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Solubility of carbon monoxide in bio-oil compounds

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ABSTRACT

The solubility of carbon monoxide is measured in four different bio-oil compounds (furan, diacetyl, 2-methylfuran, and *trans*-crotonaldehyde) at temperatures (273.15, 283.15, 298.15, and 323.15 K) and pressures up to 8 MPa using a static-analytical VLE measurement method. The equipment was validated by measuring the solubility of CO_2 in methanol at 298.15 K and pressures ($P = 2.9–5.7$ MPa). The results were compared with the abundantly available literature values. PC-SAFT, Polar PC-SAFT (PPC-SAFT), and Cubic (SRK, PR) EoS, part of commercial process simulator Aspen Plus V. 8.6, are used here for modelling purpose. The pure component parameters needed for PC-SAFT and PPC-SAFT EoS models, are regressed using the experimental liquid density and vapour pressure data of the pure components. It was observed that furan, 2-methylfuran and diacetyl, having weak dipole moments ($\mu < 1.0$ D), could be modelled reasonably well without the addition of polar contribution using conventional PC-SAFT, while it is recommended to use PPC-SAFT for the description of a polar compound like *trans*-crotonaldehyde ($\mu \sim 3.67$ D).

It was observed that SRK and PR EoS have similar predictive ability in comparison to PC-SAFT for a mixture of CO with weakly polar compounds in this study. A comparison between the performances of EoS models was made in two ways: first by setting the binary interaction parameter k_{ij} to zero, and second by adjusting a temperature-dependent binary interaction parameter (k_{ij}). All the models perform with comparable accuracy with adjusted binary interaction parameters. However, due to the large differences between the chemical and physical properties of the compounds in this study, it is challenging to make a general statement on which is the best model.

1. Introduction

Thermodynamic data concerning bio-refining processes are both important and scarce. These data, especially gas solubilities in bio-based compounds, generate considerable interest not only in expanding academic research but also in designing separation processes for industrial use. However, despite the importance of such data, not much thermodynamic research is dedicated to acquire them.

In the context of bio-based fuels, "pyrolysis oil" or "bio-oil" is an important candidate. It is a thermal decomposition product of lingo-cellulosic biomass and finds particular importance in regions where there is an abundance of biomass. Bio-oil is produced from fast pyrolysis, a process in which biomass is pyrolyzed for a short time (2–3 s) at high temperatures (600–800 °C), resulting in vapors that are condensed afterwards. The condensed vapors forms thick dark brownish liquid termed as bio-oil. For detailed information on pyrolysis technologies, readers are directed to some excellent reviews available in the literature [1–3].

Bio-oil represents a complex mixture of a variety of organic compounds consisting of several different functional groups including aldehydes, alcohols, acids, ketones, and furans, to mention only a few. The major constituents of bio-oil besides these compounds are water and sugars. The presence of water (in the mixture) is detrimental because it reduces the heating value of bio-oil, rendering it less appropriate for direct use as fuel. Moreover, the oxygenated compounds present in bio-oil also deteriorates the heating value [4]. Therefore, in order to increase the heating value of bio-oil to make it into a viable fuel, it is necessary to remove water and oxygenated compounds.

The commonly used industrial processes for removing oxygen are Hydrodeoxygenation (HDO) and cracking. Cracking involves the treatment of bio-oil under high pressures over special catalysts [5]. HDO and cracking are accompanied by several complex reactions including decarbonylation, decarboxylation, hydrocracking,

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Nomenclature

a	residual Helmholtz energy (J/mol)
m	number of segments in a chain
P	pressure (MPa)
R	universal gas constant (cm^3 MPa K^{-1} mol^{-1})
T	temperature (K)
x	mole fraction
Xp	segment dipolar fraction

Subscripts and superscripts

assoc	association term
chain	chain term
disp	dispersion energy
e	estimated value, see Eq. (2)
i,j	component indices
res	residual
seg	segment

Greek letters

ε	segment energy (K)
κ	association volume
μ	dipole moment (D)
ρ	molar density (mol/dm3)
σ	segment diameter (Å)
σ_u	standard deviation on u

