Energy 35 (2010) 759–763

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Thermodynamic characterization of bio-fuels: Excess functions for binary mixtures containing ETBE and hydrocarbons

José J. Segovia*, Rosa M. Villamañán, M. Carmen Martín, César R. Chamorro, Miguel A. Villamañán

Research Group TERMOCAL (Thermodynamics and Calibration), University of Valladolid, Escuela de Ingenierías Industriales, Paseo del Cauce 59, 47011 Valladolid, Spain

ARTICLE INFO

Article history:
Received 29 October 2008
Received in revised form
9 September 2009
Accepted 16 September 2009
Available online 23 October 2009

Keywords:
Bio-fuels
ETBE
Hydrocarbons
Vapor-liquid equilibria
Excess enthalpy
Excess functions

ABSTRACT

European energy policy is promoting the use of bio-fuels for transportation. Bioethers and bioalcohols are used as blending agents for enhancing the octane number. They make gasoline work harder, help the engine last longer and reduce air pollution. They also cause changes in the fuel properties. Development of renewable fuels needs both knowledge of new thermodynamic data and improvement of clean energy technologies. In this context, the use of ethanol of vegetable origin in its manufacture process, increases the interest of ETBE or bio-ETBE as an oxygenated additive. A complete study of the behaviour of ETBE + hydrocarbons mixtures is presented. Some experimental data concerning vapor-liquid equilibria and heats of mixing were determined in our laboratory. All the techniques have a high accuracy. The data were reduced by well-known models, such as NRTL and used to model the thermodynamic properties.

1. Introduction

European energy policy is promoting the use of bio-fuels for transportation. Bioethers and bioalcohols are used as blending agents for enhancing the octane number. They make gasoline work harder, help the engine last longer and reduce air pollution. They also cause changes in the fuel properties. Development of renewable fuels needs both knowledge of new thermodynamic data and improvement of clean energy technologies [1,2].

Ethyl 1,1-dimethylethyl ether (better known as ethyl tert-butyl ether or ETBE) is being used as a blending agent in the formulation of gasolines to enhance the octane number. ETBE, is synthesized from isobutylene and ethanol by using an acidic ion-exchange-resin such as Amberlyst-15. This exothermic reaction is equilibrium limited in the industrial temperature range (40–70 °C). The main side reactions are the dimerisation of isobutylene and the hydration of isobutylene. The former can be minimized by using excess ethanol, and the latter is neglected in this process analysis because it occurs only in the presence of water. The use of ethanol of vegetable origin in its manufacture process, increases the interest of ETBE or bio-ETBE as an oxygenated additive [3,4]. Accurate knowledge of the thermodynamic properties of ETBE and hydrocarbon mixtures is important to improve the thermodynamic models used in the design, simulation and production processes.

This work is part of a research project to obtain new high quality experimental thermodynamic data to develop a model which is able to predict the properties of a synthetic gasoline with a considerable number of components as a function of temperature and pressure. The measurement of the vapor-liquid equilibrium of a mixture allows its excess Gibbs energy to be calculated but, on the other hand the excess enthalpy is obtained directly from calorimetric measurement and both give the excess entropy, completing the thermodynamic information of the mixture at a given temperature.

The vapor-liquid equilibria (VLE) and the excess enthalpies of the binary systems containing ETBE, *n*-heptane and toluene at $T = 313.15$ K have been measured, and they are used to calculated the excess Gibbs energy and the excess entropy of the systems at this temperature. The excess enthalpies have also been determined at $T = 298.15$ K to evaluate the effect of the temperature on this property.

2. Experimental section

2.1. Materials

Ethyl 1,1-dimethylethyl ether was supplied by La Coruña Refinery of REPSOL-YPF, it was purified by rectification at atmospheric pressure. The intermediate fraction was collected and

---

* Corresponding author. Tel./fax: +34 983 184690.
E-mail address: josseg@eis.uva.es (J.J. Segovia).

0360-5442/$ – see front matter © 2009 Published by Elsevier Ltd.
doi:10.1016/j.energy.2009.09.025

Nomenclature

A_{ij}, A_{ji}	adjustable parameters of the NRTL model
G_{ij}, G_{ji}	parameters of the NRTL model
G^E	excess molar Gibbs energy (J mol^{-1})
H^E	excess molar enthalpy (J mol^{-1})
p	pressure (Pa)
R	universal gas constant (J mol^{-1} K^{-1})
rms	root mean square
S^E	excess molar entropy (J mol^{-1} K^{-1})
T	temperature (K)
x_i	mole fraction of component "*i*"
α	adjustable parameter of the NRTL model
ΔH^E_{max}	maximum deviation between experimental and calculated excess enthalpies.
Δp_{max}	maximum deviation between experimental and calculated pressures

rectified again to a purity >0.997 as determined by gas chromatography (GC).

