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Thermophysical study of the furan family

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ABSTRACT

The dynamic viscosity, speed of sound, surface tension, density, refractive index, and static permittivity of furan, 2-methylfuran and 2,5-dimethylfuran have been obtained at temperatures from 278.15 to 338.15 K under atmospheric pressure, although for furan the temperature range have been 278.15–303.15 K. The vapour pressure has been determined over a temperature range from 283.16 K to 366.70 K. Besides, the $p\rho T$ behavior has been also measured using a high-pressure, high-temperature vibrating tube densimeter over a pressure range from 0.1 MPa to 60.0 MPa and a temperature range from 283.15 K to 338.15 K. However, in the case of furan, the densities have been measured at the pressure of 0.1 MPa only in the temperature range 283.15–303.15 K. Furthermore, some derived properties such as isobaric expansibilities, isothermal compressibilities, molar refraction, isentropic compressibilities or dipolar moment have been calculated using the experimental data. At the end, a comparative study has been carried out taking into account the molecular structure of the chemicals investigated.

1. Introduction

The chemistry of the furan heterocycle has been studied because of its relevance in organic chemistry, pharmaceuticals, and liquid crystals [1]. Furthermore, the polymers that can be obtained from this chemical compound are important due to their renewable character and the availability of the monomers precursors that can be considered a counterpart of the petroleum-based materials [2]. Additionally, furan derived chemicals are also important in technology because some of its derivatives (2-methylfuran and 2,5-dimethylfuran) may be used as biofuels [3].

Specifically, furan is used for resins and lacquers productions, reactive or in pharmaceutical industry [4,5]. In the case of 2-methylfuran is generally used as an additive. In addition, 2,5-dimethylfuran is used as an additive and standard chemical for ^{1}H RMN techniques [6] or as a marker to determinate the environmental pollution [7]. One of the most important biofuels is 2,5-dimethylfuran (DMF) whose production by Roman-Leshkovet al. [8] from D-fructose, by means of an intermediate 5-hydroxymethylfurfural (HMF), raised interest in this "next-generation" biofuel [9].

Furan can be obtained from biomass from amylose (starch) pyrolysis [10] while other furan derivatives can be obtained through the pyrolysis of D-glucose [11,12].

A thermophysical study of these chemicals is important to understand their properties depending on factors such as intermolecular interactions and the structures. Considering these properties, the industrial processes can be designed and improved. Additionally, several models, including EOS or group contribution methods, can be developed to predict their behavior in liquid state [13]. For instance, viscosity is an important transport property which is considered in a number of industrial processes. Taking into account the structure and the interactions between molecules, molecular information can be obtained from the analysis of this property. Furthermore, other properties such as surface tension, viscosity or melting and boiling point give information about the bulk interactions. On the other hand, volumetric properties are related to the structural organization of the molecules in the liquid state [14,15].

A review of the literature shows that there is not a systematic study of furan and the related compounds which compare their properties. In the case of furan, there are density values at some temperatures; Timmermans and Hennaut-Roland obtained densities at the following temperatures 273.15, 284.05, 288.15, 293.15 and 298.15 K [16], Guthrie et al. measured densities at 283.15, 288.15 and 298.15 K [17] and finally Murakami et al. reported density values at 298.15 and 303.15 K [18]. There is also a work reporting densities at high pressures [19] but a lower

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temperatures than in our study, so no comparison is possible. Additionally viscosity values have been published by Timmermans and Hennaut-Roland at 284.05, 293.15 and 298.15 K [16]. Moreover, experimental data for refractive index have been measured by Murakami et al. at three temperatures 293.15 K, 298.15 K and 303.15 K [18]; furthermore Kobe et al. have obtained values for this property at the following temperatures 293.15, 298.15 and 303.15 K [20]. In addition, Foss et al. have performed refractive index at several wavelengths at 298.15 K [21]. Surface tension values at 289.55, 293.15 and 298.15 were reported by Timmermans and Hennaut-Roland [16]. Static permitivitties have been measured by Murakami et al., 298.15 and 303.15 K [18]. There are also some papers that have reported vapour pressures in the range 275.702–334.58 K in the case of Guthrie et al. [17] and 366–483 K in the case of Kobe et al. [20]. Finally it is worth mentioning that Nala et al. [22] reports the vapour–liquid equilibrium for the mixture formed by furan and hexane or toluene.

In the case of 2-methylfuran, densities, refractive index and static permitivitties have been measured by Murakami et al. at the temperatures of 293.15, 298.15 and 303.15 K [18]; on the other hand, Kobe et al. have obtained values for refractive index at the following temperatures: 293.15, 298.15 and 303.15 K [20]. Vapour pressures were measured by Kobe et al. [20] in the range 383–527 K, and by Pommier and Guiochon between 333.45 K and 373.45 K [23]. In addition, some papers have been published about vapour–liquid equilibrium involving 2-methylfuran [24–26].

With respect to 2,5-dimethylfuran, Verevkin and Welle [27] report nine vapour pressure data in the temperature range 271–308.4 K, and there are also two works reporting vapour–liquid equilibrium data [28,29]. Finally, some densities and surface tension in a range of temperatures from 293.15 K to 358.15 K [28] and the kinematic viscosity at 293.15 K [30] have also been reported.

