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Thermophysical properties of lactates

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ABSTRACT

In this work, a thermophysical study of lactates compounds (methyl, ethyl and butyl lactate) has been made to get an idea of the suitability of these chemicals in order to be considered as green. New data about the physicochemical behavior of these chemicals (density, refractive index, speed of sound, viscosity, vapour pressure, static permittivity, surface tension and derived properties such as molar refraction, isentropic compressibility and enthalpy of surface formation) have been measured under atmospheric pressure at temperatures from 278.15 K to 338.15 K, while the vapour pressure was determined over a temperature range from 303.15 K to 378.15 K.

1. Introduction

During the last century, Chemistry has improved our quality of life thanks to pharmaceutical development, new chemicals or materials used in several manufacture processes. However, these kinds of processes could be associated with the production of harmful chemicals that can be released to the environment or considered dangerous to the human health. Nowadays Chemists and Engineers are trying to develop safer processes through the knowledge of chemicals and their behavior. Besides, the main challenge for the chemical industry is to continue providing benefits that we have come to rely on. This can be achieved through development of more environmentally benign products using less hazardous processes and raw materials [1].

Furthermore, Green Chemistry, which nowadays is considered as an essential driving force in the quest for sustainable chemical processes [2], has demonstrated how fundamental methodologies may be revised and applied to protect human health and the environment in an economically beneficial manner. However, significant progresses are underway in several key research areas, such as development of renewable feedstock, biosynthesis, biocatalysis, photocatalysis, design of safer chemicals and environmentally benign solvents, biochemical engineering, heterogeneous catalysis, etc. [3].

At the present time, it is a big challenge to design and produce green products and processes. However, there is no a unique method to quantify whether the chemical processes implemented can be considered green. There have been several attempts to verify if a proposed manufacturing process is better than other alternatives based on persistence and spatial range methods (PSRM) [4] and life cycle assessment (LCA) [5]. LCA is an internationally accepted and recognized methodology for assessing environmental loads that takes in account the global process. Specifically, LCA represents the assessment and quantification of the environmental impact of processes, products or services at every stage: from raw materials to final disposition. Both methods, PSRM and LCA can be useful for assessing if a chemical process or a chemical, solvent or auxiliary means the lowest environmental [6,7]. However, it is possible to get an idea of the suitability of chemical process from the green point of view making use of the "Twelve Principles of Green Chemistry" described by Anastas and Warner [8].

One of these principles of Green Chemistry is linked with solvents not only because they are important components very used in almost every chemical reactions but also because they are used for cleaning equipment, regulating temperatures, isolating and purifying compounds by recrystallization or extractions and assisting structural characterization. However, it is well known that some of these solvents could result in serious environmental and health problems. For that reason it is important to develop new less toxic and hazardous solvents [9].

These kinds of solvents are generally named "green solvents". The idea of "green" chemicals expresses the goal to minimize the environmental impact resulting from the use of them in chemical production. An ideal green solvent should have a low vapour pressure, a high boiling point, should be non-toxic and recyclable, be biodegradable (and degradation products should be non-toxic), be able to dissolve as many chemical compounds as possible,

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inexpensive and coming from renewable resources. Although the universal green solvent cannot be applied in all situations, several alternatives have been evaluated during the last years (water, solvents from biomass, ionic liquids, supercritical fluids, etc.) [10].

Solvents from sustainable sources including those from biomass, which are usually obtained by fermentation, enzymatic or esterification processes, are one of the new families of solvents classified as green that can be used for a number of industrial processes [11,12]. Some solvents from biomass are glycols, lactates, terpenes, furfural or fatty acid esters.

Taking into account all above, this work is focused on the lactate family compounds; generally considered as green solvents are widely used as paints, gums, dyes, oils, detergents, food additives, cosmetics, in pharmaceuticals, etc. [13]. The consideration as green solvents is given to their origin from carbohydrate feedstock. The case of ethyl lactate is particularly attractive for industry due to its physicochemical properties such as high boiling point, low surface tension and low vapour pressure. Moreover, ethyl lactate has replaced solvents such as toluene, acetone and xylene, in several chemical processes resulting in a much safer workplace [14]. This means that there is an alternative way through the use of the lactate family solvents for a wide range of industrial and consumer uses, replacing environment-damaging solvents including several volatile organic compounds and ozone depleting fluids [15]. Furthermore, it is important to note that alkyl lactates are important compounds in pharmaceutical industry, for instance, they are used as a penetration enhancer for some drugs in transdermal administration [16].

A review of the literature shows that the thermophysical properties of lactate compounds are not complete. It has been reported that physical properties and phase behavior of fluids and fluid mixtures can be used to develop environmentally friendly processes [17]. Some of these properties allow knowing how the chemicals are in the environment and how they behave and interact with it.

