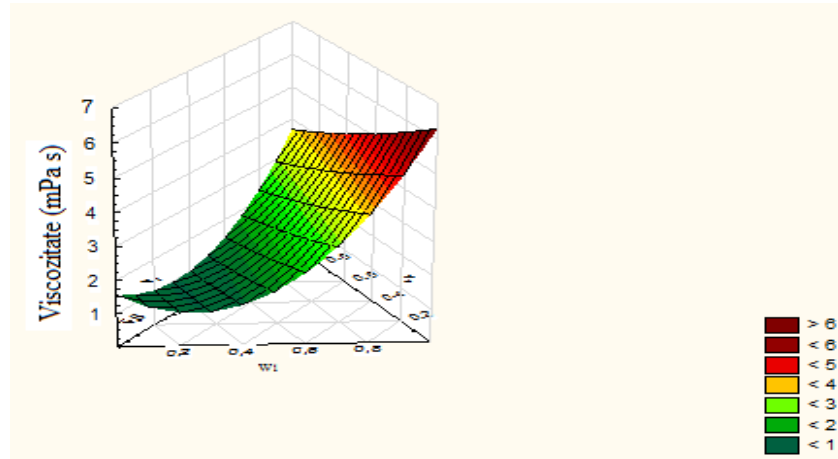


Fig. 6.21. Variation of viscosity of ternary blends biodiesel(1)+diesel(2)+benzene(3) with composition at temperatures of 298.15K, a) 3D representation, b) curves for the ternary system

- Experimental data; (—) and (•) correlated with ec. 6.3.

6.2. CORRELATION AND PREDICTION OF THE PROPERTIES

Experimental data was modeled by composition and temperature using the equations for binary systems extended to three-component systems expressing the composition by mass fraction or molar fraction.

6.2.1 Modeling data on the density

The following equations were used:

$$\rho = w_1\rho_1 + w_2\rho_2 + w_3\rho_3 \quad (6.1)$$

$$\rho = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} + \frac{x_3 M_3}{\rho_3}} \quad (6.2)$$

$$\rho = aw_1 + bw_2 + cw_3 + dw_1w_2 + ew_1w_3 + fw_2w_3 \quad (6.3)$$

$$\rho = aT + b \quad (6.4)$$

Equation 6.1 allows a prediction of ternary system density with relative percent deviations of 0.2% -1.3%, equation 6.2 shows errors (RPMD) of 0.1-1.3%, and equation 6.3, errors of 0.06-0.18% [113, 114]. Equation 6.4 that correlates the density with temperature with errors between 0.2-1.4%, has a good dependence .

The obtained equations can be used to calculate the density of the ternary mixture at various compositions and temperatures.

6.2.2. Modeling data on the viscosity

Experimental viscosity data was used to test the fitting capacity of some existing equations in literature.

Correlation with composition

The Grunberg-Nissan equation [57] was used in the simple, non-parametric form, with three binary parameters and with four parameters: three binary and one ternary parameters:

$$\ln \eta = w_1 \ln \eta_1 + w_2 \ln \eta_2 + w_3 \ln \eta_3 \quad (6.9)$$

$$\ln \eta = w_1 \ln \eta_1 + w_2 \ln \eta_2 + w_3 \ln \eta_3 + w_1w_2G_{12} + w_1w_3G_{13} + w_2w_3G_{23} \quad (6.9a)$$

$$\ln \eta = w_1 \ln \eta_1 + w_2 \ln \eta_2 + w_3 \ln \eta_3 + w_1w_2G_{12} + w_1w_3G_{13} + w_2w_3G_{23} + w_1w_2w_3G_{123} \quad (6.9b)$$

McAllister equation is a seven-parameter equation:

$$\begin{aligned} \ln \eta = & x_1^3 \ln(\eta_1 M_1) + x_2^3 \ln(\eta_2 M_2) + x_3^3 \ln(\eta_3 M_3) - \ln M_{av} + 3x_1^2 x_2 \ln M_{12} + 3x_1^2 x_3 \ln M_{13} \\ & + 3x_2^2 x_3 \ln M_{23} + 3x_2 x_3^2 \ln M_{32} + 3x_1 x_3^2 \ln M_{31} + 3x_2^2 x_1 \ln M_{21} + 6x_1 x_2 x_3 \ln M_{123} + 3x_1^2 x_2 \ln \eta_{12} + \\ & 3x_1^2 x_3 \ln \eta_{13} + 3x_2^2 x_3 \ln \eta_{23} + 3x_2 x_3^2 \ln \eta_{32} + 3x_1 x_3^2 \ln \eta_{31} + 3x_2^2 x_1 \ln \eta_{21} + 6x_1 x_2 x_3 \ln \eta_{123} \end{aligned} \quad (6.10)$$

The Orbey and Sandler (1993) equation :

$$\eta = \left(w_1 \eta_1^{1/3} + w_2 \eta_2^{1/3} + w_3 \eta_3^{1/3} \right)^3 \quad (6.11)$$

$$\eta = aw_1 + bw_2 + cw_3 + dw_1w_2 + ew_1w_3 + fw_2w_3 \quad (6.14)$$

The correlation with temperature was tested with equations 5.17-18 used for binary systems(noted in this chapter 6.15-16).

