Liquid/liquid equilibrium data measurement of iso-butanol + diethyl carbonate + water ternary system at 303.15 - 313.15 K and atmospheric pressure

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Abstract. Oxygenate compounds are organic compounds that can be mixed into fuel to increase the oxygen content. The effect of these additions to the fuel is increased combustion efficiency and reduced environmental pollution. Diethyl carbonate (DEC) is an ideal additive to replace toxic fuel additives such as methyl-tertiary-butyl ether (MTBE). DEC has high oxygen content, low vapour pressure, high octane mixture value, reduces emissions of hydrocarbons, CO, NOx, and other particles. DEC can be used as a single additive in gasoline or a co-additive in combination with alcohol such as iso-butanol. The aim of this study were to obtain liquid-liquid equilibrium (LLE) data of DEC (1) + iso-butanol (2) + H2O (3) ternary system at temperature of 303.15 - 313.15 K and atmospheric pressure. The LLE data were obtained by experiment using equilibrium cell equipped with heating jacket. This equipment has a pressure deviation of ±100.72 kPa. Each liquid sample was taken separately to analyse its composition as an equilibrium composition using gas chromatography with a standard deviation of 0.1% mol. Based on LLE data result, it shows that iso-butanol + H2O and DEC + H2O binary mixtures are partially miscible while iso-butanol + DEC mixture is total miscible. The experimental data were then correlated with thermodynamic models Non-Random Two-Liquid (NRTL) and Universal Quasi-Chemical (UNIQUAC) equations with RMSD values of 0.72% and 0.62%.

1. Introduction
An alternative to increase the efficiency of fuel combustion and to reduce pollution is reformulating the fuel with additives that has function to enrich the oxygen content in the fuel. Oxygenate additives in fuel function to increase the octane number and oxygen atoms in the fuel which act to oxidize soot and carbon monoxide (CO) gas so that the combustion system becomes more environmentally friendly [1-3]. This additive will create free radicals in the carbon chain of the fuel. With free radicals, it will be easier for the carbon chain to form new branches [4]. The effect of the emergence of new branches is an increase in the octane value and the caloric value. However, many oxygenate substances such as methyl-tertiary-butyl ether (MTBE) and tetraethyl lead (TEL) have adverse effects on the environment and are carcinogenic [5-7].

To overcome this problem, several studies have been carried out on new alternatives to fuel additives that can increase the octane value and meet emission standards, including: Diethyl carbonate (DEC). DEC is an ideal additive to replace MTBE because it has a high oxygen content, low vapour pressure,
value high octane mixture, reducing emissions of hydrocarbons, CO, NOx, and other particles. DEC has been used as a sole additive to gasoline and as an additive to simple alcohol combinations (gasohol). Ethanol is a type of alcohol that has potential as a fuel additive. Several studies have been carried to evaluate ethanol performance in various engine [8] and vehicle [9]. However, the use of ethanol causes a high fuel consumption due to the insufficient fuel value of ethanol [10]. The use of butanol is one way to get gasohol with a smaller fuel consumption because the fuel value of butanol is higher and can reduce the possibility of phase splitting. The combustion mechanism and kinetics of ethanol and butanol were simulated from the previous study [11]. It showed that ethanol may not be the suitable for single additives and alcohols with larger molecular weight such as butanol possibly can be suitable fuel additive. The use of butanol is one way to get gasohol with a smaller fuel consumption because the fuel value of butanol is higher and can reduce the possibility of phase splitting. Butanol has 4 kinds of isomers, n-butanol, 2-butanol, iso-butanol and tert-butanol. From table 1 it can be seen that iso-butanol have the highest octane value among the others so that the use of this component in the fuel mixture can produce a better octane value. Another advantage of using butanol as an additive is butanol which comes from biomass [12]. This is an opportunity for butanol to be developed and mass produced because Indonesia is rich in biomass.

| Additive       | RON  |
|----------------|------|
| n-Butanol      | 94   |
| 2-Butanol      | 101  |
| Tert-Butanol   | 104 - 110 |
| Iso-Butanol    | 113  |

The availability of liquid-liquid equilibrium (LLE) data is needed to understand the behaviour and thermodynamic properties of systems containing water, alcohol, and oxygenates. Research on phase equilibrium containing DEC, alcohol and water has been carried out by previous research [13-19]. In the butanol isomer system with dialkyl carbonates, the previous LLE studies that have been carried out are using n-butanol [20] at 298. These limitations lead to the need for the development of an LLE study using iso-butanol and an operating condition suitable for the Indonesian environment which is at temperature of 303.15 – 313.15 K. Based on the description above, the aim of this research is to obtain data on the liquid-liquid equilibrium of the ternary system DEC (1) + iso-butanol (2) + H₂O (3) at temperatures of 303.15 K and 313.15 K at atmospheric pressure. The availability of this equilibrium data can be the basis for mixing for fuels that have good performance and are environmentally friendly.