Furthermore, it is evident that accurate information of the potential green solvents in a wide range of pressure and temperature is needed to carry out a cost-effective and reliable process design in order the use these green compounds in any chemical process. Additionally, properties such as solubility, thermal behavior, volumetric, surface, electric, or transport can be used to get information regarding their potential properties as green compounds. On the other hand, characterization of solvents through thermophysical properties has been highlighted as an immediate requirement to elucidate any correlation between the structures of chemicals, their interactions and their features [18]. Moreover, the knowledge of these properties has a practical importance since they are fundamental to consider the suitability of these compounds. A review of the literature shows that no depth studies about this family of chemicals have been carried out. We have found few articles in which some properties of these compounds have been obtained. One of these papers has been published by Rehberg and Dixon [19] in which some experimental values of solubility in water at 298.15 K and refractive index, density, molecular refraction, viscosity at 293.15 K and 313.15 K have been measured for methyl, ethyl and butyl lactate [19]. For methyl lactate, a theoretical study of the properties and molecular level structure has been reported by Aparicio [15]. Moreover, Sanz et al. have reported density values at T = 298 K and the vapour liquid equilibrium at pressures of 33.33, 66.66 and 101.33 kPa [20]. Additionally, Chen and Chu have been reported some density and viscosity values for methyl lactate at 298.15 K, 308.15 K and 318.15 K [21].

In case of ethyl lactate, Aparicio et al. have presented a report in which the refractive index and the density for ethyl lactate from T = 278.15 K to 343.15 K were measured [22]. Besides, Chen et al. have measured viscosities and densities at the temperatures of 298.15 K, 308.15 K and 318.15 K [21]. Also, the vapour pressure, the liquid heat capacity, the thermal conductivity and the densities have been measured by Pereira et al. [6]. Furthermore, the surface tension of ethyl lactate has been found in two papers. In one case, this property has been measured from 318.33 K to 381.53 K and, in the other one, from 288.14 K to 313.13 K [23]. Moreover, Resa et al. have been measured some properties such as density, refractive index, speed of sound at 298.15 K and de vapour–liquid equilibrium at 101.3 kPa for binary mixtures of methanol + ethyl lactate, 1-propanol + ethyl lactate, ethyl acetate + ethyl lactate and methyl acetate + ethyl lactate [24,25].

For butyl lactate, refractive index, densities at T = 293.15 K and boiling points have been reported by Peña-Tejedor et al. [13]. Furthermore, several experimental measurements of refractive index, density and viscosity have been measured by Bajic et al. [26]. Finally, the $p\rho T$ behavior of these compounds has been previously reported [27,28].

This revision of literature shows that the study of the family is not systematic and it seems to be incomplete; therefore, results cannot be analyzed as a whole and a relationship between the structure of the compounds and their properties cannot be stated. Therefore, new data about the physicochemical behavior of these chemicals have been obtained (density, refractive index, speed of sound, viscosity, vapour pressure, static permittivity, surface tension and derived properties such as molar refraction, isentropic compressibility and enthalpy of surface formation) and a comparative study between studied chemicals has been made. Furthermore, properties such as vapour pressure, solubility or ALOGP, have been used to get information about the greener character.

2. Materials and methods

This work includes an exhaustive thermophysical study of three chemicals: methyl lactate, ethyl lactate and butyl lactate. The information about the three racemic liquids used is summarized in Table 1. No additional purification was carried out because the impurities are in such a low concentration that the physical properties of the compound are almost unaffected within the quoted uncertainty limit [29].

Measurements were performed in a range of temperatures with intervals of 2.5 K from T = 278.15 K to 328.15 K, with the exception of refractive index, whose measurements were carried out from T = 283.15 K to 328.15 K.

Densities, ρ, and speed of sounds, u, of the pure compounds were determined simultaneously with an Anton Paar DSA 5000 vibrating tube densimeter and sound analyser, automatically thermostated at ±0.005 K. The calibration was carried out with ultra-pure water supplied by SH Calibration Service GmbH and dry air. The final uncertainty of density and speed of sound can be estimated in $\pm 1 \times 10^{-5}$ g cm^{-3} and ±0.1 m s^{-1}, respectively.

Refractive indices at 589.3 nm sodium D wavelength, n_D, were measured using a high precision automatic refractometer Abbemat-HP from DR. Kernchen whose temperature was internally controlled at ±0.01 K. The uncertainty of the measurements is 5×10^{-6}.

Surface tensions, σ, were determined using a drop volume tensiometer Lauda TVT-2 [30]. The temperature was kept constant within ±0.01 K by means of an external Lauda E-200 thermostat. The uncertainty of the surface tension measurement is ±0.05 mN m^{-1}.

Kinematic viscosities, ν, were measured using an Ubbelohde viscosimeter with a Schott-Geräte automatic measuring unit model AVS-440. The temperature was kept constant at ±0.01 K by means of a Ct52 Schott-Geräte thermostat. The viscosimeter was calibrated with ultra-pure water supplied by SH Calibration service GmbH. The estimated uncertainty of kinematic viscosity