Fluid Phase Equilibria 372 (2014) 85–99

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Isothermal vapor–liquid equilibrium and excess molar enthalpies of the binary mixtures furfural + methyl isobutyl ketone, +2-butanol and +2-methyl-2-butanol

Anna Zaitseva*, Helena Laavi, Juha-Pekka Pokki, Petri Uusi-Kyyny, Ville Alopaeus

Department of Biotechnology and Chemical Technology, School of Chemical Technology, Aalto University, Kemistintie 1, 02150 Espoo, Finland

ARTICLE INFO

Article history:
Received 8 November 2013
Received in revised form 28 March 2014
Accepted 31 March 2014
Available online 12 April 2014

Keywords:
Vapor–liquid equilibria
Excess enthalpy of mixing
Furfural
2-Butanol
2-Methyl-2-butanol
Methyl–isobutyl ketone
Experimental method
Headspace gas chromatography
COSMO-RS
UNIFAC

ABSTRACT

Isothermal vapor–liquid equilibria (VLE) of the binary mixture of furfural + methyl isobutyl ketone (MIBK), furfural + 2-butanol and furfural + 2-methyl-2-butanol were measured at 333, 346 and 353 K with three equipment: a static total pressure apparatus, a recirculation still apparatus and a gas chromatograph connected to a headspace sampler (HS–GC). Excess molar enthalpy (h^E) was measured for the three binary mixtures at 298.15 K by using a SETARAM C80 calorimeter equipped with a flow mixing cell. Gas chromatography–mass spectrometry was employed for the analysis of furfural impurities. A comprehensive consistency analysis was performed for the obtained data. The experimental data were correlated with the NRTL, UNIQUAC and Wilson activity coefficient models. The results were compared with the UNIFAC-Dortmund and COSMO-RS predictive models. All investigated mixtures show positive deviation from Raoult's law.

1. Introduction

Lignocellulosic biomass is one of the main sources of renewable energy. Several routes for biofuels production from biomass exist currently, but their feasibility and commercial potential are still under research and not fully explored. Optimization of processing costs is the bottleneck of most bio-refinery technologies [1]. Thus, commercialization of the processes has to incorporate efficient process design that requires reliable and accurate knowledge of the physico-chemical properties of the process compounds and their mixtures.

Furfural is one of the products of thermal and chemical hydrolysis of lignocellulosic biomass. It has been commercially produced from biomass since 1921. Furfural is used as a solvent, as an important chemical intermediate and as a resin precursor [2]. Rich furfural chemistry allows upgrading of furfural to various end products, such as biofuel components [3]. Such furfural derivatives as methylfuran or ethyltetrahydrofurfuryl ether have high energy density and excellent gasoline blending properties [4]. However, the technology of furfural production is not currently cost efficient and the produced gasoline additives are too expensive [4].

Development of efficient furfural recovery and optimal conditions for the furfural upgrading requires deep understanding of complex furfural chemistry and also basic knowledge of thermodynamics and equilibrium properties of the processed chemicals. The availability of thermodynamic property data for furfural and its derivatives is limited in the literature [5,6], whereas the number of compounds observed at furfural production and within further upgrading of furfural are numerous. In the absence of the thermodynamic data needed for the furfural process development, predictive models, such as UNIFAC, can be used. However, group contribution predictive models often show deviations in predictions for the smallest molecules in the homological series. That is why these small compounds are often treated as separate groups, e.g. methanol and furfural in the UNIFAC model. In this work, we have tested the predictive capabilities of two models (the UNIFAC-Dortmund and the COSMO-RS) with respect to new experimental data for furfural + 2-butanol, furfural + 2-methyl-2-butanol (*tert*-pentanol) and furfural + methyl isobutyl ketone (MIBK) mixtures.

---

* Corresponding author. Tel.: +358 50 361 5082; fax: +358 9 4702 2694.
E-mail addresses: anna.zaytseva@aalto.fi, zaytseva.anna@gmail.com (A. Zaitseva).

http://dx.doi.org/10.1016/j.fluid.2014.03.033
0378-3812/© 2014 Elsevier B.V. All rights reserved.

