



Experimental and modeled volumetric behavior of linear and branched ethers



Victor Antón, José Muñoz-Embid, Manuela Artal, Carlos Lafuente*

Departamento de Química Física, Facultad de Ciencias, Universidad de Zaragoza, 50009, Zaragoza, Spain

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ABSTRACT

Ethers are known to be suitable octane enhancers for gasoline whose combustion process is optimized in direct-ignition spark-ignition engines, where the fuel is directly injected in the chamber at pressures up to 20 MPa. To know and predict the thermodynamic behavior of the fluid will be very convenient to study these processes. In this work, we report density experimental data for nine linear and branched ethers (butyl methyl, methyl tert-butyl, butyl ethyl, ethyl tert-butyl, dipropyl, diisopropyl, dibutyl, dipentyl, and diisopentyl) in the pressure and temperature range from 0.1 to 65 MPa and from 283.15 to 333.15 K (for methyl tert-butyl ether the temperature range was 283.15–323.15 K). From our measurements, we studied the effect of temperature and pressure on density by calculating isobaric expansibility and isothermal compressibility. Other properties such as internal pressure and solubility parameter, which describe the degree of cohesion of the molecules, were obtained. We compared the experimental and calculated data with the literature and a good agreement is found. Finally, we modeled the phase and volumetric behavior using two Equations of State: PC-SAFT and CPA. The needed parameters were obtained from literature or by fitting of their vapor liquid equilibrium and density data; several linear correlations for these parameters were found. Both EoS provided similar deviations in the density but PC-SAFT predicted better than CPA the phase equilibrium (saturation pressure and density) and the solubility parameter.

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1. Introduction

A gasoline additive is a chemical that improves the fuel properties. The methyl tert-butyl ether (MTBE) has been used intensively as a gasoline additive since 70s. Besides increasing the octane, its presence reduces the fuel vapor pressure and vapor emissions during the combustion process, particularly carbon monoxide, aromatic hydrocarbons and particulate matter. Therefore, using MTBE in gasoline has a beneficial effect in reducing air contamination. However, it is quite soluble in water, difficult to biodegrade and does not adsorb on the soil. So MTBE has become an important source pollution water. In 1996, a U.S. Geological Survey study [1–3] found MTBE worrying levels in the urban groundwater; MTBE, in 2000, was classified as a health risk threat by EPA [4]. Several countries (France, Germany, Spain, Japan, ...) are replacing this additive by more innocuous oxygenates compounds

such as ethyl tert-butyl ether (ETBE). This replacement of additives is still slow because the ETBE production cost is higher than that of MTBE [5].

Significant progress in the automotive engineering has been made with the purpose to fuel economy and reduce emissions. The direct injection of fuel into the combustion chamber which is produced in the engines with in-cylinder direct-injection (DI) has clear advantages over the traditional system of port-fuel injection (PFI). The high injection pressures, up to 20 MPa, reached in DI engines increase both the fuel atomization degree and the fuel vaporization rate so that combustion processes are optimized [6]. The knowledge of the thermodynamic behavior of fuel mixtures will be useful to understand the phenomena accompanying combustion, such as the formation of spray and cavitation [7]. The modeling using equations of state, EoS, of the pure compounds of the mixture will enable the prediction its thermodynamic behavior in various pressure, temperature and composition conditions.

Moreover, the ethers are good solvents for chemical analysis, chemical reactions (Grignard synthesis), production of pesticides,

* Corresponding author.

E-mail address: celadi@unizar.es (C. Lafuente).

or oil or resins extractors. Even its effect on the dissolution of gallstones is being evaluated [8].

In this work, experimental density measurements of nine linear and branched ethers (butyl methyl, methyl tert-butyl, butyl ethyl, ethyl tert-butyl, dipropyl, diisopropyl, dibutyl, dipentyl, and diisopentyl) in a wide range of pressure, p , and temperature, T , are collected. Derived properties such as isobaric expansibility, α_p , isothermal compressibility, κ_T , internal pressure, π , and solubility parameter, δ_V , are calculated to evaluate the effect of pressure and temperature on the density and the degree of cohesion of the molecules. Finally, we model the phase and volumetric behavior of these compounds using two equations of state: PC-SAFT and CPA EoS.

