Interfacial tensions of binary mixtures of ethanol with octane, decane, dodecane, and tetradecane

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ABSTRACT

This contribution is devoted to the experimental characterization of interfacial tensions of a representative group of binary mixtures pertaining to the (ethanol + linear hydrocarbon) series (*i.e.* octane, decane, dodecane, and tetradecane). Experimental measurements were isothermically performed using a maximum differential bubble pressure technique, which was applied over the whole mole fraction range and over the temperature range 298.15 K < T/K < 318.15 K.

Experimental results show that the interfacial tensions of (ethanol + octane or decane) negatively deviate from the linear behavior and that sharp minimum points on concentration, or aneotropes, are observed for each isotherm. The interfacial tensions of (ethanol + dodecane or tetradecane), in turn, are characterized by combined deviations from the linear behavior, and inflecting behavior observed on concentration for each isotherm. The experimental evidence also shows that these latter mixtures are close to exhibit aneotropy.

For the case of (ethanol + octane or decane) mixtures, aneotropy was clearly induced by the similarity of the interfacial tension values of the constituents. The inflecting behavior of the interfacial tensions of (ethanol + dodecane or tetradecane), in turn, was observed in the vicinity of the coordinates of the critical point of these mixtures, thus pointing to the fact that the quasi-aneotropic singularity that affects these mixtures was provoked by the proximity of an immiscibility gap of the liquid phase.

Finally, the experimental data of interfacial tensions were smoothed with the Scott–Myers expansion, from which it is possible to conclude that the observed aneotropic concentrations weakly depend on temperature for all the analyzed mixtures.

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1. Introduction

The interfacial behavior of (ethanol + hydrocarbon) mixtures plays a central role in the formulation and rational application of oxygenated gasolines and biofuels. This is so due to the fact that the magnitude of the interfacial tension may conveniently control the ignition kinetics as well as it may affect the atomization of liquid fuels inside the engine's combustion chamber [1–3]. The interfacial tensions of the mixtures under study are also important for designing potentially convenient strategies able to prevent – or at least, minimize – eventual risks related to the pollution of aquifers during gasoline distribution. Other important risks where interfacial tensions of the study mixtures need to be considered are summarized in references [3–5]. Besides these technological and environmental issues, the interfacial tensions of (ethanol + hydrocarbon) mixtures exhibit the singular behavior known as surface azeotropy [6] or aneotropy [7,8], as it has been

experimentally reported for mixtures composed of perfluoroalkanes and heptane or octane. Aneotropy corresponds to a physical state in which the interfacial tension of a mixture reaches a stationary point on concentration at isothermal conditions, a phenomenon that has been experimentally observed in mixtures that are close to critical points of immiscibility or for cases in which the mixture's constituents are characterized by similar interfacial tension values [9–11]. From the point of view of the specific interfacial activity, aneotropic states imply nil relative Gibbs isothermal adsorption (*i.e.* the surface and bulk composition are identical) [6,8,9], a potentially attractive condition which may be exploited in surfactant engineering applications.

Previous works concerning the experimental characterization of the (ethanol + hydrocarbon) mixtures considered here only report the case of {ethanol (1) + octane (2)} at T = 298.15 K and p = 101.3 kPa [12], for which it has been observed that interfacial tensions exhibit moderate negative deviation from the linear behavior, and aneotropy is present at $x_1 \approx 0.528$.

Since scarce experimental data are available for (ethanol + hydrocarbon) mixtures and, additionally, little is known

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about their aneotropic behavior, this work is undertaken to experimentally characterize the interfacial behavior of four binary mixtures composed by (ethanol + octane, decane, dodecane, and tetradecane). From these representative data, we describe the mechanisms that induce existence and persistence of aneotropy in (ethanol + linear hrydrocarbon) series.

2. Experimental

2.1. Purity of materials

All chemicals were purchased from Merck and, after testing their quality, they were used directly without further purification. Table 1 reports the purity of the components (as determined by gas chromatography, GC), together with the densities of pure liquids at $T = 303.15$ K, the refractive indexes at $T = 298.15$ K, and the interfacial tensions of pure fluids over the experimental temperature range.