List of symbols

A, B, C, D, E	parameters of the pure component vapor pressure correlation
A_i	integral of the natural logarithm of activity coefficient ratio
$a_{ij}{}^0$, $a_{ij}{}^1$	coefficients of equation for binary interaction parameters of a model
a_n, i = 1, 4	nth parameter of the Legendre polynomial
F_i	consistency test coefficients
G^E	the excess Gibbs energy
h^E	molar excess enthalpy (J mol^{-1})
M	molality (mol kg^{-1})
N	number of measurements
n_i	moles of components i injected in static apparatus equilibrium cell
P	pressure
$P_i{}^0$	vapor pressure of pure compound i at system temperature
P_i	vapor pressure of pure component i
Q	quality factor
Q_i	area parameter of components i in the UNIQUAC model
R_i	volume parameter of components i in the UNIQUAC model
T	temperature (K)
$V_i{}^L$	liquid molar volume of the component i
V_t	volume of the static apparatus cell
x_i	mole fraction of the component i in the liquid phase
y_i	mole fraction of the component i in the vapor phase
z_i	total molar fraction of component i

Greek letters

α_{ij}, α_{ji}	non-randomness constant for binary ij interactions in NRTL model
Δ	difference
$\phi_i{}^0$	fugacity coefficient of pure component i at the mixture temperature and vapor pressure of pure component i
ϕ_i	fugacity coefficient of component i at the system temperature and pressure
γ_i	activity coefficient of component i
ρ	density (kg m^{-3})
ω_{SRK}	acentric factor for use with the SRK equation of state

Subscripts

exp	experimental
C	critical
calc	calculated
i, j	component of a mixture
leg	from Legendre polynomial
lit	literature
max	maximum
min	minimum

The new measured data have been obtained with different experimental techniques that provide a reliable source of information for furfural containing mixtures.

For the binary mixture of furfural + 2-butanol some excess enthalpy measurements (h^E) were reported by Naorem and Suri at 308.15 K [7]. Unfortunately no vapor liquid equilibrium (VLE) data were found for this mixture. For the furfural + MIBK mixture the VLE data were published by Hauschild et al. [8] at 368.09 K and 383.09 K, but no h^E data are available in the literature. For the furfural + *tert*-pentanol mixture neither VLE nor h^E data were found in the literature [5].

2. Materials and methods

2.1. Materials

The chemicals supplied by Sigma Aldrich were distilled under vacuum before the experiments. The purity of the distilled chemicals was always above 99.7 mass% in accordance with gas chromatography (GC) analysis, as presented in Table 1. The distilled chemicals were stored in flasks connected to drying tubes filled with molecular sieves. Water content was measured before the experiments by Karl–Fischer titration (Mettler-Toledo DL38, Hydra point solvent G and Hydra point titrant 2 mg H_2O ml^{-1}).

For the static total pressure apparatus measurements all chemicals were degassed under vacuum inside an ice containing ultrasound bath for at least 1 h as described in [9]. For the measurements with the recirculation still, degassing of the components significantly reduced the rate of furfural oxidation, which was observed during the measurements related to furfural + *tert*-pentanol binary mixture.

Furfural has to be purified before experiments because it undergoes resinification and oxidation reactions during storage. Furfural was distilled into three fractions. The middle fraction was used in the measurement. A similar procedure has been described in Mertes and Colburn [11]. The furfural was stored under nitrogen and used within 3–4 days after the distillation. The measurements were carried out at minimum contact of the distilled furfural with water and oxygen. At the beginning of all measurements, the furfural was colorless but it was slightly yellowish in the end of the measurements. The color indicates the presence of very small amount of furan-based resins (<10^{-5} M) [3].

The concentration of furfural reaction products in the measurements was checked by GC analysis of vapor and liquid phases. One mass percent of impurity, detectable by GC analysis, was found at the end of the recirculation still measurements in the liquid phase of the furfural + 2-butanol mixture (i.e. after the mixture has been boiled for 2–3 h), whereas only 0.2 mass% of impurities were found in the gas samples. Less than 0.5 mass% of impurities was found in the liquid phase after measurements with the static apparatus. The direct GC analysis was made for all mixtures. The potential presence of heavy impurities was checked once using silylation of the mixture prior to the analysis as described in [12]. No additional impurities were found in comparison with the GC analysis of the same mixture without silylation.

The main impurity is known to be of non-acidic nature [13,14]. The yellowish color shows the presence of furan-based resins containing conjugated double bonds [15] and the resinification process is relatively slow even above 471 K [14]. Accordingly, we did not observe significant change of color during several hours of experiments as the temperature in our measurements was lower than 471 K. The purity of the mixtures was checked by GC analyses. The furfural based resins are too heavy to be analyzed by GC, but other impurities were observed. Following the GC procedure described in [16] we confirmed the presence of 5-methyl-furfural and 2-acetyl-furan as the main impurities in our samples. The impurities are common for commercially produced furfural where they originate from biomaterial used for furfural production [3]. Contrary to the report by Hauschild [8], the presence of the 2-furoic acid was not confirmed by either GC–MS or GC analysis. Titration of the water extracts of the furfural mixtures with sodium hydroxide was used for the determination of the overall mixture acid content [11,14]; no substantial amount of acids was found, i.e. the acid content was less than 0.06 mol%. The heated binary mixtures containing