Table 6.8 shows the results of the correlation with several equations: parameters and correlation errors, similarly, the Figure 6.8.

Viscosity-temperature dependence equations were obtained on the 293.15-323.15K range that can be used practically to calculate the viscosity of the ternary mixture at various compositions and temperatures with RPMD of 0.1-0.3% (equation 6.15) and 1-2% (equation 6.16).

Table 6.8. Dynamic viscosity correlation parameters with composition for ternary mixtures at different temperatures

Equation		Temperature (K)						
		293.15	298.15	303.15	308.15	313.15	318.15	323.15
Grunberg– Nissan	G ₁₂	-0.7498	-0.7738	-0.6982	-0.6587	-0.7999	-0.6430	-0.5828
	G ₁₃	-1.1331	-1.0509	-1.0086	-0.9327	-0.9436	-0.6512	-0.8461
	G ₂₃	-1.9848	-1.9804	-1.8472	-1.8404	-1.8439	-1.6303	-1.7271
	RPMD (%)	3.0185	2.9759	2.6638	2.5951	2.7227	3.3804	3.2265
Grunberg– Nissan	G ₁₂	-1.0200	-1.0448	-0.9514	-0.9156	-1.1120	-0.7195	-0.8579
	G ₁₃	-1.3839	-1.3023	-1.2436	-1.1711	-1.2332	-0.7222	-1.1015
	G ₂₃	-2.2573	-2.2537	-2.1026	-2.0994	-2.1586	-1.7075	-2.0040
	G ₁₂₃	3.3407	3.3501	3.1315	3.1758	3.8585	0.9465	3.4015
	RPMD (%)	2.8644	2.8226	2.2563	2.4559	2.4426	3.5236	2.2927
McAllister	η_{12}	2.7371	2.5489	2.4195	2.2166	2.0014	3.3729	1.3511
	η_{13}	5.2709	4.5897	3.9616	3.5223	3.0643	2.3979	2.8047
	η_{23}	2.0420	1.8353	1.6990	1.5568	1.4043	1.2130	1.4466
	η_{21}	2.9018	2.5200	2.2895	1.9947	1.7237	2.3659	1.2485
	η_{31}	2.8937	2.6558	2.4985	2.2845	2.1055	2.4658	1.8580
	η_{32}	1.0553	0.9722	0.8988	0.8243	0.7625	0.8286	0.5878
	η_{123}	7.4308	6.4883	5.4739	4.9649	4.6249	2.4690	3.9354
	RPMD (%)	1.8118	1.6772	1.5397	1.4987	1.5162	2.6724	2.8561

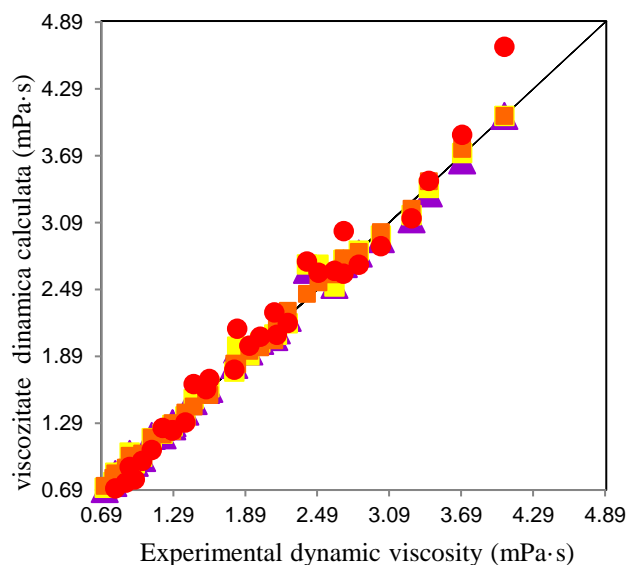


Fig.6.8. Viscosity calculated with different equations *versus* experimental viscosity at 298.15K for biodiesel(1)+diesel(2)+benzene(3) system;
■ eq. (6.9A); ▲ eq. (6.9B); ■ eq. (6.10); ● eq. (6.14);

6.2.3. Modeling data on the refractive index

The equations of refractive index dependence on the blends concentration can be used to determine the biodiesel concentration in the blends with diesel [111].