2.2. Apparatus and procedure

2.2.1. Concentration measurements

Concentrations were determined by gas chromatography (GC) in 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. The detector temperature was always held at $T = 493.15$ K. The temperatures of the column and injector were fixed according to the mixture. Specifically, $T = 383.15$ K and $T = 413.15$ K were used for (ethanol + octane); $T = 363.15$ K and $T = 423.15$ K for (ethanol + decane); $T = 413.15$ K and $T = 423.15$ K for (ethanol + dodecane), and $T = 423.15$ K and $T = 443.15$ K for (ethanol + tetradecane). Good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. The pertinent polynomial fit had a correlation coefficient R^2 better than 0.99. At least three analyses were made of each sample. Concentration measurements were accurate to better than ±0.001 in mole fraction.

2.2.2. Density and refractive indexes

The densities of pure liquids were measured using an Anton Paar DMA 5000 densimeter (Austria), and the refractive indexes were measured using a Multiscale Automatic Refractometer RFM 81 (Bellingham + Stanley, England). During the operation of these equipments, temperature was controlled to within ±0.01 K by means of a thermostatic bath (Haake DC3, Germany). The uncertainties in density and refractive index measurements are $5 \cdot 10^{-6}$ g · cm^{-3} and ±10^{-5}, respectively.

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 different orifice radii ($r_1 = 0.125 \pm 0.01$ mm and $r_2 = 2.0 \pm 0.01 \cdot$ mm) are immersed in a vessel that contains the sample to be measured. In order to guarantee high accuracy and reduce the measurement errors, the small orifice is $2.5 \cdot$ mm below to the large orifice. Ultra high purity nitrogen (UHP = 99.995%) is then blown through the probes and the differential pressure (ΔP) between them is recorded. The differential pressures measured were in the range (279 to 373) Pa (approximately), while bubbling frequency was in the range $(1.50$ to $1.80) \cdot$ bubbles/seg.

According to the Laplace's equation, ΔP and r_1, r_2 are related to the interfacial tension, σ, as:

$$\Delta P = P_1 - P_2 = 2\sigma(r_1^{-1} - r_2^{-1}), \tag{1}$$

where P_i is the pressure exerted by the gas flow in the probe of radius r_i. The gas flow is controlled by a sensor unit connected to a personal computer through an interface board (PCI-DAS08, Measurement Computing, USA). Besides a constant volume flow controller, this sensor unit includes a differential pressure transducer, a temperature transducer and a pressure regulator. The temperature of the sample in the vessel is measured by means of a Pt 100 probe, and maintained constant to within ±0.01 K using a thermostatic bath (Julabo, Germany).

The experimental method for determining interfacial tensions proceeds as follows: the mixture to be analyzed is prepared by adding appropriate volumes of each pure fluid. The sample is then placed into the vessel, where it is heated to the experimental temperature and stirred during 30 min by a magnetic stirrer. At that moment, the concentration of the sample is determined in triplicate by means of GC. Thereafter, UHP nitrogen flows through the probes, and the sensor unit translates the measurement of voltage signal (Δv) to a ΔP signal. The relation between $\Delta v - \Delta P$ is obtained by calibrating the sensor unit software using two reference fluids with well-characterized interfacial tensions over the range of

TABLE 1
Gas Chromatography (GC) purities (mass fraction), refractive index (n_D) at Na D line, densities (ρ), and interfacial tensions (σ) of pure components as a function of temperature (T).

Component (purity/mass fraction)	n_D T/K = 298.15		ρ/(g · cm^{-3}) T/K = 303.15		σ/(mN · m^{-1})		
	Exp.	Lit.[a]	Exp.	Lit.[a]	T/K	Exp.	Lit.[a]
Decane (0.998)	1.41116	1.40970	0.72238	0.72230	303.15	22.90	22.91
					308.15	22.50	22.43
					318.15	21.66	21.49
Dodecane (0.998)	1.42128	1.41510	0.74172	0.74163	298.15	24.90	24.92
					303.15	24.73	24.47
Ethanol (0.999)	1.36068	1.35940	0.78078	0.78141	298.15	22.10	22.10
					303.15	21.70	21.68
					308.15	21.30	21.26
					313.15	20.71	20.83
					318.15	20.40	20.40
Octane (0.997)	1.39576	1.39510	0.69468	0.69523	298.15	21.10	21.13
					308.15	20.20	20.17
					318.15	19.20	19.22
Tetradecane (0.998)	1.42848	1.42690	0.755936	0.75593	313.15	24.80	24.79

[a] Daubert and Danner [13].