Isothermal vapor–liquid equilibria for the binary system of dimethyl ether (DME) + methyl iodide (CH$_3$I)

Hyun Cho, Ji Eun Kim, Jong Sung Lim *

Department of Chemical and Biomolecular Engineering, Sogang University, C.P.O. Box 1142, Seoul 100-611, South Korea

ABSTRACT

Isothermal vapor–liquid equilibrium data for the binary system of dimethyl ether (DME) + methyl iodide (CH$_3$I) were taken with a circulation-type equilibrium apparatus in which both vapor and liquid phases were recirculated still at five temperatures: 283.15, 293.15, 303.15, 313.15 and 323.15 K. This binary mixture system showed negative deviation from the Raoult's law and no azeotrope observance. The equilibrium compositions of vapor and liquid phases and pressures were reported at each temperature. The measured data were correlated with the Peng–Robinson equation of state(PR-EoS) using the Wong–Sandler mixing rules combined with the NRTL excess Gibbs free energy model and Peng–Robinson equation of state (PR-EoS) using the Universal mixing rule (UMR) as well as with the UNIQUAC model. The calculated results with this combination of equations show good agreement with experimental data taken in this study.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Dimethyl carbonate (DMC) that is useful material in broad chemical industry used as methylation and carbonylation agent, fuel additive, electrolytes in lithium batteries and starting material for polycarbonate. So it is expected to substitute for phosgene, dimethyl sulfate and MTBE that are toxic and harmful to the environment, because DMC is non-toxic, biodegradable and eco-friendly substance [1–6].

There are various existing methods for synthesis of DMC: (1) phosgene route, (2) the oxidative carbonylation of methanol with carbon monoxide and oxygen that was introduced by EniChem [7], and (3) methyl nitrite that was introduced by UBE [8]. However, the aforementioned processes require materials that are toxic, explosive and flammable gases such as phosgene, hydrogen chloride and carbon monoxide. Also, these routes have not only problem that is harmful to the environment, but also many drawbacks that are corrosion of equipment, difficulty of separation process among the products, and etc.

Alternatively, direct synthesis of DMC using supercritical carbon dioxide and methanol has been suggested to overcome aforementioned drawbacks. This method uses carbon dioxide and methanol as raw materials and produces DMC and water as product and

by-product. Unlike old-fashioned process, there are few risks or hazards of the manufacturing process because this method does not use and produce undesirable and potentially lethal compound. But DMC yield in the direct synthesis reaction is too low to commercialize because of next two reasons. First, the reversible reaction under the thermodynamic equilibrium hinders final production quantity; and second, the inactivation of catalysts slows the reaction due to water by-products [6,9,10].

To improve these problems, many researchers have been studying development of catalyst and dehydration process. Among the numerous catalysts that have been researched [11–14], the use of base catalysts such as K$_2$CO$_3$ and CH$_3$I promoters is considered one of the appealing for getting optimum results [13,15].

The direct synthesis system includes carbon dioxide, methanol and CH$_3$I or other reaction products (DMC, water and DME) at different pressures and temperatures. Therefore, vapor liquid equilibrium data is essential for evaluating the performance of DMC synthesis processes, determining their optimal composition, and designing the optimum separation process. For entire these reasons, its thermodynamic properties have recently studied. Until now, we have been researched VLE data that are related to the direct synthesis of DMC and reported DME + methanol [16], DMC + CO$_2$ [17], DME + CO$_2$ [18] and CO$_2$ + CH$_3$I system [19] in the series. However, VLE data for the binary system DME + CH$_3$I have not been reported yet. So we conducted a study on this binary system.

In this paper, isothermal VLE data for the binary mixture of dimethyl ether + methyl iodide at five equally spaced temperatures

$a(T)$	temperature dependent
a	attraction parameter
b	molecular volume
c	pure compound parameters as defined in Mathias–Copeman expression
P, P_c	pressure, critical pressure (MPa)
R	gas constant 8.3144 (J mol^{-1} K^{-1})
k_{ij}	interaction Parameter
T, T_c	absolute temperature, critical temperature, reduced temperature (K)
ν	molar volume
x	liquid mole fraction
y	vapor mole fraction
A_∞^E	excess Helmholtz free energy at infinite pressure
G, g	excess Gibbs energy (J mol^{-1})