The refractive index of a ternary mixture can be predicted based on the refractive indices of the components of the mixture, similarly to binary systems using the same equations: Lorentz-Lorenz, Gladstone-Dale, Eykman, Newton and Arago-Biot Terrestrial Systems [66,69]. The

equations allow the predictive calculation of the refractive index and further estimation of other properties of the ternary mixtures.

CONCLUSIONS

C.1. GENERAL CONCLUSIONS

The blends of traditional fuels with renewable biofuels are the preoccupation of technical and theoretical research in the field, for which obtaining experimentally determined data accurately on broad areas of composition and temperature is necessary. In this study it is presented the results regarding the (pseudo) binary and (pseudo) ternary mixtures of gasoline with bioalcohols and diesel fuel with biodiesel and benzene for technical applications and fundamental research.

Gasoline physico-chemical characteristics

- Characterization of gasoline used in the work was carried out by chemical composition, molar mass, volatility (Reid vapor pressure and distillation curve) and Research Octane number. The chemical composition of the catalytic reforming gasoline was determined chromatographically. The studied gasoline contains 1% (v / v) paraffin, 25.33% (v / v) olefins, 1% (v / v) naphthenic and 72.63% (v / v) aromatics.
- For biodiesel, the chemical composition and molar mass was determined by chromatographic method. For diesel fuel and biodiesel, the molar mass was determined by cryoscopic method.

Gasoline-alcohol physico-chemical characteristics

Volatility

- The volatility (Reid vapor pressure and the distillation curve) and the Research octane number for gasoline blends and (bio) alcohols: ethanol, i-propanol and n-butanol were determined to assess the influence of alcohol in gasoline.
- The addition of ethanol and i-propanol increase the Reid vapor pressure (RVP), especially in the range (0-10%) of alcohol concentration. N-butanol insignificantly influences RVP.
- The distillation curves of gasoline and alcohol blends show deviations from the pure gasoline distillation curve, more pronounced for blends with ethanol and i-propanol and lower for that with n-butanol. The distillation curves of the blends are below the gasoline distillation curve;
- The T10, T50 and T90 parameters (temperatures at which 10%, 50% and 90% of gasoline is distilled) are determined according to ASTM D4814. The T10, T50 parameters decrease with the addition of alcohol; ethanol and i-propanol have the greatest influence, but n-butanol influences less the parameter values.
- VLI (Vapor Lock Index) and DI (Driveability Index) index have been calculated. For VLI, the alcohol blends shown the values within limits according to the standards in force (EN228) across the studied concentrations range; the blends of gasoline with alcohols show DI values corresponding to the standards at concentrations above 20% alcohol.

Octane number

- The addition of ethanol and i-propanol determine a RON linear increase with the concentration of alcohol in the mixture. The addition of n-butanol does not significantly change the octane number, RON.

- The gasoline blends with ethanol falls within the RON range and complies with RVP rules across the range of composition according to ASTM D323.

Physico-chemical properties of the gasoline mixtures with ethanol, i-propanol and n-butanol

Density

- The density of binary benzine systems with alcohols varies monotonously, slightly nonlinear with alcohol concentration. The density increases with increasing ethanol and n-butanol content and decreases as the content of i-propanol increases in the blend.
- The density is uniformly influenced by temperature across the range of gasoline-alcohol mixtures. The density values remain in the range recommended by the European Norm EN 228 for catalytic reforming gasoline of max. 0.830 g/cm^3 .
- Gasoline blends with alcohol (ethanol, i-propanol and n-butanol) have utility as a fuel mixture.

Viscosity

- The viscosity of gasoline blends with alcohols increases with increasing alcohol concentration in the mixture. Variation of viscosity with alcohol concentration is monotonous of exponential type at all compositions and studied temperatures.
- Temperature affects the viscosity of alcohols more than that of gasoline. Viscosity decreases by up to two units in the case of i-propanol and n-butanol on the studied temperature range, being less obvious for ethanol.
- The variation of mixtures viscosity with temperature are higher for blends with higher alcohol concentrations. With the increase of gasoline concentration, the decrease in viscosity with temperature is less important.
- In the literature, there is little data on the viscosity of gasoline blends with alcohols, the present study being an important contribution to the database on blends of gasoline with alcohols.

