



Equilibrium data and GC-PC SAFT predictions for furanic extraction



Eric Auger^a, Christophe Coquelet^{a,b,*}, Alain Valtz^a, Mqondisi Nala^{a,b},
Paramespri Naidoo^b, Deresh Ramjugernath^b

^a Mines ParisTech, PSL Research University, CTP - Centre of Thermodynamics of Processes, 35 Rue Saint Honoré, 77305, Fontainebleau, France

^b Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, King George V Avenue, Durban, 4041, South Africa

ARTICLE INFO

Article history:

Received 24 June 2016

Received in revised form

24 August 2016

Accepted 13 September 2016

Available online 13 September 2016

Keywords:

Furfural

Furan

Solvent

Phase diagram

Ebulliometer

Equipment

ABSTRACT

The present study concerns phase equilibria measurements involving oxygenated components (furan and furfural) and potential solvents of extraction (n-hexane, ethanol and n-octanol) using an ebulliometer at atmospheric pressure. New liquid-liquid equilibrium data concerning the ternary system furan + furfural + n-hexane are also presented. The experimental technique used for the liquid-liquid equilibrium measurements is based on the static analytic method. The two liquid phases are sampled using a syringe and analyzed using gas chromatograph. Two thermodynamic approaches are considered for the data treatment: the first considers a dissymmetric approach using the NRTL activity coefficient model, and the second considers a group contribution model based on the PC-SAFT EoS (GC-PPC SAFT). The experimentally measured data were successfully correlated with the models proposed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The development and improvement of second-generation bio-fuels and green chemistry relies on accurate phase equilibrium computations of molecules involved. Among these molecules, there is a specific growing interest on selective production of furfural from renewable biomass. Indeed, a number of chemical products and fuel (additives) can be produced from the starting material called furfural. Current uses of furfural include, mainly the production of furfuryl alcohol (resin production), linking foundry sand, and lubrication oil extraction. Moreover, acidic biomass hydrolysis and subsequent dehydration of the obtained C5 sugar xylose leads to furfural [1] and glucose into furans [2]. Therefore, extraction of furfural is a key point of the development of second generation biorefinery [3–7]. Finally, furan, which is industrially synthesized from furfural, is also used for the production of the solvent tetrahydrofuran, some polymers used as additives for detergents, and herbicides.

In biorefining, the determination of the process for separation or purification requires an accurate thermodynamic model. In the case

of liquid-liquid extraction, information about the liquid-liquid equilibria (LLE) between solvent and solute permits the determination of selectivity between the solute and the solvent. Concerning the distillation processes, residue curves are used to determine the feasibility of the separation process. The residue curve is obtained by solving the Rayleigh distillation equation ($\frac{dx}{dt} = x - y$, x and y are the compositions of liquid and vapor phases, respectively). Parameters of the thermodynamic models are determined from experimental data, but can also be determined from group contribution methods.

In this publication, we present new sets of data: vapor-liquid equilibrium (VLE) data at atmospheric pressure for furan + ethanol, furan + n-octanol, and furan + furfural binary systems and LLE data at atmospheric pressure for the furfural + n-hexane binary system and furan + furfural + n-hexane ternary system. The authors have previously published VLE data concerning the furan + n-hexane binary system [8]. The models used in this work are the same as used in the previous paper [8].

A review of the literature shows that there are a few publications describing the modeling of binary mixtures similar in nature to those presented in this study with the GC-EoS with associating terms (Gonzalez Pietro et al., [9]). To the best of our knowledge there is no VLE data in the literature concerning the three binary systems or LLE data concerning the ternary system. The literature reveals that only Kolyuchkina et al. [10] has published two sets of

* Corresponding author. Mines ParisTech, PSL Research University, CTP - Centre of Thermodynamics of Processes, 35 Rue Saint Honoré, 77305, Fontainebleau, France.
E-mail address: christophe.coquelet@mines-paristech.fr (C. Coquelet).

LLE data concerning the furfural + n-hexane binary system. Moreover, it should be noted that literature contains some system measurements for components fairly similar to those measured in this study, for example, VLE data for 2,5 dimethyl furan + alcohols (ethanol, butanol, hexanol [11,12]), 2-methylfuran + furfuryl alcohol, isopropyl alcohol + furfuryl alcohol, furan + furfural [13], and furan + n-hexane [8,14]. There was also data in the literature for ternary systems such as alkanes + aromatics + furfural [15].

The new data are correlated using thermodynamic models, viz. the NRTL activity coefficient model [16]. The new data have also been used to extend the predictive thermodynamic model GC-PPC-SAFT. The extension of such models containing furfural and furan is challenging because of the polarity and the aromatic core of these molecules.

The first objective of this work is to present 3 new VLE, one LLE and one ternary data sets and their data treatments which are of high interest for design of separation units in biorefining. The second objective of this study is aimed to assess the predictive character of the thermodynamic model GC-PPC-SAFT.

