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Need for Vapour-Liquid Equilibrium Data Generation of Systems Involving Green Solvents

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ABSTRACT
Much has been said and written over the years regarding green chemistry concept and use of green solvents. The green solvents can potentially replace the traditional or classical solvents in order to reduce the environment footprint or their harmful impact on human being and/or environment. Vapour-liquid equilibrium data is indispensable for the design of distillation columns for separation processes which account for a large percentage of total costs in a typical chemical plant. Though extensive approach has been made for the replacement of traditional solvents, but not enough consideration been given for vapour-liquid equilibrium data, required for designing separation processes in case of replacement with green solvents. So this paper aims at encouraging vapour-liquid equilibrium data generation for design of efficient separation for binary systems involving ethereal green solvents such as cyclopentyl methyl ether (CPME) and 2-methyl tetrahydrofuran (2-MeTHF). A brief review and outline of procedure for generating vapour-liquid equilibrium data is presented here.
Keywords - Green solvents, CPME, 2-MeTHF, vapour-liquid equilibrium

I.   INTRODUCTION
1.1 Green Chemistry
Twelve principles of green chemistry were developed by P. T. Anastas and J. C. Warner in 1991. The focus of green chemistry is to reduce the environment pollution by various means such as reduction of hazardous chemical synthesis, use of renewable materials, use of safer chemicals, solvents and auxiliaries, design for increased energy efficiency, increased safety, etc. The green chemistry is aimed at reducing chemical related hazardous impact on human health and environment by preventing contamination of environment through a set of instructions or principles. These principles are set to lessen utilization and production of hazardous chemicals at various stages of design, synthesis and application of chemical products [1, 2].

1.2 Green Solvents
Solvents constitute a large part of chemical process industries and hence a major contributor in the environmental performance of processes [3]. Petroleum based organic solvents are used in organic chemical industries for purification of various chemicals. Despite huge number of useful solvents available for routine organic reactions, most of the commercially available solvents are not recommended to use for various reasons such as volatility, flammability, hazardousness, etc [4]. So it is the need of time to develop and promote use of

environment friendly and highly tuneable solvents which can be useful as replacements to traditional solvents. The solvents with the least toxicity to human health and environment are called green solvents. Cyclopentyl methyl ether (CPME) and 2-methyl tetrahydrofuran (2-MeTHF) are found to be promising ethereal green solvents that are fairly new to the market, and whose environmental, health, and safety (EHS) characteristics are comparatively more favourable to other ethers [5].

II.   LITERATURE SURVEY
2.1 Cyclopentyl methyl ether
CPME is commercially available from Zeon Corporation since November 2005 and it is approved by the Toxic Substances Control Act (TSCA) and the European List of Notified Chemical Substances (ELINCS) [4]. CPME becomes a valid alternative to other ether solvents such as dioxane, tetrahydrofuran, diethyl ether, methyl *tert*-butyl ether and 1, 2-dimethoxyethane with the properties such as low formation of peroxides, high boiling point and better stability in acidic and basic conditions. It is suitable for organometallic reactions due to its hydrophobic nature [1]. CPME has the lowest evaporation energy, and thus, facile recovery through distillation can be attained because of high boiling point which is similar to that of toluene. CPME can maintain anhydrous conditions without any particular precautions which makes it more preferable solvent for Grignard-type reactions [4]. S.

Kobayashi, H. Kuroda, et al. demonstrated that CPME is an effective solvent for radical additions and reductions [7]. CPME has also been proven as a suitable solvent in various catalytic reactions. It has been already used for the production of pharmaceuticals, aroma chemicals, electronic materials and so on as a process solvent, and has been already registered or listed under the corresponding legislation for new chemical substances of USA, EU, Japan, Korea, Taiwan and China and it is commercially available in these countries and others. CPME has relatively low acute toxicity with negative skin sensitization (LLNA) and negative mutagenicity, but shows moderate to severe irritation to skin and eye [6]. 8 out of 12 widely recognized principles of green chemistry set by Anastas and Warner are satisfied by CPME. Innovations such as one-pot synthesis and telescoping become feasible by the virtue of unique properties of CPME [8]. By the utilization of 4N-HCl solution in CPME as a solvent, the classical Pinner reaction has been improved and by simple filtration direct isolation of the product was made possible [9]. The biphasic system H_2O/CPME using H_2SO_4 as catalyst allows the selective conversion of lignocellulosic pentoses into furfural, improving the overall furfural yield up to values near to 100% [10]. CPME has seven notable physical properties that can be summarized as follows: (i) low peroxide formation, (ii) high hydrophobicity, (iii) relative stability under acidic and basic conditions, (iv) high boiling point and low melting point, (v) low heat of vaporization, (vi) narrow explosion area, (vii) low solubility of salts [6].

