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Measurement and modeling of isobaric vapor – Liquid equilibrium and isothermal interfacial tensions of ethanol + hexane + 2,5 – Dimethylfuran mixture

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ABSTRACT

Isobaric vapor-liquid equilibrium data have been measured for the ternary system ethanol + hexane + 2,5 – dimethylfuran at 94 kPa and in the temperature range 330–344 K. Equilibrium determinations were performed in a vapor-liquid equilibrium still with circulation of both phases. The dependence of interfacial tensions of the ternary mixture on concentration was also experimentally determined at atmospheric pressure and 298.15 K, using the maximum differential bubble pressure technique.

From the experimental results, it follows that the ternary mixture exhibits positive deviation from ideal behavior. Furthermore, the determined interfacial tensions exhibit negative deviations from the linear behavior, and ternary aneotropy is observed.

The vapor-liquid equilibrium (VLE) data of the ternary mixture past the consistency test and were well correlated by Redlich–Kister expansion and predicted by the nonrandom two-liquid (NRTL), Wilson and universal quasichemical (UNIQUAC) activity coefficient models using binary parameters only. The interfacial tensions (IFT) were smoothed using the Myers-Scott expansion, showing an important contribution of parameters that describe three-body interactions, thus suggesting that the ternary interfacial tensions data cannot be initially predicted from the binary contributions.

The experimental isobaric VLE and isothermal IFT data of the ternary mixture were accurately characterized by applying the linear square gradient theory to the Peng–Robinson Stryjek–Vera equation of state (EoS) appropriately extended to mixtures by means of the modified Huron–Vidal mixing rule. This model allows directly transferring the experimental excess Gibbs energy function to the EoS model for equilibrium and interfacial tension calculation purposes. This theoretical framework shows that both experimental VLE and IFT data can be accurately predicted by using binary contributions and provide a route to interpolate values phase equilibrium and interfacial tension.

1. Introduction

Current environmental regulations and energy directives recommend and promote to increase the use of renewable energy sources. These polices have been stimulated the development of alternative combustibles that can be used as a fuel or additives for fossil gasoline [1,2]. One of the most innovative route to produce a renewable fuel has been proposed by Román-Leshkov et al. [3]. In their original work, a novel biochemical route is described to efficiently produces 2,5-Dimethylfuran (or 2,5-DMF) from sugar with a potentially high yield. Posteriorly, Binder and Raines [4] have been demonstrated that 2,5-DMF exhibits an energy density that not only it is comparable to gasoline but also 40% higher than ethanol. Additionally, Nakata et al. [5] measured the Research Octane Number (RON) for 2,5-DMF and demonstrated that this fluid improves de fuel economy because it can be used in higher compression ratio engines. Complementary, 2,5-DMF displays a stoichiometric air/fuel ratio lower than traditional gasoline, resulting on a reduction of the air needed to burn the fuel. Finally, the 2,5-DMF has been already tested as a fuel in direct-injection spark-ignition engines, showing an excellent performance [6], transforming the 2,5-DMF as a potentially attractive and highly efficient biofuel. [3,6–9].

Despite its innovative and potential use as fuel or additive for fossil fuel, the evaluation of some key thermodynamic properties, such as vapor – liquid equilibrium (VLE) and interfacial tensions (IFT), are

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limited to few cases. The importance of VLE is to provide information about the distillation curve (*i.e.*, fuel concentration during vaporization) and the Reid vapor pressure (volatility indicator), which are useful for predicting technical properties of gasoline blends. In addition, IFT defines the size of fuel drops and controls their ignition kinetics, thus providing useful information for the purpose of designing engine injectors.

Previous experimental works related to the VLE cover the 2,5-DMF as a pure fluid [10,11] and only a reduce number of binary mixtures have been measured (i.e., 2,5-DMF + 1-butanol, or 2-butanol or 1-hexanol [12]; 2,5-DMF + hexane [10]; 2,5-DMF + 2,2′ - oxybis[propane] or DIPE [13]; 2,5-DMF + ethanol [14]; 2,5-DMF + methyl-*tert*-butyl ether or MTBE [11]). From these experimental works, it is possible to conclude that 2,5-DMF mixtures exhibits positive deviation from ideal behavior and positive azeotropic behavior can be observed for the case of 2,5-DMF + lower alcohols (ethanol, 1-butanol, 2-butanol). For the case of IFT, the available information is more scare than VLE. In fact, IFT measurements have been reported for 2,5-DMF as a pure fluid [10] and four binary mixtures (i.e., 2,5-DMF + hexane [10], 2,5-DMF + DIPE [13], 2,5-DMF + ethanol [14] and 2,5-DMF + MTBE [11]). For the case of 2,5-DMF + ethers, the experimental reports show a negative deviation from the linear behavior, whereas IFT for 2,5-DMF + ethanol mixture exhibits a positive deviation from the linear behavior.