The hydrocarbons were purchased from Fluka Chemie AG and were of the highest purity available, chromatography quality reagents. Their purities were checked by gas chromatography and found to be >0.997 (GC).

2.2. Experimental techniques

A static VLE apparatus, consisting of an isothermal total pressure cell, was used to measure the vapor-liquid equilibrium of binary mixtures. The apparatus and measuring technique are based on that by Van Ness and co-workers [5,6] and its performance was described in a previous paper [7].

Two positive displacement pumps, of 100 mL capacity (Ruska, mod. 2200-801), are used to inject known volumes of pure degassed components into the cell. This is immersed in a high precision water bath (Hart Scientific model 6020) assuring a temperature stability of ±0.5 mK and thermostatted at $T = 313.15$ K. The pump resolution is 0.01 mL and the resulting uncertainty in the volume injected is ±0.03 mL.

The cell is a cylindrical stainless steel piece with a volume of about 180 mL and is provided with an externally-operated magnetic stirrer. Initially about 50 mL of one component are injected into the evacuated cell, and the vapor pressure is recorded. The second component is then injected in an appropriate proportion to achieve the desired composition. The total mass injected is accurately determined from the volume differences corresponding to the initial and final positions of the pistons, the temperature of the pumps and the densities of the components. The estimated uncertainty in the mole fraction is ±0.0005. The composition of the liquid phase is close to the overall composition but is corrected by taking into account the vapor space of the cell and using the virial equation, whereas the composition of the vapor phase is calculated by data reduction.

Experimental values of the total vapor pressure for the binary mixtures are obtained in two overlapping runs starting from opposite ends of the composition range.

Excess enthalpies have been measured with a quasi-isothermal flow calorimeter developed in our laboratory (Fig. 1). Two precision isocratic pumps (Agilent 1100 normally used in HPLC chromatography) deliver the liquids through the cell at programmable constant flow rates into the mixing coil placed in the flow cell. The flow cell is immersed in a water bath, (Hart Scientific, model 7041) thermostatted at the same temperature at which the mixing process is taking place. The bath temperature is measured with a calibrated standard Pt-100 thermometer using an a/c resistance bridge (ASL model F250) as indicator. Isothermal calorimetry is based on measuring the energy required to maintain the mixing vessel at a constant temperature. To achieve this condition, a Peltier cooler removes energy at a constant rate from the flow cell and a control-heater compensates this energy as well as the additional energy liberated (exothermic mixing) or absorbed (endothermic mixing) by the mixing process. The variation of temperature is detected by a control sensor, an NTC thermistor. The resistance is measured by a 4-wire resistance bridge with a micro-ohm meter from Hewlett-Packard, model HP-34420A. The Peltier cooler, the control-heater and the calibration heater are each connected to their own DC power supply. These devices are controlled using a computer through a GPIB connection and specific software that has been developed using a VEE-Agilent program. The change in heating power of the control-heater before, during and after measurements is a direct measure for the excess enthalpy. The calibration of the measurement system is done by simulating an exothermic mixing process by a calibration resistor.

The measured directly properties and their corresponding uncertainties are: flow rate ±0.15% (1–10 mL/min); temperature ±10 mK; the heating and cooling systems have a stability better

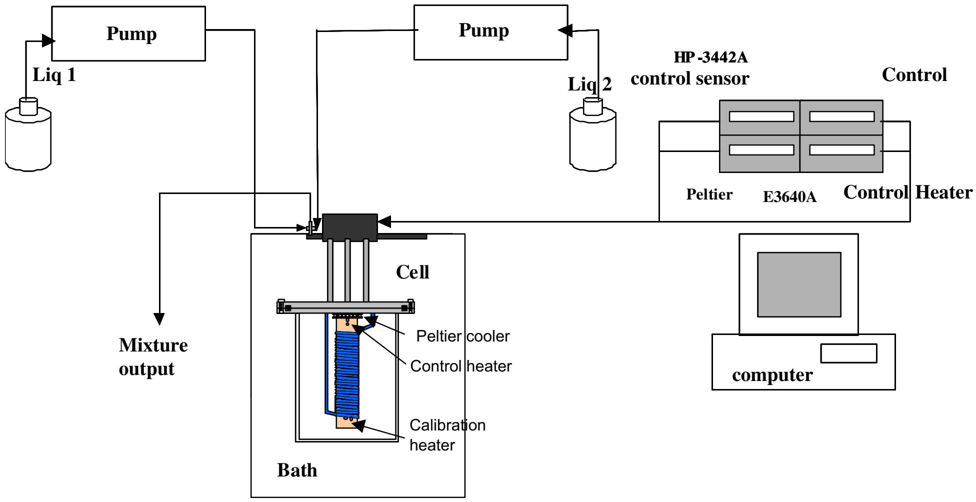

Fig. 1. A schematic view of the isothermal flow calorimeter.