Measurement of activity coefficient at infinite dilution for some bio-oil components in water and mass transfer study of bubbles in the dilutor

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A B S T R A C T

Activity coefficients at infinite dilution (γ^∞) values are of great importance when designing separation processes like distillation, liquid–liquid extraction and gas stripping. In this study the γ^∞ values were determined for four compounds in water that are present in bio-oil. Henry's law constants (H_{12}), Partial molar excess enthalpies at infinite dilution $\left(\overline{H}_i^{E,\infty}\right)$ and air–water partition coefficients (K_{aw}) are also reported. The measurements were performed using inert gas stripping equipment (dilutor) in the 298–340 K temperature range. Mass transfer study was also performed to investigate the equilibrium between the solution and the gas leaving the cell.

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1. Introduction

Depletion of conventional fossil fuels has largely affected the scientific research in energy sector in the previous few decades. The increase in the use of more sustainable and renewable energy is imminent. Bio-fuels have been anticipated to be the next refuge for the energy crisis. There are conversion processes that can be utilized to produce liquid fuels from different types of bio-mass which make it certainly important to acquire accurate experimental data for designing and optimizing such industrial processes. The phase equilibrium for multicomponent reaction mixtures can be represented with advanced chemical thermodynamic models but the accuracy of these models depends largely on the accuracy of the experimental data used to fit their adjustable parameters. Fast pyrolysis oil/bio-oil is one strong candidate in the list of potential bio-fuels [1]. It is a complex mixture arising from the fast pyrolysis of bio-mass. The composition of bio-oil containing large variety of

polar and non-polar compounds largely depends on the bio-mass source [2]. The number of individual compounds in bio-oil is high although the quantity of each individual component is low. A major portion of the pyrolysis oil in addition to solids is water (15–35% by mass) [1] which makes the overall production and modeling process cumbersome. The potential use of bio-oil is adversely affected by the presence of water. It reduces the higher heating value (HHV) of the bio-oil to 19 MJ/Kg compared to 44 MJ/Kg for mineral oil [2]. HHV is also affected by the oxygen content. Thermal separation processes are not a suitable option for bio-oil because excessive heating of bio based compounds may result in polymeric products. Therefore, separation of the valuable compounds in the production of fuel from bio-oil becomes intricate.

Despite the high importance of bio-oil in the near future, not enough attention has been paid to the investigation of its thermodynamic properties. Phase equilibrium properties are the backbone of any chemical separation process and are needed for process modeling. One very important thermodynamic property needed in designing and optimization of separation processes is the activity coefficient at infinite dilution (γ^∞). It is helpful in deriving important thermodynamic parameters such as Henry's law constants (H_{12}), excess enthalpies at infinite dilution $\left(\overline{H}_i^{E,\infty}\right)$, air–water partition coefficients (K_{aw}), G^E-model parameters and also for predicting azeotropes in mixtures [3]. The most challenging stage in any separation process occurs when a product of high purity is needed. This is the region where the unwanted compound

Nomenclature

List of Symbols

a	Slope, 1/s
C	Solute concentration, mol/m^3
D_b	Diameter of bubble, m
$D_{i,j}$	Diffusion coefficient of solute in gas mixture, m^2/s
F_{in}	Corrected flowrate of the inert gas, cm^3/min
F_{meas}	Measured flowrate, cm^3/min
Fo	Fourier number
G^E	Gibbs energy
h	Liquid level, m
H_{12}	Henry's law constant, kPa
$\left(\overline{H}_i^{E,\infty}\right)$	Partial molar excess enthalpy at infinite dilution, J/mol
k	Mass transfer coefficient, m/s
K_{aw}	Air–water partition coefficient
M	Molar mass of component, g/mol
n	Number of moles, mol
P	pressure, Pa
Pe	Peclet number ($=D_b \cdot v_b/D_{i,j}$)
R	Universal gas constant, J/molK
Re	Reynolds number
Sh	Sherwood number
$\overline{Sh}$	Time-averaged Sherwood number
T	Temperature, K
τ	Mass transfer approach
V	Volume, m
v_b	Bubble rise velocity, m/s
x	Liquid mole fraction
y	Vapor mole fraction

Superscripts

i	Ideal gas
l	Liquid
Sat	Saturated
app	Approach
s	Solute

Subscripts

a	Air
cell	Dilutor cell
Fm	Flow meter
g	Gas phase
i	Component "i"
Slv	Solvent
Solu	Solute
w	Water
vap	Vapor

Greek letters

∞	Infinite dilution
ϕ	Fugacity coefficient
γ	Activity coefficient
ρ	Density, kg/m^3
μ	Dynamic viscosity, Pa s
ω	Acentric factor
$v_{i,j}$	Group contribution parameter for atoms, groups and structural features

is present in the mixture in a trace quantity but it is the region where in most cases maximum departure from ideality is observed. Thus, it becomes necessary to have accurate experimental data to avoid unwanted expenditures in separation processes.

In this study the activity coefficients at infinite dilution (γ^∞), Henry's law constants, air–water partition coefficients and partial molar excess enthalpy values are reported for four bio-oil components in water over a temperature range from 298 to 340 K for which the data are either missing or are not reliable enough. The same properties are also reported for a reference compound (1-butanol). The experiments were carried out using inert gas stripping (IGS) equipment, the details of which are presented in the Section 2.2. Detailed mass transfer study was also carried out to validate the equilibrium between the solution and gas leaving the cell.

2. Experimental

2.1. Materials

The list of solutes, with corresponding purities and suppliers is presented in Table 1. The solutes were used without further purification. Distilled water was used in all the experiments.

2.2. Apparatus and procedure

The apparatus is composed of three major sections including:

1. Cell assembly.
2. Gas analysis using FID.
3. Data logging.

These sections are shown in Fig 1 .

The inert gas stripping equipment as presented in Fig. 1, similar to the design of Richon [4] and Afzal [5], consists of two similar cylindrical glass cells ($19.3 \, cm^3$), one acting as a presaturator and the other as a dilutor. It is important to use the presaturator cell in conjunction with the dilutor cell to keep the number of moles of solvent in the dilutor cell constant. In the pre-experimental procedure the dilute solutions (mole fraction $< 10^{-3}$) were prepared. The solution was mixed overnight in case of hydrophobic compounds but for readily soluble compounds few minutes were sufficient for efficient mixing. The presaturator cell was filled with the solvent, water in this case and the dilutor cell with the dilute solution prepared beforehand. The dilutor cell was weighed before and after each experiment to ensure the fixed number of moles of

Table 1
Materials with their purities and vapor pressures at 298.15 K from DIPPR [18].

Compound	CAS number	Supplier	Purity[a]	Vapor pressure (Pa) at 298.15 K error $< 3\%$
1-Butanol	71-36-3	Sigma–Aldrich	99.9 wt%	901
Valeraldehyde	110-62-3	SAFC	97 wt%	4940
Furan	110-00-9	Aldrich	99 wt%	80032
Acrolein	107-02-8	Fluka	99 wt%	36538
Crotonaldehyde	123-73-9	Fluka	99 wt%	4698
Water	7732-18-5	–		3142
Helium	7440-59-7	Aga Oy	99.996 V%	
Nitrogen	7727-37-9	Aga Oy	99.999 V%	

[a] Purity information according to the supplier.