



Thermophysical study of 2-acetylthiophene: Experimental and modelled results



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ABSTRACT

Several thermophysical properties have been studied for 2-acetylthiophene: (i) vapour pressure was determined at temperatures within 336.16–445.02 K; (ii) density, speed of sound, static permittivity, refractive index, surface tension, and kinematic viscosity were measured at $p = 0.1$ MPa and at temperatures from 278.15 K (or 283.15 K for the refractive index) to 338.15 K; (iii) volumetric properties were also determined at temperatures in the (283.15–338.15) K range and at pressures up to 65.0 MPa. From these experimental values, different derivative properties have been calculated such as enthalpy of vaporization, isobaric expansibility, isothermal and isentropic compressibility, dipole moment, entropy and enthalpy of surface formation, and dynamic viscosity. All experimental properties were correlated and the results were explained through the intermolecular interactions. Moreover PC-SAFT EoS was used to model the thermodynamic behaviour of the compound. Finally, this EoS combined with the Density Gradient Theory allowed obtaining the influence parameter for the surface tension of 2-acetylthiophene.

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1. Introduction

Thiophene is a five heterocycle compound with an atom of sulphur and can be extracted, as well as its derivatives, from fossil fuels [1,2]. The presence of thiophene-based compounds in plants provides specific organoleptic characteristics. Thus, it was detected 2-acetylthiophene in different foods such as flour extrudes or yeast extracts producing a sulfurous odor like disinfectant [3,4].

This compound can be employed for various purposes such as: synthesis of several drugs for depressive disorder and anxiety (duloxetine and others) [5,6]; drugs synthesis for treatment of anti-inflammatory [7]; synthesis of antiparasital drugs [8]; metal complexes synthesis [9]; organic synthesis [10]. Despite the many industrial applications of 2-acetylthiophene, the study of its thermophysical properties is very scarce [11,12]. The knowledge of these properties in a wide range of temperature and pressure and its dependence on structure and intermolecular interactions is fundamental in the chemical industry: the volumetric properties give the necessary information about the structural organization and packing of the molecules in liquid state. Furthermore additional information about the intermolecular interactions can be

obtained through boiling point, viscosity or surface tension; and the permittivity and refractive index allow to characterize the compound polarity [13–15].

In this contribution, we present experimental values for several properties: (i) vapour pressure from $T = 336.16$ – 445.02 K; (ii) density in the following pressure and temperature ranges ($p = 0.1$ – 65 MPa) and ($T = 278.15$ – 338.15 K); and (iii) speed of sound, static permittivity, surface tension, and kinematic viscosity at $p = 0.1$ MPa and the temperature interval 278.15–338.15 K (or 283.15–338.15 K for the refractive index). From these properties, we calculate others such as: enthalpy of vaporization, isobaric expansibility, isothermal compressibility, isentropic compressibility, dipole moment, entropy and enthalpy of surface formation per unit surface area, and dynamic viscosity. Finally, we use the PC-SAFT EoS [16] to model the phase, volumetric and acoustic behaviour of the studied compound as well as to find the influence parameter [17] for surface tension.

2. Experimental section

2.1. Chemicals

2-Acetylthiophene was provided by Sigma-Aldrich and the purity was checked by GC chromatography; this purity, expressed as mass percentage, was 99.6%. An automatic titrator Crison KF 1S-2B

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was employed to determine the water content of the liquid, being this content less than 100 ppm. Table 1 reports at $p = 0.1$ MPa the density, ρ , and the refractive index, n_D , at $T = 293.15$ K, and the surface tension, σ , and the dynamic viscosity, η , at $T = 303.15$ K obtained in this work along with the literature values [11].

2.2. Apparatus

Different facilities were used to measure the properties studied in this study, all the devices were periodically checked and rearranged if necessary. The proper operation of these devices is checked by measuring the properties of some reference fluids. Table S1 of the Supporting Information reports our experimental thermophysical data of benzene along with literature values [18–20] for comparison.

An all-glass dynamic recirculating ebulliometer (Fischer-Labodest) equipped with a Cottrell pump allowed determining the vapour pressure, p_v , with uncertainties in the temperature and pressure of equilibrium of 0.01 K and 0.05 kPa, respectively. The pressure was measured with a Digiquartz 735-215A-102 pressure transducer (Paroscientific) and the temperature with a thermometer model F25 with a PT100 probe (Automatic Systems Laboratories).

Density, ρ , and speed of sound, u , at atmospheric pressure were simultaneously obtained using an Anton Paar DSA 5000 vibrating tube densimeter and sound analyser (at a frequency of 3 MHz), automatically thermostated at ± 0.005 K. The estimated uncertainties in the measure of density and speed of sound were 0.1 kg m^{-3} and 0.5 m s^{-1} , respectively. Densities at high pressure were measured by means a high pressure, high temperature Anton Paar DMA HP cell connected to an Anton Paar DMA 5000 unit. The high pressure cell includes a Peltier thermostat to control the temperature, on the other hand to achieve working pressure a hand pump 750.1100 from Sitec (Switzerland) was used, this pressure was measured by a pressure transducer US181 from Measuring Specialties (USA). The uncertainties in this apparatus were: 0.05 MPa in pressure, 0.01 K in temperature and 0.2 kg m^{-3} in density. The device was calibrated using several fluids (dry air, hexane, water and dichloromethane) of known density, more details about calibration and procedure can be found in our previous paper [21].