2. Experimental Section

2.1. Description of Materials

The chemicals used in this work were iso-butanol, diethyl carbonate (DEC), and water. The chemicals were used without further purification and its specifications are given in table 2.

| Component     | Source                | Purity (%) | Molecular Weight (g.mol⁻¹) |
|---------------|-----------------------|------------|----------------------------|
| Diethyl carbonate | Wuhan Fortuna Chemical, China | 99         | 118                        |
| Iso-butanol   | Merck, Germany        | 99.9       | 74                         |
| Distilled water | -                     | -          | 18                         |

2.2. Experimental Procedures

The experiment used an equilibrium cell which equipped with heating jacket to keep the temperature constant and a magnetic stirrer to stir the solution. The experimental apparatus is shown in figure 1 which consists of an equilibrium cell equipped with a PID controller and a Pt100 RTD to control the temperature. The experiment was conducted by mixing the known chemical composition into the cell.
equilibrium. The mixture was then stirred at temperatures of 303.15 and 313.15 K at atmospheric pressure for 4 hours. After 4 hours of stirring, the mixture was then settled to allow phase splitting for 20 hours. After equilibrium was reached, samples were taken from each phase to be analysed using the Gas Chromatography (GC) Shimadzu 2010 Plus using the Rtx-5 column to get the phase equilibrium composition. The next step was to correlate the experimental data using the NRTL [21] and UNIQUAC [22] equation models.

![Experimental apparatus](image)

**Figure 1.** Experimental apparatus; (1) Equilibrium Cell, (2) Stirrer, (3) Magnetic Stirrer, (4) RTD Pt100, (5) Temperature Display, (6) PID Controller ANLY AT-502, (7) Water bath, (8) Pump, (9) Sampling port and (10) Capillary pipe

### 3. Results and Discussion

The results of the liquid-liquid equilibrium experiment are the composition of the aqueous and organic phases at equilibrium. In the liquid-liquid equilibrium, the Diethyl Carbonate (1) + iso-butanol (2) + H₂O (3) system at temperatures of 303.15 and 313.15 K was distributed into aqueous and organic phases. The experimental liquid-liquid equilibrium (LLE) data are shown in table 3. The experimental data is correlated with the Bachman-Brown equation [23-24] which is used to ensure the reliability of the experimental data. This correlation is based on the consistency of data distribution both in the aqueous and organic phases. The Bachman-Brown equation is shown in equation (1) where A is gradient, B is intercept, \( x_{1}^{or} \) is DEC mole fraction in organic phase and \( x_{3}^{aq} \) is H₂O mole fraction in aqueous phase.

\[
\frac{x_{1}^{or}}{x_{3}^{aq}} = Ax_{1}^{or} + B
\]  

(1)

The equilibrium composition data of the experimental results for each operating temperature is depicted in the ternary system LLE diagram which can be seen in figure 2. It can be seen that the DEC (1) + iso-butanol (2) + H₂O (3) system is a system with ternary diagram Treybal Type II [25] because the system has two partially miscible binary pairs, DEC (1) + H₂O (3) and iso-butanol (2) + H₂O (3). From figure 2, it can be seen that the temperature difference can have a significant effect on the resulting two-phase area. This can be seen from the two-phase area of experimental data at a temperature of 303.15 K which is greater than the two-phase area at a temperature of 313.15 K. The parameter Bachman-Brown equation is shown in table 4 with a regression value of \( R^2 \) close to 1, which indicates that the experimental data is consistent and reliable.
Figure 2. Experimental LLE Data of DEC (1) + iso-butanol (2) + H₂O (3) system at (●) 303.15 K and (▼) 313.15 K at atmospheric pressure

