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Phase equilibrium measurements and thermodynamic modeling of binary mixtures containing a diesel compound *n*-dodecane + biodiesel compounds: Ethyl dodecanoate and ethyl octanoate

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ABSTRACT

The vapor pressures of two binary systems ethyl dodecanoate (1) + *n*-dodecane (2) and ethyl octanoate (1) + *n*-dodecane (2), were measured by means of a static apparatus at temperatures between 373.15 K and 453.15 K. The data were correlated with the Antoine equation. From these data, the molar excess Gibbs energies G^E were obtained with Barker's method and fitted to the Redlich-Kister equation. The binary mixture (ethyl octanoate (1) + *n*-dodecane (2)) exhibits maximum azeotropic behavior. Positive values of the excess Gibbs energy are obtained for all the investigated constant temperatures and over the whole composition range. The data were also correlated by using Wilson equation and good results were obtained in the prediction of the total pressure and thermodynamic excess properties; however deviations were observed with respect to the experimental and predicted G^E, using modified UNIFAC (Dortmund) group contribution model. Additionally, the NRTL model was applied to regress the experimental G^E. The investigated systems were successfully represented by the NRTL model.

1. Introduction

Nowadays, there is a growing interest in biodiesel, considerable attention has been made to biodiesel as an alternative and a promising substitute to petroleum-based fuels due to the depleting of limited resources, growing emissions of combustion-generated pollutants and the environmental problems caused by the use of fossil sources (petroleum, coal and natural gas).

The demand of energy in transportation sector has hiked with the growth of population and it keeps increasing. This has led to a rapid depletion in the world's reserve of fossil fuel [1,2]. The energy crisis has become one of the most crucial issues in recent years. The unstable price of petroleum fuel in the world market and recent environmental concerns on gas emission during combustion have led to an intensive search for alternative energy sources that are not only renewable but also sustainable [3].

Usage of biodiesel will allow a balance to be sought between agriculture, economic development and the environment [4,5].

Biodiesel is a potential renewable and biodegradable fuel source comprising of fatty acid methyl esters (FAME) or Fatty Acid Ethyl Esters (FAEE), it is an eco-friendly biofuel produced from renewable energy sources (vegetable oils and animal fats). It is also worth to mention that; biodiesel favors biodegradability, non-toxicity, reduces global warming, promotes rural development and lowers emission of pollutants.

Recently algae have emerged as one of the most promising sources for biodiesel production [6–10]. According to Shay, algae were one of the best sources of biodiesel [11]. In fact, algae are the highest yielding feedstock for biodiesel. It can produce up to 250 times the amount of oil per acre as soybeans. In fact, producing biodiesel from algae may be only the way to produce enough automotive fuel to replace current gasoline usage [6]. As demonstrated by Yusuf Chisti [8], microalgae appear to be the only source of renewable biodiesel that is capable of meeting the global demand for transport fuels.

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Biodiesel consists of a mixture of fatty acid alkyl esters [12]. The most common way used to make biodiesel is transesterification of vegetable oils and animal fats [7,13] at the industrial level in which, oil or fat is reacted with a monohydric alcohol, short chain alcohol such as methanol or ethanol in the presence of a catalyst, yielding a mixture of fatty acid alkyl esters and glycerol [13]. The acyl group chain of the esters produced normally ranges from 12 to 24 carbon atoms and the number of unsaturated bonds normally ranges from 0 to 3, both chain length and unsaturation varies significantly depending on the feedstock used [14].

On one hand, biodiesel can be used blended with petrodiesel (paraffinic fuel) in any percentage without affecting the performance of most diesel equipment. On the other hand, by blending biodiesel with diesel fuel, the combustion efficiency is enhanced and a cost-reduction in the distribution system is obtained [15].

Vapor liquid equilibrium (VLE) study is very important to accurately characterize diesel/biodiesel blended fuel to optimize the injection and ignition steps of the engine. In our knowledge, only few researchers have published some experimental data of systems containing fatty acid ester and nonvolatile alkanes [2–27].

The knowledge of vapor-liquid equilibria of mixtures containing fatty acid ethyl esters (biodiesel) and alkane (paraffinic fuel) is also essential in industrial scale operations. It allows an understanding of the problems of volatility, stability, and security during the exploitation, transport, and storage of diesel/biodiesel blends [15].

This study is a continuation of research works on the thermodynamic properties of organic compounds present in diesel/biodiesel blends and phase equilibria of their mixtures [12,14,15,17,28–30]. We present a complete set of data on vapor pressures for (FAEE + *n*-dodecane) mixtures: Ethyl dodecanoate (1) + *n*-dodecane (2) and Ethyl octanoate (1) + *n*-dodecane (2), for temperatures from (373.15 to 453.15) K. The excess molar Gibbs energies G^E evaluated by Barker's method are examined on the basis of the modified universal functional activity coefficient (UNIFAC) model and the NRTL model. In addition, the experimental results obtained in the previous work [14] were correlated using the NRTL model.

The experimental excess molar Gibbs energies G^E data were satisfactorily correlated by NRTL model.

2. Experimental section

2.1. Chemicals

The suppliers, thermophysical and the purities of the two saturated FAEE and *n*-dodecane are reported in Table 1. These compounds were used without any further purification.

2.2. VLE measurements

The vapor pressure measurements were carried out using a static apparatus. The description of the apparatus and the experimental procedure can be found elsewhere [14,17,31–36].

The vapor and the sublimation pressures of water and naphthalene were measured to check the calibration of the apparatus. [14,17,37]. Furthermore, the equipment was validated in many previous work [15,17,37–40].

2.3. Uncertainty on the vapor pressures system temperature and molar fraction

The uncertainties of the measurements are estimated to be:

Table 1
Source, thermophysical properties, functional groups and purity (mass fraction) of products.

Chemicals name	Synonym	Chemical formula	CAS n°	P_c/(bar)	T_c/(K)	T_m/(K)	T_b/(K)	ω	Functional groups for UNIFAC (Dortmund) correlation			Source	Purity/Mole as stated by the supplier
									$-CH_3$	$-CH_2$	$-CH_2COO$		
Ethyl octanoate	Ethyl caprylate	$C_{10}H_{20}O_2$	106-32-1	21.600[a,f]	656.390[a,f]	230.35[a,f] 229.17[f,g]	482.150[i]	0.5817	2	6	1	Sigma Aldrich	≥99%
Ethyl dodecanoate	Ethyl laurate	$C_{14}H_{28}O_2$	106-33-2	15.970[a,f]	719.130[a,f]	272.59[a,f] 272.31[f,g]	542.150[i]	0.6756	2	10	1	Sigma Aldrich	≥99%
n-Dodecane	–	$C_{12}H_{26}$	112-40-3	18.170[b] 18.239[c] 17.900[e] 18.200[j]	658.100[b] 658.154[c] 659.000[e] 658.250[h] 658.000[j]	263.58[d]	489.47[h]	0.5745	2	10	0	Janssem Chimica	>99%

[a] Ref. [46].
[b] Ref. [47].
[c] Refs. [47,48].
[d] Ref. [49].
[e] Ref. [50].
[f] Ref. [51].
[g] Ref. [52].
[h] Ref. [53].
[i] Refs. [54,55].
[j] Ref. [56].