A capacitive method was used to determine the static permittivity, ϵ , at a frequency of 2 MHz. To do this, an Agilent 4263BA precision LCR meter connected to an Agilent 16452A terminal dielectric test was used. The temperature was controlled by means of a CT52 Schott-Geräte thermostat. The uncertainties for temperature and static permittivity were 0.01 K and 1%, respectively.

A Digital Abbe Refractometer Zuzi WAY-1S with an external Lauda E-200 thermostat that keeps the temperature constant were used to measure the refractive index at sodium D wavelength (589.3 nm), n_D , being the uncertainty in temperature 0.01 K and the

Table 1

Density, ρ , refractive index, n_D , surface tension, σ , and dynamic viscosity, η , at $p = 0.1$ MPa and at two temperatures of 2-acetylthiophene. Comparison between experimental and literature values.^a

T = 293.15 K			T = 303.15 K		
Property	Exp.	Lit. [11]	Property	Exp.	Lit. [11]
$\rho/(\text{kg m}^{-3})$	1171.07	1170.9	$\sigma/(\text{mN m}^{-1})$	42.59	44.5
n_D	1.5658	1.5667	$\eta/(\text{mPa s})$	2.316	2.32

^a Standard uncertainties u are $u(T) = 0.005$ K for density and $u(T) = 0.01$ K for the rest of properties, $u(p) = 0.5$ kPa, and the combined expanded uncertainties U_c are $U_c(\rho) = 0.1 \text{ kg m}^{-3}$, $U_c(n_D) = 10^{-4}$, $U_c(\sigma) = 1\%$, $U_c(\eta) = 1\%$ with 0.95 level of confidence ($k = 2$).

uncertainty in refractive index 10^{-4} .

Surface tension, σ , measurement was carried out by the drop volume technique with a tensiometer Lauda TVT-2. The temperature was controlled by an external Lauda E-200 thermostat. The estimated uncertainties for the temperature and the surface tension were 0.01 K and 1%, respectively.

Kinematic viscosity, ν , was measured with an Ubbelohde capilar viscosimeter including a Schott-Geräte AVS-440 automatic unit and a CT52 Schott-Geräte thermostat to attain a constant temperature. The uncertainty in temperature is 0.01 K and the uncertainty of kinematic viscosity, expressed as percentage, was 1%.

3. Model

3.1. PC-SAFT

PC-SAFT EoS is widely described in the literature so that, in this section, we summarize its most important features; all expressions can be found in the paper of Gross and Sadowski [16]. In this model, the dimensionless Helmholtz energy, \tilde{a} , is written as a sum of an ideal gas contribution, and a residual contribution, which is calculated by perturbation theory. The hard-chain fluid is established as a reference system for the repulsive interactions and the attractive ones are considered a disturbance to that. Thus,

$$\tilde{a}^{\text{res}} = \tilde{a}^{\text{hc}} + \tilde{a}^{\text{dis}} + \tilde{a}^{\text{assoc}} + \tilde{a}^{\text{polar}} \quad (1)$$

where represent the hard-chain contribution obtained from Chapman's approach [22]; is the dispersive attractive contribution calculated using the Barker and Henderson's theory [23,24]; is the association contribution; and include multipole contributions. In this work, we do not consider multipole interactions and the studied compound is not associated.

It is clear that an advantage of this model is that only three parameters are necessary in order to describe each non-associating pure compound: the chain segment number, m , the segment diameter, σ_{SAFT} , and the segment energy, ϵ_{SAFT} . Usually, they are obtained by fitting the thermodynamic properties of the compound.

3.2. Density gradient theory

In this theory, extended by Cahn and Hilliard [25], the Helmholtz free energy density for a two-phase system is written as a Taylor series whose expression keeping the two lowest-order terms is:

$$f[\rho(z)] = f_0[\rho(z)] + k_{ii}(T)[\nabla\rho(z)]^2 \quad (2)$$

where $\rho(z)$ is the density of molecules at position z ; $f_0[\rho(z)]$ is the free energy in the homogeneous part of the system; and $k_{ii}(T)$ is the influence parameter.

The Helmholtz free energy is calculated as the following:

$$A[\rho(z)] = \int \{f_0[\rho(z)] + k_{ii}(T)[\nabla\rho(z)]^2\} dz \quad (3)$$

For a system in equilibrium, this equation has a minimum and this is used to calculate the density profile in the interface. However, it is more adequate to replace the unbounded domain; for this, the z -origin is located at a density $\rho(z_0) = (\rho^v + \rho^l)/2$ being ρ^v and ρ^l the equilibrium densities for vapour and liquid phases, respectively. The density profile, $\rho(z)$, in the direction perpendicular to the surface can be calculated by:

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