1.1. Experimental work

1.1.1. Materials

Table 1 presents the characterisation of the chemicals used in this work. No further purification of the reagents was employed after gas chromatography analysis showed no significant impurities.

2. Experimental

2.1. Equipments

All experimental work were done at CTP laboratory.

2.1.1. The vapor–liquid equilibrium apparatus and procedure

The apparatus and experimental procedure are identical to that presented in a previous publication (Nala et al. [8]). Briefly, the ebulliometer is an all-glass recirculating still equipped with a Cottrell pump. The still allows for the circulation of both liquid and vapor phases. The operating principle of the ebulliometer used is similar to the Othmer dynamic VLE still [17]. Sufficient heat was supplied to the reboiler contents to ensure continuous and smooth boiling and a high circulation rate (judged by counting the condensate drop rate). The equipment is used for atmospheric pressure measurements and therefore no pressure control system is included. Experimental uncertainties for temperature and equilibrium phase compositions are $u(T, k = 2) = 0.01$ K and $u(z) = 0.007$, respectively.

2.1.2. The vapor-liquid-liquid equilibrium apparatus and procedure

The newly designed VLLE cell is equipped with stainless steel end-caps which enclose the cell completely, preventing any loss of material. The new design comprises of three sampling points allowing sampling of liquid phase I, liquid phase II, and the vapor phase. The sampling points are equipped with air-tight rubber

septa to prevent any loss of pressure within the cell. The temperature is measured using a type Pt100 Ω platinum probe which is inserted through a port at the top of the stainless steel cap. The port is designed to fit the Pt100 Ω with an adjustable bolt fitting which also eliminates the loss of pressure within the cell. The pressure inside the cell is regulated by the chemicals used. The glass used for this cell is capable of withstanding pressures of up to 4 bar. The pressure testing was undertaken by introducing nitrogen gas in the cell at room temperature. The recommended safe operating pressure is 3 bar, taking into account the effect of temperature on the glass. The capacity of the cell is up to 60 ml, which is adequate for continuous measurements and sampling without disturbance of equilibrium. A vacuum pump line is installed at the top of the cap. This is suitable during loading of the cell by inducing a small vacuum and allowing materials to flow into the cell. Air which may be present after loading of the cell is removed by inducing the vacuum. Figs. 1 and 2 shows a mechanical drawing of the VLLE cell and the schematic diagram of VLLE apparatus setup used for measurements, respectively.

The LLE cell used in this work was operated under atmospheric pressure, and thus only temperature was monitored. A standard probe Fluke–Hart Scientific 5628 was used for calibrating the platinum probe temperature sensor used in the LLE cell. The two probes were placed in an Ultra Kryomat[®] Lauda temperature controlled waterbath, which was allowed to reach stable thermal equilibrium. The accuracy of the equilibrium temperature is estimated to be ± 0.01 K. The cell was dismantled and thoroughly cleaned with ethanol and allowed to dry in the fumehood for at least 1 h. The cleaning procedure was employed prior to introducing a new system into the cell. The chemicals were introduced into the cell in adequate amounts such that a two phase mixture is formed and also to ensure that the interface is above the dense phase sampling point (i.e. the interface must be between the sampling points for the liquid phases). The cell was then immersed in the waterbath, the temperature set to a desired value and the magnetic stirrer switched on. The speed of stirrer motor had to be controlled during stirring to prevent emulsion of the liquid mixture. The two phase mixture was then stirred for at least 2 h, thereafter the motor was switched off and the mixture was allowed to reach equilibrium. In 30-min intervals, the liquid samples for each phase were withdrawn using a 5 μ L gas tight liquid syringe and injected into a Perichrom Gas Chromatograph. GC detectors were calibrated by injection of known quantities of each chemical using a GC syringe. Equilibrium is deemed to have been achieved when the composition in each phase remains constant, at which time the mixture temperature is also recorded. For each system, a new value of temperature is set and procedure above repeated to get the next equilibrium point. Experimental uncertainties for temperature and composition are $u(T, k = 2) = 0.01$ K and $u_{\max}(z) = 0.007$, respectively.

2.2. Systems studied and experimental data

Each of the binary systems studied are representative of mixtures which play a role in biorefinery processes. They are listed in

Table 1
Chemical characterisation.

Chemical	CAS number	Supplier purity (weight %)	Supplier	Method of analysis
n-Hexane	110-54-3	≥ 99	Acros	GC
Furan stabilized	110-00-9	≥ 99	Acros	GC
Furfural	98-01-1	≥ 99	Acros	GC
Ethanol	645-17-5	> 99.8	Fluka	GC
n-Octanol	111-87-5	≥ 99	Acros	GC

GC: Gas Chromatograph.

Download English Version:

<https://daneshyari.com/en/article/4768123>

Download Persian Version:

<https://daneshyari.com/article/4768123>

[Daneshyari.com](https://daneshyari.com)