



# Measurement and theoretical prediction of the vapor–liquid equilibrium, densities and interfacial tensions of the system hexane + 2-methoxy-2-methylbutane

Andrés Mejía\*, Hugo Segura\*, Marcela Cartes

Departamento de Ingeniería Química, Universidad de Concepción, POB 160 – C, Correo 3, Concepción, Bio-Bio, Chile

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## ABSTRACT

Experimental vapor–liquid equilibrium have been measured for the binary system hexane + 2-methoxy-2-methylbutane at 50, 75 and 94 kPa, and over the temperature range 321–357 K using a vapor–liquid equilibrium still with circulation of both phases. In addition mixing volumes were determined at 298.15 K and atmospheric pressure with a vibrating tube densimeter, while maximum differential bubble pressure tensiometry was used to measure atmospheric interfacial tensions at 303.15 K. According to experimental results, the mixture exhibits slight positive deviation from ideal behavior over the experimental range. The mixing volumes of the system are positive over the whole mole fraction range, and the interfacial tensions exhibit slight negative deviation from the linear behavior. The vapor–liquid equilibrium data of the binary mixture satisfy the Fredenlund's consistency test and were well correlated using the  $\gamma$ - $\phi$  approach with the Wohl, NRTL, Wilson and UNIQUAC equations for all the measured isobars. Mixing volumes and interfacial tensions, in turn, were satisfactorily correlated using the Redlich–Kister equation.

The experimentally determined phase equilibrium, mixing volume and interfacial tension data were theoretically predicted using the Peng–Robinson Stryjek–Vera equation of state (EoS), which was extended to mixtures using the modified Huron–Vidal mixing rule. In such an approximation, the  $\phi$ - $\phi$  approach was directly linked to the Square Gradient Theory, while the experimental excess Gibbs energy data were directly transferred to the EoS model for calculation purposes. According to the results, accurate predictions of the experimental data were obtained for the vapor–liquid equilibrium and interfacial tensions, while qualitatively correct results were obtained for the mixing volumes.

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## 1. Introduction

Experimental determinations and theoretical modeling of the phase equilibrium, densities and interfacial tensions for ether-based mixtures are important for the purpose of understanding the thermodynamics of oxygenated fuels. Certainly, the vapor–liquid equilibrium (VLE) of the quoted mixtures plays an important role in the formulation and production of commercial gasolines with an adequate octane index and low carbon monoxide emissions. Densities (or excess volumes –  $V^E$ ) are also important to design adequate vessels for storage and transportation. Interfacial tensions (IFT), in turn, regulate the formation of gasoline drops that control the optimum fuel atomization on the combustion chamber. Therefore, accurate interfacial tension data are required for designing fuel injection systems [1]. In fact, high interfacial tension prevents the generation of small fuel drops from the liquid gasoline [2]. In

addition, VLE,  $V^E$  and IFT are also important for evaluating the environmental impact of the fuels in air, ground, and aquifers during distribution.

Due to the relevance of the synergistic effect produced when blending alcohol and ether in commercial fuels, a considerable amount of experimental – as well as theoretical – research have been carried out considering branched ethers (e.g. methyl-tert-butyl ether or MTBE, ethyl-tert-butyl ether or ETBE, 2,2'-oxybis[propane] or DIPE, and 2-methoxy-2-methylbutane or TAME) mixed with aliphatic hydrocarbons (e.g. hexane, heptane, cyclohexane, aromatic hydrocarbons (e.g. benzene, etc.) and alcohols (e.g. ethanol, propanol, butanol, etc.). Besides the variety of ether-based binary and ternary systems already studied, some gaps have been detected in the case of mixtures composed by TAME as co-oxygenate [3]. Compared to MTBE, a significant advantage of TAME for gasoline blending is that it exhibits similar thermo-physical properties, although significantly reducing possible environmental impacts. The water solubility of TAME is 51% less than that of MTBE however, as the latter, it has been used to formulate gasoline blends with high degradation index [4],

\* Corresponding authors. Tel.: +56 412203897; fax: +56 412247491.  
E-mail addresses: [amejia@udec.cl](mailto:amejia@udec.cl) (A. Mejía), [hsegura@udec.cl](mailto:hsegura@udec.cl) (H. Segura).