2.2 2-methyl tetrahydrofuran

2-MeTHF can often replace tetrahydrofuran and diethylether in organometallic reactions; the reaction yields are often superior, the stability of solvent to acid and base is increased and the work-up is simplified [11]. The additional advantage with 2-MeTHF is that it is derived from renewable sources. In Grignard and organometallic reactions also, it gives superior efficiency and reactivity. It is an aprotic solvent and not miscible with water which makes it suitable for reactions in biphasic environments, such as amidations and nucleophilic substitutions [1]. It is derived from 2-furaldehyde (also known as furfural), which is produced from naturally occurring pentoses in agricultural waste like corncobs or bagasse (sugar cane), in a two-step hydrogenation process via 2-methylfuran [11]. It is also used as a solvent for other organometallic reagents as well as for electrolytic solutions in lithium batteries [12]. Some physical properties of CPME and 2-MeTHF have been listed in the Table 1.

Table 1. Physical Properties CPME and 2-MeTHF

Properties	CPME	2-MeTHF
MW	100.16	86.14
ρ at 293.15K	860	850
T_b	379.15	353.15
T_m	< 133.15	137.15
T_f	272.15	262.15
λ_v at T_b	289.74	375.57
μ	0.55 (293.15K)	0.6 (298.15K)
n_D at 293.15K	1.4189	1.406

2.3 Identification of Potential Process Systems with Green Solvents

The approach of this work is the experimental determination of vapour-liquid equilibria (VLE) data of CPME and 2-MeTHF in different binary systems. Therefore it is necessary to explore potential process systems in which hazardous solvents can be replaced by green solvents. To identify these systems, various applications of CPME and 2-MeTHF should be studied thoroughly and also rigorous study can be made of the systems involving targeted solvents for replacements. The identified process systems then should be chosen for experimental work.

III. EXPERIMENTAL DETERMINATION OF VLE DATA

The task of measurement, modelling, and computation of multicomponent phase equilibria has been one of the most compelling problems in chemical engineering. The variety of experimental and computational methods has been developed by chemical engineers and physical chemists for the measurement and thermodynamic interpretation of VLE probably surpasses that of all other areas of chemical engineering research [13]. For the synthesis, design, and optimization of distillation processes and selection of solvents, a reliable knowledge of the vapour-liquid equilibrium behaviour is necessary [14]. Very limited work has been accounted on VLE study of binary mixtures involving green solvents such as CPME and 2-Me-THF till now. Group contribution methods provide an alternative to experimental measurements of VLE data but the equations used for data prediction in these methods have some limitations. Thus, experimental determination of VLE data of these systems becomes necessary.

3.1 Review & Selection of Equipments

Hundreds of static, recirculating, and other types of equipment for VLE measurement have been proposed, tested, and published in the open literature. In this paper, experimental procedure for the determination of vapour-liquid equilibrium at normal pressure has been presented. The quest for