Abbreviations

AAD	absolute average deviation
CAS	chemical abstract service
CALC	calculated
CK-SAFT	Chen-Kreglewski SAFT
EoS	equation of state
EXP	experimental
GC-EOS	group contribution equation of state
HDO	hydrodeoxygenation
LJ-SAFT	Lennard Jones SAFT
NIST	National Institute of Standards and Technology
PC-SAFT	perturbed chain statistically associating fluid theory
PCP-SAFT	polar SAFT version of Gross and Vrabec
PPC-SAFT	Polar PC-SAFT
PR	Peng Robinson
ROLSI™	rapid on line sampler injector
SAFT-VR	statistical associating fluid theory for attractive potentials of variable range
SRK	Soave-Redlich-Kwong
VLE	vapour-liquid equilibrium

and polymerization. Due to the complexities of these reactions the process design of such separation processes are usually impaired by the lack of experimental thermodynamic data.

Phase equilibrium data are particularly important for the design and development of separation processes. Moreover, in order to be able to have a rigorous process model, which is able to predict the process behaviour at various process conditions, reliable and accurate thermodynamic data is needed. Experimental VLE, especially gas solubility data are needed in many applications concerning bio-fuels.

Gas solubility data are needed for example in designing HDO processes where gases are released as a result of different reactions discussed earlier [6]. Such data are also wanted in the bio-oil gasification process where bio-oil is gasified into CO, CO_2, CH_4, and H_2O. These gases are further treated via Fischer-Tropsch syntheses to obtain value added products such as methanol, dimethyl ether, and many others [7]. Furthermore, the phase equilibrium data are also needed in the optimization of the storage conditions for bio-oil. This is relevant because bio-oil is a non-equilibrium product and its composition changes during storage. This compositional change is known as ageing and is attributed to various phenomenon, including polymerization of oil fragments, decomposition of unstable species, phase separation and evolution of gases such as CO and CO_2.

Despite the necessity of such experimental data, insignificant attention has been paid in acquiring the same. It was revealed after a critical assessment of the existing open literature that gas solubility data in bio-oil compounds are present only for most common compounds such as low molecular weight alcohols, aldehydes, acids, ketones and phenols. The gas solubility data in most relevant bio-fuel compounds such as furans are still missing and must be obtained for reliable process modeling.

Thermodynamic modelling of bio-oil compounds is also challenging. One important difficulty in modelling these compounds emerge from the presence of oxygen in these compounds. Oxygenated compounds induce association and solvation effects and thus are not easy to model [4]. Rigorous thermodynamic models are required for the accurate representation of pure compounds and mixtures. However, in spite of the modelling complexities these compounds present, there has been few attempts to model such mixtures. One important piece of work is by Feng et al. [8], which proposed a method for the optimization of SAFT pure component parameters based on the critical properties, density and boiling points of the compounds. They further validated their method by applying it to predict the solubility of sugars (found in bio-oil) in mixed solvents and water.

A few researchers have applied SAFT EoS [9–11] while some have used an EoS in combination with group contribution methods (GC-EoS) [12,13] for bio-oil mixtures. Nguyenhuynh et al. [14] carried out a successful attempt in modelling polar and oxygenated systems utilizing polar GC-SAFT. A more recent study encompassing the phase equilibria of bio-based oxygenated compounds was made by Soria et al. [15] in which a group contribution method with association (GCA-EoS) was used successfully.

The aim of this paper is the investigation of phase equilibria involving bio-oil compounds and CO at different pressures and temperatures with the goal of enhancing the development of a working model capable of accurately predicting the phase behaviour for these complex systems. The validation of the measurements from the equipment was carried out using a reference system of CO_2–methanol.

2. Experimental

2.1. Materials

Information on the purities and suppliers of each chemical is given in Table 1. The chemicals were used without any further purification. The molecular structures of the compounds are shown in Fig. 1.

2.2. Apparatus

The method used in this study for the measurement of vapour-liquid equilibria is based on the static-analytical technique, which allows withdrawal of the sample from the liquid and vapour phases at equilibrium and their online analyses through gas chromatography [17]. The static methods for VLE measurements