Greek letters

ω	acentric factor
α	non-randomness parameter

Superscripts

res	residual term
SG	Staverman–Guggenheim contribution

Subscripts

AC	activity coefficient model
c	critical property
cal	calculated
exp	experimental
i, j	ith, jth component of the mixture
r	reduced property

from 283.15 to 323.15 K were measured by using a circulation-type equilibrium apparatus in which both phases were continuously recirculated. The experimental data were correlated with two combinations of equations: (1) the Peng–Robinson equation of state (PR-EoS) [20] using the Wong–Sandler mixing rule [21] combined with the NRTL excess Gibbs free energy model which is one of the most widely and often used combinations of equations which show good agreement with various VLE experimental data (2) the Peng–Robinson equation of state (PR-EoS) using the Universal mixing rule combined with the UNIQUAC model [22,23], suggested by Voutsas et al., which is used in literatures and then they concluded that UMR for cubic EoS provided satisfactory results for various thermodynamic properties even at high pressure. In the previously stated range of experimental temperatures, the average absolute deviations of pressure and vapor phase compositions between experimental and calculated values were determined, and the relevant parameters were presented.

2. Experimental

2.1. Materials

High-grade chemicals of dimethyl ether and methyl iodide were used for VLE measurement. The high purity dimethyl ether (greater

than 99.9 mass%) and methyl iodide (greater than 99.5 mass%) were purchased from Sigma Aldrich, Co., USA. We analyzed these two pure components with a gas chromatography (GC).The resulted mass fraction purities of dimethyl ether and methyl iodide were higher than 99.9 and 99.5 mass%, respectively. So, all the chemicals were used without any further purification. The purity data and properties of these components are shown in Tables 1 and 2, respectively.

2.2. Experimental apparatus

The schematic diagram of the experimental apparatus that was used for this study is shown in Fig. 1. The vapor–liquid equilibrium apparatus used in this investigation is identical to the one used in previous works [20–29].The aforementioned apparatus uses a circulation-type mechanism in which both liquid and vapor phases were recirculated continuously. The equilibrium cell (10) is made from a type 316 stainless steel vessel with an inner volume of about 85 cm^3. The central part is composed of two Pyrex glass windows of 20 mm thickness installed in the front and back so that the liquid level, mixing and circulating behaviors, and critical phenomena are able to be observed using a backlight during operation. A stirrer (13), rotated at variable speeds by an external magnet, was used to accelerate the attainment of the equilibrium state and to reduce concentration gradients in both phases. The temperature of the equilibrium cell in the water bath (14) was maintained by a circulator (4) from Thermo Fisher Scientific, USA. The temperature in the cell was measured with a platinum-resistance sensor and a digital temperature indicator (17) Model F250MkII precision thermometer from Automatic Systems Laboratories, Ltd., United Kingdom. They were both calibrated by a National Measurement Accreditation Service accredited calibration laboratory. The total uncertainty in temperature measurements is estimated to be within0.01 K, including sensor uncertainty, temperature resolution, 0.001 K, and a measurement uncertainty within 0.001 K. The pressure was measured with a pressure transducer, Model XPM60, and a digital pressure calibrator (2), Model PC106, from Beamex, Finland. Pressure calibrations are traceable to National Standards (Center for Metrology and Accreditation Cert. No. M-95P077, 14.11.1995, M-M 730, 16.11.1995, and M-95P078, 16.11.1995). The calibrator uncertainty was 0.0005 MPa, the sensor uncertainty was 0.001 MPa, and the measurement uncertainty was 0.001 MPa. Therefore, the total uncertainty of the pressure measurement is estimated to be within0.001 MPa.

To reach the equilibrium state rapidly in the cell, the vapor and liquid phases in the equilibrium cell were continuously recirculated with a dual-head circulation pump, which includes a vapor circulation pump (5) and a liquid circulation pump (6) powered simultaneously by an electric motor (7).This pump was manufactured by the Milton Roy Company, USA. After equilibrium was reached, the liquid and vapor samples were withdrawn from the recycling loop and injected on-line into GC (15) by a liquid sampling valve (11) and a vapor one (12). The liquid and vapor sampling valves were manufactured by the Valco Instruments Co., USA and have 20 and 0.5 μl sampling volumes, respectively. The composition of both phases was determined by means of a GC (15) of model YL 6100GC from Young-Lin Instrument Co., Korea connected online to the liquid and vapor sampling valves. This GC was equipped with a thermal conductivity detector (TCD) and a Porapak Q column

Table 1
The purity data of chemicals.

Chemical	Chemical formula	Source	Purity (mass %)	Purification method	Analysis method
Dimethyl Ether (1)	CH_3OCH_3	Sigma–Aldrich	99.9	None	Gas-chromatography
Methyl iodide (2)	CH_3I	Sigma–Aldrich	99.5	None	Gas-chromatography