**Table 1**  
Gas chromatography (GC) purities (mass fraction), refractive index ( $n_D$ ) at Na D line, densities ( $\hat{\rho}$ ), normal boiling points ( $T_b$ ) and interfacial tensions ( $\sigma$ ) of pure components.<sup>a</sup>

Component (purity/mass fraction)	$n_D$ $T/K = 298.15$		$\hat{\rho}/\text{g cm}^{-3}$ $T/K = 298.15$		$T_b/K$ $p/\text{kPa} = 101.33$		$\sigma/\text{mN m}^{-1}$ $T/K = 303.15$	
	Exp.	Lit. <sup>b</sup>	Exp.	Lit. <sup>b</sup>	Exp.	Lit. <sup>b</sup>	Exp.	Lit. <sup>b</sup>
Hexane (0.996)	1.37374	1.37230	0.65519	0.65603	341.94	341.88	17.40	17.37
TAME (0.997)	1.38712	1.38590	0.76580	0.76587	359.52	359.51	22.00	22.01

<sup>a</sup> The measurement uncertainties are:  $n_D \pm 10^{-5}$ ;  $\hat{\rho} \pm 5 \times 10^{-6}$  g cm<sup>-3</sup>;  $\sigma \pm 0.1$  mN m<sup>-1</sup>;  $p \pm 0.03$  kPa;  $T \pm 0.01$  K.

<sup>b</sup> Daubert and Danner [14].

showing similar RVP (Reid Vapor Pressure) and RON (Research Octane Number).

Following with our ongoing research program in the characterization of TAME as a potential oxygenate [5], in this work we report new experimental data and estimate theoretical modeling for the phase equilibrium, densities and interfacial tension for the case of hexane + TAME.

Previous works reporting VLE data of hexane + 2-methoxy-2-methylbutane or TAME only cover isothermal conditions ranging from 298.15 K to 328.15 K [6,7]. According to these works, this zeotropic mixture exhibits slight positive deviation from ideal behavior, and positive  $V^E$  over the whole mole fraction range at 298.15 K [8]. In contrast to the experimental VLE and  $V^E$  characterization – and to the best of our knowledge – no IFT data have been previously reported for this mixture.

Consequently a primary goal of this contribution is to report experimental VLE data, namely isobaric VLE data (50, 75 and 94 kPa),  $V^E$  at 298.15 K based on purified TAME (>99%), together with new IFT data for the hexane + 2-methoxy-2-methylbutane (or TAME) mixture. A secondary goal of this work is to simultaneously predict both bulk phase and interfacial properties of the quoted mixture by using a  $\phi$ - $\phi$  approach, namely combining the Peng–Robinson equation of state [9] extended to mixtures using the modified Huron–Vidal mixing rule (MHV) [10], and the Square Gradient Theory (SGT) proposed originally by van der Waals [11] and reformulated by Cahn and Hilliard [12]. As we demonstrated in a previous work [13], this  $\phi$ - $\phi$  approach provides a full predictive route for both VLE and IFT because the required information (the parameters involve excess Gibbs energy  $G^E$  models) are transferred from  $\gamma$ - $\phi$  to  $\phi$ - $\phi$  approach by means of the MHV mixing rule, while the interfacial parameters (particularly, influence parameters) can be obtained from the interfacial tension data of pure fluids.