new measurement procedures dates back to 1913, when Jamaguchi [1913] and subsequently Sameshima [1918] developed the first recirculating stills for low-pressure VLE measurement. There are several reviews of experimental procedures and equipment in the literature for both high and low pressure VLE measurement, such as those of Hala et al. [1967], Malanowski [1982], Abbott [1986], and Raal and Muhlbauer [1994]. There are many hundreds of publications have been done on low pressure vapour liquid equilibrium measurement alone [13]. Important contribution in this field are given by the following: Carveth [1899], Inglis [1906], Rosanoff et al. [1909], Sameshima [1918], Cottrell [1919], Washburn [1919], Swietoslawski and Romer [1924], Lee [1931], Chilton [1935], Scatchard et al. [1938], Jones, Schoenborn and Colburn [1943], Gillespie [1946], Marshall and Pigford [1947], Kretchmer et al. [1948], Brown and Ewald [1950], Brown [1952], Ellis [1952], Rose and Williams [1955], Heertjes [1960], Dvorak and Boublik [1963], Yerazunis et al. [1964], Leslie and Kuehner [1968], Raal et al. [1972], Rogalski et al. [1977, 1980], Kassman and Knapp [1980], Malanowski [1982], and Raal and Muhlbauer [1998].

Raal modification of the Yerazunis et al. [1964] dynamic still was designed by Raal and Mulhbauer [1998] which is believed to have eliminated all major sources of error and it is recommended here to use for VLE measurements at atmospheric pressure. The VLE apparatus constructed with some modifications in this design by a scientific company in Mumbai has been acquired for the experimentation. The schematic diagram of the VLE apparatus is given in Fig. 1.
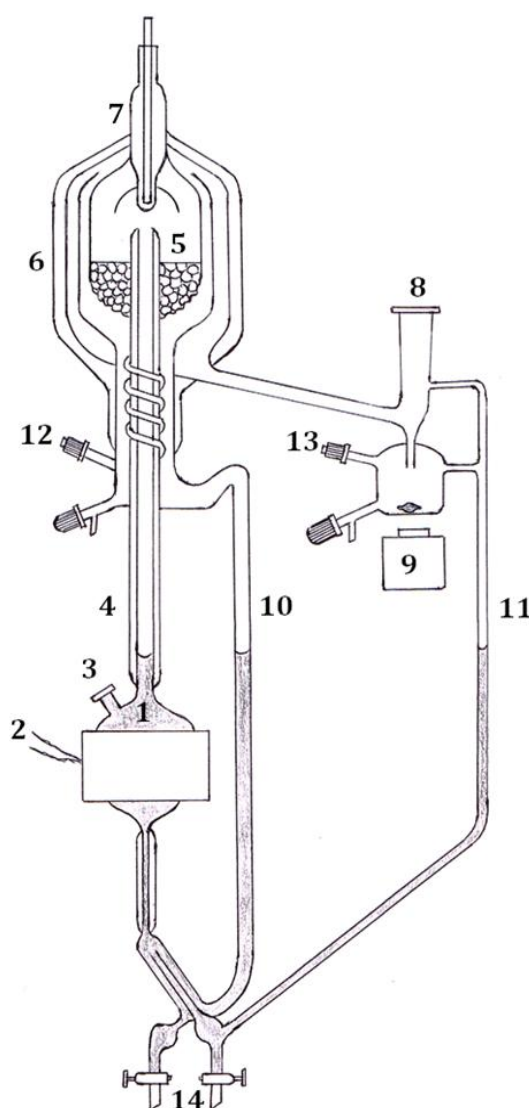

Fig. 1. Experimental VLE apparatus

(1) Boiling chamber (2) Heater cartridge (3) Feed Point (4) Vacuum jacketed Cottrell pump (5) Packed equilibrium chamber (6) Vacuum jacket for the equilibrium chamber (7) Thermo well (8) Condenser (9) Magnetic Stirrer (10) Liquid return line (11) Vapour return line (12) Liquid Sample point (13) Vapour sample point (14) Drain valves

The detailed description of the apparatus with its salient features is given in the book phase equilibria measurement and computation by J. D. Raal and A. L. Muhlbauer [13]. However, requirement of slightly higher volume of mixture for boiling chamber is the disadvantage of this apparatus because it increases the overall cost of experimentation particularly when system involves costly compounds.

3.2 Experimental Procedure

The purities of all chemicals can be determined by gas chromatography or by measuring refractive indices for pure compounds and comparing them

with those reported in the literature or by UV-Spectrophotometry. The equilibrium temperature and compositions of the coexisting vapour and liquid phases will be measured after establishment of the equilibrium which may take approximately 30-45 minutes. The accurate composition measurement of liquid and vapour phases is an important part of the VLE experimentation which can be achieved by a gas chromatograph or a refractometer or a UV-spectrophotometer whichever is suitable for the system under experimentation.