Refractive index

- The refractive index of all blends of gasoline with ethanol, i-propanol or n-butanol increases with increase of gasoline content in the mixture due to pure component values. Refractive index-concentration dependencies are practically linear in the studied blends, making it possible to use as calibration curves to determine blends composition and for correlation with other properties.
- The temperature causes the refractive index decrease for gasoline blends with ethanol, i-propanol and n-butanol. The influence of temperature is more pronounced for ethanol and i-propanol and less obvious for n-butanol.
- In the literature, there are no studies on analysis of the refractive index of gasoline blends with alcohol.

Correlation and prediction of the properties

Density

- The predictive equations, eqs. 5.1 (Kay's equation) si 5.2, give very good results for all systems, especially for the gasoline + n-butanol system with errors (RPMD) between 0.04 and 0.12%.
- The density for all gasoline- alcohol systems is correlated with very good results with the second degree empirical equation (equation 5.3, $(p-w_I)$) across the entire studied temperature range, especially for the n-butanol system, for which a degree equation one $(p-w_I)$.
- The correlation and predictive equations used show close results.

- For the dependence ρ - T , the linear equation 5.4 correlates very well all gasoline- alcohol systems with values for R^2 of 0.9997-1.
- Equations of the Ramirez p - w_1 - T dependence obtained by the simultaneous correlation of density with composition and temperature allow the calculation of density at a temperature and composition with errors (RPMD) of 3.7-3.8% for gasoline systems with ethanol and i-propanol and of 5.2-5.5% for the mixture with n-butanol.
- The equations can be used practically in the calculation of the temperature density, in the studied area.

Viscosity

Viscosity-composition correlation (η - w_1)

- The Grunberg-Nissan, Orbey, and Sandler *predictive equations* give good and very good results for the gasoline- ethanol system (with RPMD values of 1.1-1.4% and 2.3-3.5%, respectively) and poor results for gasoline blends with i- propanol and n-butanol. The Wielke equation gives satisfactory results (RPMD of 2.8-5.1%) for gasoline-ethanol system. For gasoline-i-propanol and gasoline- n-butanol systems, the equation can not be used for the viscosity estimation, having errors of over 10%.
- *The correlative equations* (η - w_1) give far better results than predictive, behavior commonly encountered in the properties modeling.
- For gasoline-ethanol blends, the equations: Grunberg-Nissan with a parameter, McAllister - semi-empirical equation and polynomial empirical equation (5.16) correlate very well the experimental viscosity data (errors less than 1%).
- For gasoline with i-propanol and n-butanol, the McAllister and polynomial equations correlate well the experimental data with errors below 1%, and the Grunberg-Nissan equation with satisfactory results (errors between 2 and 4%) .
- The three-parameter empirical equation has very good results in viscosity versus composition correlation, and the Grunberg-Nissan and McAllister semi-empirical equations with one and two parameters, respectively, show good and satisfactory results. From a practical point of view, the polynomial equation, more simple to use, can be used to calculate viscosity by composition. From a theoretical point of view, is worthy of notice that the complex equations as well as Grunberg-Nissan and McAllister can be used to represent the viscosity of pseudo-binary systems.
- Gasoline blends with ethanol give better results both in the predictive calculation and in the representation of properties by correlation equations. This can be explained by the fact that gasoline blends with n-butanol and gasoline with i-propanol show different structures than those with ethanol, which implies different interactions in systems that influence the the blends properties.
- The viscosity – composition equations are useful in practice for estimating the viscosity of different blends of gasoline.

Viscosity-temperature correlation (η - T)

- The Andrade and Andrade equations extended by Tat and van Gerpen correlate very well the experimental viscosity data for gasoline-alcohol systems.
- Viscosity calculated with the Andrade equation shows errors of approx. 0.2-0.8% for the gasoline-ethanol system, 0.2-0.5 for the gasoline system with i-propanol and 0.1-0.3 for the gasoline system with n-butanol on the 293.15-323.15K temperature range.
- The Andrade extended three-parameter equation does not bring a higher accuracy than the

Andrade equation with two parameters, describing with 0.1-1.9% errors the viscosity-temperature dependence.

Viscosity-composition-temperature correlation (η - w_1 - T)

- The Krisnangkura equation (equation 5.19) shows the best results for the gasoline + ethanol system with errors of 0.7-1.1%, satisfactory for the gasoline + n-butanol system with errors of 3.9% and weaker for gasoline+ i-propanol with errors of 6.2-7.4%.
- Krisnangkura equations can be practical for estimating viscosity at a given composition and temperature.