To increase the knowledge of this family, we have performed a systematic thermophysical study of these chemicals as we have done with other families [31,32]; more than a few thermophysical properties (surface tension, speed of sound, density, refractive index, dynamic viscosity and static permittivity) of furan, 2-methylfuran and 2,5-dimethylfuran obtained from hydrocarbons [11,12] have been measured at atmospheric pressure from 278.15 K to 338.15 K. In the case of vapour pressure, it has been obtained over a temperature range from 278.15 K to 363.15 K.

Moreover, a $p\rho T$ study has been carried out over a pressure range from $p = 0.1$ to 60.0 MPa and a temperature range from $T = 283.15$ K to 338.15 K for the studied chemicals, in the case of furan, the densities were measured only in the temperature range 283.15–303.15 K at the pressure of 0.1 MPa. The TRIDEN equation has been used to fit the experimental density values. Furthermore, isobaric expansibility, α_p, and isothermal compressibility, κ_T, have been calculated. The results have been analyzed taking into account the structure and the molecular interactions.

2. Materials and methods

The chemical structures of the chemicals are shown in Fig. 1. The provenance and purity of the studied compounds is shown in Table 1. An automatic titrator Crison KF 1S-2B has been used to determine the water content of the compounds.

The measurements have been carried out in a range of temperatures with intervals of 2.5 K from 278.15 K to 338.15 K except in the case of refractive index that has been performed from 283.15 K to 338.15 K. It is important to note that the normal boiling point of furan is 304.46 K. These properties have been measured at atmospheric pressure.

For the study of the $p\rho T$ behavior, a high pressure and high temperature Anton Paar DMA HP cell connected to an Anton Paar DMA

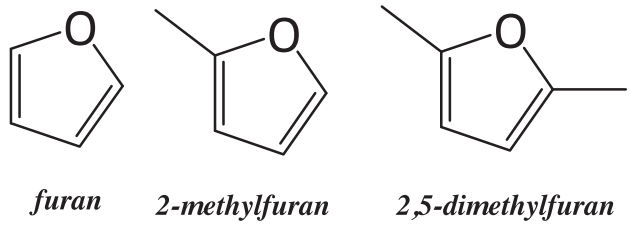

Fig. 1. Chemical structures of the studied compounds.

5000 evaluation unit has been used. The density values have been measured using an oscillation period of the U-shaped tube made with Hastelloy C-276. An integrated Peltier thermostat keeps constant the cell at ± 0.01 K. On the other hand, a hand pump 750.1100 from Sitec, Switzerland is used to create the required pressure. Additionally, the pressure has been measured by a pressure transducer US181 from Measuring Specialties, USA. In this case, the uncertainty for the pressure is estimated in ±5 kPa. A vacuum pump has been used to empty the apparatus. More details about the procedure and calibration have been reported in a previous paper [33]. The uncertainty of density values has been estimated in 0.1 kg m^{-3}.

Densities, ρ, and speed of sounds, u, of the chemicals have been determined at the same time with an Anton Paar DSA 5000 vibrating tube densimeter and sound analyzer thermostated at ±0.005 K. The operating frequency of the sound analyzer is around 3 MHz. The equipment has been calibrated using ultra-pure water supplied by SH Calibration service GmbH and dry air. The uncertainty of speed of sound and density and can be estimated in 0.5 m s^{-1} and 0.05 kg m^{-3} respectively.

The values of refractive index at 589.3 nm sodium D wavelength, n_D, have been obtained using a high precision automatic refractometer Abbemat-HP from Dr. Kernchenwith controlled temperature at ±0.01 K. The uncertainty of the measurements is 2×10^{-5}.

The surface tensions, σ, have been measured with a drop volume tensiometer Lauda TVT-2. A Lauda E-200 thermostat has kept the temperature constant at ±0.01 K. The uncertainty of the surface tension measurement is 0.1 mN m^{-1}.

The kinematic viscosities, ν, have been measured using an Ubbelohde viscosimeter with a Schott-Geräte automatic measuring unit model AVS-440. A CT52 Schott-Geräte thermostat has kept the temperature constant at ±0.01 K. The calibration has been carried out with ultra-pure water from SH Calibration service GmbH. In this case, the estimated uncertainty (expressed as percentage) of kinematic viscosity measurements is ±1%. To calculate the absolute viscosity, $\eta = \rho \cdot \nu$, values of kinematic viscosity and density has been used. For absolute viscosity, the estimated uncertainty is 1%.

The vapour pressures have been measuredusing dynamic recirculating still, Fischer-Labodest which has been equipped with a Cottrell pump. To determine the temperature, a thermometer model F25 with a PT100 probe from Automatic Systems Laboratories has been used. Besides, the pressures have been obtained using a Digiquartz 735–215A-102 pressure transducer from Paroscientific with a Digiquartz 735 display unit. In this case, the uncertainty in the pressure equilibrium measurement and temperature is 0.1 kPa and 0.01 K respectively.

The static permittivities, ε, at a frequency of 2 MHz have been calculated through a capacitive measurement method. The capacitances between parallel plates have been performed using an Agilent 4263BA precision LCR meter connected to a four terminal Agilent 16452A liquid dielectric test fixture through an Agilent 16048A test leads. To keep constant the temperature at ±0.01 K, a CT52 Schoot-Geräte thermostat has been used. The uncertainty of the static permittivities values is less than 0.5%.