## 2. Experimental

### 2.1. Purity of materials

Hexane was purchased from Merck, and it was used without further purification. TAME was purchased from Aldrich, and then was further purified to 99.7+ mass% by rectification in a 1 m height and 30 mm diameter Normschliffgerätebau adiabatic distillation column (packed with 3 × 3 mm stainless steel spirals), working at a 1:100 reflux ratio. Table 1 reports the purity of the components (as determined by gas chromatography, GC), together with the normal boiling points of the pure fluids ( $T_b$ ), the mass densities ( $\hat{\rho}$ ) of pure liquids, the refractive indexes ( $n_D$ ) at 298.15 K, and the interfacial tensions ( $\sigma$ ) of pure fluids at 303.15 K. The reported values are also compared with those given by Daubert and Danner [14].

### 2.2. Apparatus and procedure

#### 2.2.1. Vapor–liquid–equilibrium cell

An all-glass vapor–liquid equilibrium apparatus model 601, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used in the equilibrium determinations. In this circulation-method apparatus, the mixture is heated to its boiling point by a

250 W immersion heater. The vapor–liquid mixture flows through an extended contact line (Cottrell pump) that guarantees an intense phase exchange and then enters to a separation chamber whose construction prevents an entrainment of liquid particles into the vapor phase. The separated gas and liquid phases are condensed and returned to a mixing chamber, where they are stirred by a magnetic stirrer, and returned again to the immersion heater. The temperature in the VLE still is determined with a Systemtechnik S1224 digital temperature meter, and a Pt 100 probe, which was calibrated against the experimental fusion and boiling points of distilled water. The reliability of such a calibration procedure was successfully checked using the experimental boiling temperature data of the pure fluids used in this work. The accuracy is estimated as  $\pm 0.02$  K. The total pressure of the system is controlled by a vacuum pump capable of work under vacuum up to 0.25 kPa. The pressure is measured with a Fischer pressure transducer calibrated against an absolute mercury-in-glass manometer (22 mm diameter precision tubing with cathetometer reading), the overall accuracy is estimated as  $\pm 0.03$  kPa.

On average the system reaches equilibrium conditions after 2–3 h operation. 1.0  $\mu\text{L}$  samples taken by syringe after the system had achieved equilibrium, were analyzed by gas chromatography on a Varian 3400 apparatus provided with a thermal conductivity detector and a Thermo Separation Products model SP4400 electronic integrator. The column was 3 m long and 0.3 cm in diameter, packed with SE-30. Column, injector and detector temperatures were 373.15, 413.15, and 493.15 K, respectively. Good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak area ratio to the mass composition of the sample. The pertinent polynomial fit of the calibration data had a correlation coefficient  $R^2$  better than 0.99. At least three analyses were made of each sample. The maximum standard deviation of these analyses was 0.08 in area percentage. Concentration measurements were accurate to better than  $\pm 0.001$  in mole fraction.

#### 2.2.2. Density and refractive indexes measurements

For density measurements, samples of known mass were prepared on an analytical balance (Chyo Balance Corp., Japan) with an accuracy of  $\pm 10^{-4}$  g. Densities ( $\hat{\rho}$ ) of the pure components and their mixtures were measured at 298.15 K using a DMA 5000 densimeter (Anton Paar, Austria) with an accuracy of  $5 \times 10^{-6}$  g cm<sup>-3</sup>. The density determination is based on measuring the period of oscillation of a vibrating U-shaped tube filled with the liquid sample. During the operation, the temperature of the apparatus was maintained constant to within  $\pm 0.01$  K.

The refractive indexes ( $n_D$ ) of pure liquids were measured at 298.15 K using a Multiscale Automatic Refractometer RFM 81 (Bellingham + Stanley, England). During the operation, temperature was controlled to within  $\pm 0.01$  K by means of a thermostatic bath (Haake DC3, Germany). The uncertainties in refractive index measurements are  $\pm 10^{-5}$ .

#### 2.2.3. Interfacial tension measurements

A maximum differential bubble pressure tensiometer model PC500-LV manufactured by Sensadyne Inc. (USA) was used in interfacial tension measurements. In this equipment, two glass probes of

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