Refractive index

- The predictive equations give good and very good results for all gasoline-alcohol binary systems, with errors between 0.01 and 0.1%. Eykman equation shows the best results for all systems, with errors of 0.01-0.05%.
- Refractive index-composition- temperature (η - w_1 - T) equations give very good results on the studied temperature range, with RPMD values between 0.02 and 0.05 for the studied systems.
- The obtained complex refractive index-composition- temperature (η - w_1 - T) equations can be successfully used to calculate the composition of mixtures at a given temperature from experimental refractive index values.

Corelation between properties

- Various equations for density or viscosity connection with the refractive index were tested . Density-refractive index equations, density-refractive index-temperature and similarly, viscosity-refractive index, viscosity-molar mass-temperature were tested.
- All equations tested for density give good and very good results. Equation 5.27 allows a good prediction of density in refractive index and molar mass, and has a relative percentage mean deviation (RPMD) of 0.020-0.023%. Polynomial equation 5.28 correlates very well the density with the refractive index with correlation coefficients above 0.99. The equations 5.27-28 can be used practically and are recommended for density calculation from experimental data of refractive index and temperature.
- The relationship viscosity–refractive index and viscosity-temperature-molar mass give good and very good results. A prediction of viscosity from refractive indices at a given temperature can be made, as well as a viscosity calculation at different temperatures, knowing the molar mass of the mixture.
- Viscosity-refractive index correlation equation 5.30 allows for a satisfactory prediction of viscosity from refractive index for the gasoline system with ethanol and i-propanol with errors between 3-7%. The equation shows poor results for the n-butanol gasoline system.
- For the viscosity -molar mass-temperature relationship, the equation 5.31 gives good results, with errors (RPMD) of 0.3-2.8%, which allows the practical use of the equation.

Physico-chemical properties of diesel blends with biodiesel and benzene

Density

- The experimental data obtained for diesel fuel blends with biodiesel and benzene show that the density of the ternary mixtures varies monotonously with the composition with values in the range of the pure component densities.
- The equations 6.1 (Kay) and 6.2 give a satisfactory prediction of the density of the ternary system from the pure component densities with relative deviations of 0.2% -1.3% and of 0.1-1.3%, respectively. The equation 6.3 with 6 parameters correlates very well the experimental data with errors of 0.06-0.18%.

- Dependence of temperature density is well represented by equation 6.4 with errors between 0.2-1.4%.
- The equations tested can be used practically to calculate the density of the ternary mixture at different compositions and temperatures.

Viscosity

- The viscosity of the ternary mixtures varies monotonously with the composition, with values in the range limited to the viscosities of the pure components. The viscosity of the mixtures decreases with the temperature increase for all the studied mixtures more intensively for mixtures where biodiesel and diesel predominate over the studied 293.15-323.15K range.
- Grunberg și Nissan predictive equations without parameters and Orbey-Sandler equation are not recommended for estimating the viscosity of the mixture from pure component values.
- The Grunberg-Nissan equations with 3 and 4 parameters as well as the 7-parameter McAllister semiempirical equation correlate well the experimental data. The Grunberg-Nissan equation with 3 parameters can be used practically due to the small number of parameters and the reduced error values. Using the large number of parameters does not make significant improvements.

Refractive index

- The Lorentz-Lorenz, Gladstone-Dale, Eykman, Newton and Arago-Biot predictive equations (RPMD of 0.2%) and the 6.20 correlative equation (RPMD of 0.003%) present good and very good results that authorize the use of the refractive indices to estimate other properties.

C2. ORIGINAL CONTRIBUTIONS

- Characterization of fuels and biofuels with molar mass, chemical composition, volatility (Reid vapor pressure and distillation curve) in order to reproduce the experimental data and to compare it with the literature data.
- Obtaining experimental properties data for (pseudo) binary and (pseudo) ternary blends of conventional biofuel with biofuels non-studied or partially studied until now on large composition and temperature ranges. The study of the specialized literature showed the lack of similar studies at this level. Generally, the system properties are studied only in conditions of technical and purely applicative interest.
- Performing a thermodynamic modeling study of the properties of (pseudo) binary and (pseudo) ternary systems with predictive and correlative equations.
- Obtaining the equations (property- composition), (property- composition-temperature) and of correlations between properties (density-refractive index, viscosity-refractive index), equations that can be used in practical applications.

C3. PERSPECTIVES OF FURTHER DEVELOPMENT

- Extending the study to blends of gasoline with other (bio) alcohols of interest or additives to improve the properties of combustible mixtures.
- Making correlations between properties that are useful for practice and contributing to the understanding of the thermodynamic behavior of the studied systems, the basis for future theoretical and practical applications.
- Developing a methodology for experimental study of the properties of fuel blends to be adopted by the research community and making it possible to obtain reproducible and comparable data.

WORKS PUBLISHED IN THE FIELD OF THE THESIS

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