From a theoretical perspective, the VLE of 2,5-DMF mixtures have been correlated by using the $\phi - \gamma$approach, where the vapor phase is modeled using the second virial equation of state, whereas the behavior of the liquid bulk phase is approached by using activity coefficient (γ) models (e.g. Wilson, NRTL, UNIQUAC, etc) and the Redlich–Kister expansion. For the case of the IFT, its dependence on concentration has been correlated using the following Myers-Scott expansion. Additionally, for the case of 2,5-DMF + ether [11,13], the experimental VLE and IFT have been simultaneously treated by using van der Waals square gradient theory [15] couple to an equation of state (EoS). Specifically, the Cubic-Plus-Association EoS (see Kontogeorgis and Folas [16] and references therein) was used for the case of 2,5-DMF + DIPE mixture [13] whereas the Peng – Robinson EoS [17] with the modified Huron – Vidal mixing rules (MHV) [18] was used was used for the case of 2,5-DMF + MTBE mixture [11].

Following with our ongoing research program in the characterization of 2,5-DMF as a potential oxygenate [10,11,13,14], in this work we report new VLE and IFT experimental data for the case of the ternary mixture of ethanol + hexane + 2,5-DMF and, additionally, we discuss their theoretical modeling. Specifically, in this contribution we report isobaric VLE data at 94 kPa and isothermal IFT data at 298.15 K, together with a full predictive theoretical framework based on the application of the linear version of the van der Waals square gradient theory (LSGT) proposed by Zuo and Stenby [19,20] to Peng – Robinson EoS [17] with modified Huron – Vidal mixing rules (MHV) [18]. As it has been demonstrated in previous works [11,13,21–23], the information required in this purely predictive approach can be obtained from pure fluids and binary mixtures, together with an accurately parameterized excess Gibbs energy, G^E, function of the involved mixture. For this latter purpose, the parameters of a G^E model are regressed from isobaric binary VLE experimental data using the $\phi - \gamma$approach and the resulting function is directly used to predict isothermal VLE using the $\phi - \phi$ approach and IFT combining the $\phi - \phi$ approach to the LSGT.

2. Experimental section

2.1. Materials

Hexane (99.6 + mass%) and ethanol (99.9 + mass%) were purchased from Merck whereas 2,5 – dimethylfuran or 2,5-DMF (99.7 + mass%) was purchased from Aldrich. The chemicals were used in this work without further purification and gas chromatography (GC) test confirms a mass purity not less than indicate by the companies. Table 1 summarizes the information of the pure fluids, the purity and water content provided by the manufacturer as well as purity of the components as determined by GC. Table 2 includes normal boiling points of the pure fluids (T_b) and the mass densities (ρ), the refractive indexes (n_D) and the interfacial tensions (σ) of pure fluids at 298.15 K. Table 2 also includes the corresponding reference experimental values which have been reported in previous works [10,11,13,14,24–27] and NIST-REFPROP database [28]. In order to avoid hydration, the chemicals are stored in a dark place and lightly pressurized by an inert gas (Argon).

Table 1
Information of the pure fluids used in this work.

Chemical name	Source	Mass fraction purity (as stated by the supplier)	% Water content	Purification method	Mass fraction purity (as detected by GC[a])
Ethanol	Merck	0.999	≤0.01%	None	0.999
Hexane	Merck	0.990	≤0.005%	None	0.996
2,5-DMF	Aldrich	0.985	≤0.07%	None	0.997

[a] Gas-liquid chromatography.

2.2. Vapor – liquid equilibrium measurements

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 phase is condensed, and then both the condensed and liquid phases are returned to a mixing chamber, where they are magnetically stirred, and returned again to the immersion heater. The temperature in the VLE still is determined with a Systemteknik S1224 digital temperature meter and a Pt 100 probe, which was calibrated against the ice and steam points of distilled water, and then checked against the boiling temperature data of the pure fluids used in this work. The accuracy is estimated as ± 0.02 K. The total pressure of the system is controlled by a vacuum pump capable of working 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 ± 0.03 kPa.

On average, the ternary mixture reaches equilibrium conditions after 2–3 h operation. 1.0 μL 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 353.15, 393.15, 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 0.12 in area percentage. Concentration measurements were accurate to better than ± 0.001 in mole fraction. Additional details concerning low pressure VLE measurements have been described in depth by Raal and Ramjugernath [29].