2. Models

2.1. PC-SAFT EoS

In this model, developed by Gross and Sadowski [9] the dimensionless Helmholtz energy, \tilde{a} , is written as a sum of two terms: an ideal gas contribution \tilde{a}^{id} , and a residual contribution, \tilde{a}^{res} which contains repulsive and attractive interactions. The repulsive contribution is calculated by establishing a reference system, in this case is hard-chain fluid, and attractive interactions are considered a disturbance to that.

$$\tilde{a} = \tilde{a}^{\text{id}} + \tilde{a}^{\text{res}} \quad (1)$$

$$\tilde{a}^{\text{res}} = \tilde{a}^{\text{hc}} + \tilde{a}^{\text{dis}} + \tilde{a}^{\text{assoc}} + \tilde{a}^{\text{polar}} \quad (2)$$

where \tilde{a}^{hc} represent the hard-chain contribution; \tilde{a}^{dis} is the dispersive attractive contribution; \tilde{a}^{assoc} is the association contribution; and \tilde{a}^{polar} include multipole contributions. A complete description of these terms is collected in the literature: Chapman et al. [10] developed an expression for calculating \tilde{a}^{hc} from Wertheim's first order perturbation theory (TPT1) [11–14]; the attractive term \tilde{a}^{dis} is calculated from Barker and Henderson perturbation theory [15]; the contribution due to short range association interactions \tilde{a}^{assoc} , was proposed by Chapman et al. [16] and Huang and Radosz [17]; and finally, Jog and Chapman [18] developed a term for calculation long range electrostatic interactions of dipolar fluids, \tilde{a}^{polar} , considering the fluid as a mixture of polar and non-polar spherical segments.

Then, the number of parameters needed to describe the pure compounds is different depending on the interactions they arise. Three geometric parameters are always needed: the segment number, m , the segment diameter, σ , and the segment energy, ϵ . If the compound is auto-associated, two additional parameters (effective volume, $\kappa^{A_i B_i}$, and association strength, $\epsilon^{A_i B_i}$) and an association scheme are required. Besides, if the polar contributions are taken into account, the fraction of polar segments, $x_p = k/m$, must be defined (k is the number of polar functions in the chain). In this work, we consider $\tilde{a}^{\text{assoc}} = 0$ and $\tilde{a}^{\text{polar}} = 0$.

The geometric parameters for the ethers studied have been obtained from literature or by fitting of their vapor liquid equilibrium and density data.

2.2. CPA EoS

In this equation of state [19], physical interactions between molecules are described by a cubic equation of state such as Soave-Redlich-Kwong, while specific interactions are given by the same association term used in the SAFT models. This model does not include multipole contributions. When pure compounds are not

associated, as the ethers, this model is the Soave-Redlich-Kwong cubic-EoS with fitted parameters.

Thus, the parameters necessary to describe the non-associated compounds are the usual in cubic EoS: the covolume, b , which is related to the volume of van der Waals, V_w , and the parameters (a_0 and c_1) included in the temperature-dependent term, $\alpha(T)$. To describe associated compounds are necessary association parameters, energy and volume ($\epsilon^{A_i B_i}$, $\beta^{A_i B_i}$), and to establish an association scheme.

Again, we consider ethers as non-associated compounds so only the cubic EoS parameters (b, a_0 and c_1) are required. They have been obtained by fitting of their vapor liquid equilibrium and density data.

3. Experimental

In Table 1 the information about the liquids used is summarized. The purities of the chemicals were checked by GC chromatography and the water content was determined by a Karl-Fischer titration using an automatic titrator Crison KF 1S–2B. All chemicals were used without purification.

Pressure-density-temperature, measurements were performed using a vibrating U-tube densimeter described previously in detail [20]. A hand pump allowed to reach the required pressure which was measurement using a pressure transducer whose uncertainty is $u(p) = 5$ kPa. The uncertainty in the temperature is $u(T) = 0.01$ K and it was controlled using an integrated Peltier thermostat. The calibration was checked by measuring toluene densities in a wide T and p ranges and the estimated uncertainty of our density measurements was: $u(\rho) = 0.1$ kg m⁻³. It was not considered the influence of viscosity on density measurements due to the low viscosity of the studied compounds.

4. Results and discussion

This work reports $p\rho T$ experimental data for several linear (butyl methyl, butyl ethyl, dipropyl, dibutyl, and dipentyl) and branched (diisopropyl, diisopentyl, methyl tert-butyl and ethyl tert-butyl) ethers in the pressure and temperature range from 0.1 to 65 MPa and from 283.15 to 333.15 K, respectively. Methyl tert-butyl ether density data at $T = 328.15$ and 333.15 K are not included due to proximity at its boiling temperature ($T_b = 328.2$ K) [21].

Density results are listed in Table S1 in the Supplementary Information and were correlated with temperature and pressure using the Tait equation [22]:

$$\rho = \frac{\rho_0(T, p_0)}{1 - C \ln \left(\frac{B(T) + p}{B(T) + p_0} \right)} \quad (3)$$

where $p_0 = 0.1$ MPa is the reference pressure and ρ_0 is the corresponding density. Both parameters ρ_0 and B were assumed to be dependent on temperature in the form of a power expansion:

$$\rho_0(T, p_0) = \sum_{i=0}^n A_i \cdot T^i \quad (4)$$

$$B(T) = \sum_{i=0}^n B_i \cdot T^i \quad (5)$$

A_i parameters in Equation (4) can be simultaneously fitted to temperature-dependent experimental density data at atmospheric pressure ($p_0 = 0.1$ MPa). On the other hand, the parameter C in Equation (3) was treated as temperature independent. The

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