IV. THERMODYNAMIC CONSISTENCY TEST

Thermodynamic consistency test is carried out in order to verify the reliability of the experimental data. It is based on one form or another of the Gibbs-Duhem equation. The Gibbs-Duhem equation can be handled in a number of ways, leading to a variety of consistency tests that can be broadly classified as an area or integral test, point-to-point tests, an L-W test, an infinite dilution test, and a differential test [16]. The area or integral test was proposed by Herington [1947] and Redlich and Kister [1948]. The test is relatively simple and provides a necessary but not sufficient condition for the evaluation of thermodynamic consistency. A much better thermodynamic consistency check, pioneered by Van Ness et al. [1973] and developed with considerable rigor by Van Ness and Abbott [1982], is to generate values of one of the variables – typically pressure or vapour composition – based on measured data for the other remaining variables. This point-to-point test was developed as an improvement to the area test but it penalizes the experimental data when the model is not capable of fitting them. Thus experimental error propagates differently in each test so it is advisable not to rely on one consistency test alone but to use other tests also as an overall check of the validity of the data.

V. VLE DATA CORRELATION AND REGRESSION

The process, by which the model with the best representation of VLE data is determined, is named data reduction. The methods of VLE data regression involve determining the most suitable and accurate method of expressing measured data and calculating variables that were not directly measured. There are three general approaches to VLE data regression. These include: i) The direct equation of state method (phi-phi), ii) The combined method (gamma-phi), and iii) The model-independent methods

In the direct method of VLE data reduction, both the liquid and vapour phase non-idealities are described by fugacity coefficients. The combined method of VLE reduction employs activity coefficients to account for the liquid phase non-ideality and fugacity coefficients to account for vapour phase non-ideality. Several model independent approaches for VLE regression have been proposed in the literature. These methods can be classified as direct, where the relative volatility or vapour composition is determined initially, or indirect, where the excess Gibbs energy or activity coefficient is determined initially. In this paper, Gamma-Phi approach is recommended for data reduction because activity coefficient models give better accuracy for liquid-phase than equation of state models. The activity coefficients are evaluated using the excess Gibbs energy models and the fugacity coefficients by using the equation of state. According to Van Ness and Abbott [1998], gamma-phi method is suitable for low pressure measurements and a simple equation of state such as the virial equation of state is sufficient for calculations. The excess Gibbs energy models such as Van Laar, Wilson, NRTL, UNIQUAC, etc. can be used to correlate the experimental data to take into account the non-ideality in the liquid phase.

The estimation of parameters in thermodynamics models is an important requirement and a common task in many areas of chemical engineering because these models form basis for synthesis, design, optimization and control of process system. In the particular case of process separation, thermodynamic models play a major role with respect to energy requirements and equipment sizing.

VI. CONCLUSION

This work will be useful to generate VLE for the green solvents such as CPME and 2-MeTHF in different binary systems. Experiments can also be carried out with other green solvents in different binary systems. This kind of experimental work may lead to massive data generation which can contribute significantly to data bank and promote research activities that depend on these data. The accurate VLE data based on systematic experiments can generate accurate model which provides experimental basis not only for designing and optimizing the separation processes but also for effectively reducing the cost. This work can provide platform for substitution for hazardous solvents by green solvents with better environment, health and safety (EHS) properties such as less toxicity, flammability, ozone depletion potential, increased safety, low peroxide formation, reduced environmental footprint, solvent production from renewable sources, etc. This paper will be useful for researchers who are engaged in promoting environment friendly manufacturing processes that minimize toxicity and hazard.

NOTATION

MW – Molecular Weight, g/mol;
ρ – Density, Kg/m^3;
T – Temperature, K;
μ – Viscosity, cP;
n_D – Refractive index;
λ_v – Vaporization Energy, kJ/kg;

SUBSCRIPTS AND SUPERSCRIPTS

b – Boiling point;
m – Melting point;
f – Flash point;

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