Table 3. Experimental LLE data of ternary Diethyl Carbonate (1) + iso-butanol (2) + H₂O (3) system at atmospheric pressure

| T(K)  | Aqueous Phase | Organic Phase |
|-------|---------------|---------------|
|       | x₁  | x₂  | x₃  | x₁  | x₂  | x₃  |
| 303.15 | 0.0224 | 0   | 0.9776 | 0.9569 | 0   | 0.0431 |
|        | 0.0328 | 0.0327 | 0.9345 | 0.7482 | 0.1319 | 0.1199 |
|        | 0.04 | 0.0386 | 0.9215 | 0.5456 | 0.219 | 0.2355 |
|        | 0.0204 | 0.0576 | 0.9219 | 0.2608 | 0.2912 | 0.4481 |
|        | 0.0179 | 0.0663 | 0.9159 | 0.1214 | 0.291 | 0.5876 |
|        | 0.0296 | 0.047 | 0.9234 | 0.4012 | 0.2799 | 0.3189 |
|        | 0 | 0.1105 | 0.8895 | 0 | 0.2344 | 0.7656 |
|        | 0.0193 | 0.0977 | 0.8831 | 0.0542 | 0.2515 | 0.6944 |
| 313.15 | 0.0221 | 0 | 0.9779 | 0.9567 | 0 | 0.0433 |
|        | 0.0273 | 0.0196 | 0.9531 | 0.7287 | 0.1156 | 0.1558 |
|        | 0.0268 | 0.0212 | 0.952 | 0.5462 | 0.2118 | 0.242 |
|        | 0.027 | 0.042 | 0.9311 | 0.25 | 0.2744 | 0.4756 |
|        | 0.0236 | 0.0326 | 0.9439 | 0.4495 | 0.2511 | 0.2994 |
|        | 0.0361 | 0.06 | 0.9039 | 0.1502 | 0.2627 | 0.5871 |
|        | 0.0315 | 0.0773 | 0.8913 | 0.0419 | 0.2335 | 0.7246 |
|        | 0 | 0.0966 | 0.9034 | 0 | 0.2231 | 0.7769 |
Table 4. Bahcman-Brown Parameters

| T(K)   | A    | B    | R²   |
|--------|------|------|------|
| 303.15 | 0.962| 0.008| 0.998|
| 313.15 | 0.973| 0.008| 0.999|

Table 5. UNIQUAC parameters: molecular area (q) and volume (r)

| Chemical | r       | q   |
|----------|---------|-----|
| DEC      | 4.39684 | 3.896|
| iso-butanol | 3.45353 | 3.048|
| H₂O      | 0.92    | 1.4 |

Table 6. NRTL and UNIQUAC binary interaction parameters for DEC (1) + iso-butanol (2) + H₂O (3) system

| Model  | Parameters | %RMSD |
|--------|------------|-------|
|        | i-j        | aij   | aji   | α     |       |
| NRTL   | 1-2        | -1450.27 | 1497.56 | 0.2   | 0.72  |
|        | 2-3        | 1078.46  | 879.49  |       |       |
|        | 1-3        | 2440.13  | -133.22 |       |       |
| UNIQUAC| 1-2        | 65.50    | 115.90  | -     | 0.62  |
|        | 2-3        | -33.24   | 110.50  |       |       |
|        | 1-3        | 438.26   | 134.97  |       |       |

Figure 3. Experimental Result of correlation of DEC (1) + iso-butanol (2) + H₂O (3) system using NRTL model at temperature (A) 303.15 K and (B) 313.15 K at atmospheric pressure; (■) experiment data; (---) experiment Tie Line; (─) NRTL model.
The experimental data obtained were correlated using the NRTL and UNIQUAC. Fitting parameters with the NRTL model is calculated by setting $\alpha$ value to 0.2 where the value is chosen because there are partially miscible binary pairs. Validity testing is carried out based on the reference value of the root square mean deviation (RMSD), which is the absolute deviation of the average composition between the experimental data and the calculation results using model equations. The UNIQUAC parameters used in the calculations are presented in table 5. While the binary interaction parameters results obtained by the NRTL and UNIQUAC models are shown in table 6. Figure 3-4 illustrates the correlation performance of the DEC (1) + iso-butanol (2) + H$_2$O (3) experimental data using NRTL and UNIQUAC models. Based on the correlation results, the NRTL and UNIQUAC models show good results. This can be seen through the RMSD value is less than 1% for the two models. The correlation results obtained are good so that this single parameter set can also be used to represent equilibrium data for temperatures of 303.15 - 313.15 K.

4. Conclusions
Accurate LLE data of DEC (1) + iso-butanol (2) + H$_2$O (3) ternary system were obtained experimentally at 303.15 K - 313.15 K at atmospheric pressure. The ternary system graph shows that the system displays Type Treybal II. Temperature different has an effect on the two-phase area of the system. The NRTL and UNIQUAC thermodynamic models can correlate the experimental data very well where UNIQUAC is slightly superior.

Acknowledgment
This research was funded by Ministry of Research, Technology and Higher Education, Republic of Indonesia under contract no: 3/AMD/E1/KP.PTNBH/2020. The author also give appreciation to Bagus Rizky Pratama B and Arina Ulfa S for their efforts in experimental works.

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