Phase behavior of binary systems of carbon dioxide with dibasic esters at elevated pressures, including near critical regions

Ardila Hayu Tiwikrama,[a,*] Teofilius Kristanto,[b] Ming-Jer Lee[b]

[a]National Taipei University of Technology, Taipei, 10607, Taiwan

[b]National Taiwan University of Science and Technology, Taipei, 10607, Taiwan

*Corresponding author: ardilahayu@mail.ntut.edu.tw

1. Introduction

Dibasic esters (DBE) are potential green solvents to replace conventional high volatility and high toxicity organic solvent [1], which are commonly used as paint strippers. The major compounds of DBEs are dimethyl succinate (DMS), dimethyl glutarate (DMG), and dimethyl adipate (DMA), which can be synthesized from dibasic acids with alcohols via esterification. In the esterification reaction, an intermediate monomethyl adipate (MMA) is produced as a minor product. The dibasic acids are available from waste compounds in the intermediate stream from caprolactam plants. These waste compounds can be efficiently recycled and converted into DBE to enhance the usage of raw materials by using a reactive distillation technology. Supercritical fluid such as carbon dioxide could be a potential auxiliary agent for separation of DBE from the product mixtures.

The phase equilibrium properties mixtures containing DMS, DMG, DMA or MMA and CO_2 are fundamentally important for designing the process of reactive distillation system. No available literature vapor-liquid equilibrium (VLE) data for DBE + CO_2 systems, especially in near critical region. In order to study the VLE of these four esters completely and accurately, we measured isothermal vapor-liquid equilibrium data for DMS + CO_2, DMG + CO_2, DMA + CO_2 and MMA + CO_2 systems using a phase equilibrium analyzer (PEA) at temperatures range from 313.15 K to 413.15 K and pressures up to 29 MPa. The Peng-Robinson equation of state with the van der Waals was used to correlate the measured data to determine the optimal values of the binary interaction parameters for each binary system. The performance of each model was evaluated the deviations of experimental and correlated values. The optimal values of the binary interaction parameters determined in this work can be applied to the process development for separation of DBEs using supercritical carbon dioxide as an auxiliary agent.

2. Materials and Methods

2.1 Materials

Carbon dioxide (purity of 99.5 mass%) was purchased from Liu-Hsiang Co. (Taiwan). Dimethyl succinate (99 mass% purity), dimethyl glutarate (99 mass% purity), dimethyl adipate (99 mass% purity) and monomethyl adipate (99 mass% purity) were supplied from Acros Organics B.V.B.A. (Belgium). All the chemicals were used without further purification.

2.2 Apparatus and procedure

The schematic diagram of the visual and volume-variable phase equilibrium analyzer (PEA) has been described in our previous work [2,3]. This apparatus consists of a high-pressure generator (model 62-6-10, High Pressure Equipment Co., USA), a sapphire window (Part No. 742.0106,Bridgman closure, SITEC, Switzerland), a rupture disk, and a circulation jacket. The internal volume of the cell can be adjusted manually from 35 cm^3 to 60 cm^3 by a manual hand pump and the visual cell is operable up to 50 MPa and 473.15 K. The temperature of cell was maintained by thermostatic oil bath and was measured by an inserted thermocouple, whose reading has been calibrated to within an uncertainty of 0.1 K. A pressure transducer (PDCR 407-01, Druck, UK) connected with a digital indicator measured the cell's pressure to within an uncertainty of 0.1 %. The operation procedure is given as below. The empty cell was purged with carbon dioxide several times to remove the residual content. After evacuating the cell, two precision syringe pumps were employed to charge carbon dioxide and one of the DBEs (DMS, DMG, DMA or MMA), respectively. The loaded mixture in the cell was compressed to the desired pressure by displacing movable piston fitted within the cell. A magnetic stir bar was placed inside the cell to help the mixture became homogenous faster. The mass of each loaded

material was calculated from multiplying the known charged volume (accurate to 0.01 cm^3) by its density at feeding pressure and temperature. Density of carbon dioxide was taken from the NIST Chemistry WebBook [4] and density of DBE was measured by a high-pressure densimeter (DMA 512P, Anton Paar, Austria) to an uncertainty of 0.0001 g/cm^3. The uncertainty of the composition of the prepared mixtures was estimated to be 0.003 in mole fraction. The phase behavior of the loaded mixture in the cell was observed with a digital camera (Model: EOS M2, Canon, Japan), which was connected with an LCD monitor (Model: SE2231R. BenQ, Taiwan), and two light sources illuminating cell's content. The loaded sample was compressed to form a single-phase at a fixed temperature and the pressure was then slowly decreased until the second phase appeared by manipulating the position of piston manually. The uncertainty of the observed phase transition pressures was estimated to be 0.02 MPa.

3. Results and discussion

Experimental phase behavior of carbon dioxide (1) + dibasic esters (2) mixture was successfully measured using phase equilibrium analyzer (PEA) at high pressures, especially near the critical region. The phase behavior of dibasic esters (DBEs) including dimethyl succinate (DMS), dimethyl glutarate (DMG), dimethyl adipate (DMA), or monomethyl adipate (MMA) and carbon dioxide binary system was observed at isothermal condition from temperature range 313.15 K to 413.15 K and pressures up to 29 MPa. All phase transitions observed were vapor-liquid equilibrium (VLE) type. The VLE phase transition crossing the bubble, dew, or critical points of the studied system is described in Figs. 1-2. Fig. 1 shows an illustrative case of bubble point transition at 313.15 K. While critical phase transition of DMG with 0.8885 mole fraction of carbon dioxide at 373.15 K as presented in Fig. 2.
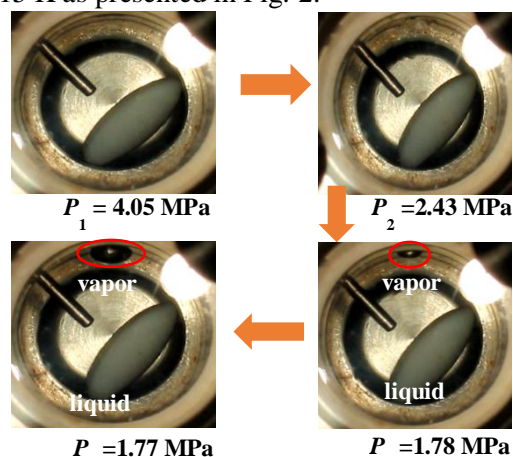

Fig. 1. Images of bubble point phase transition for CO_2 (1) + dimethyl succinate (DMS) solution (2) at 313.15 K and x_{CO2} = 0.2040.
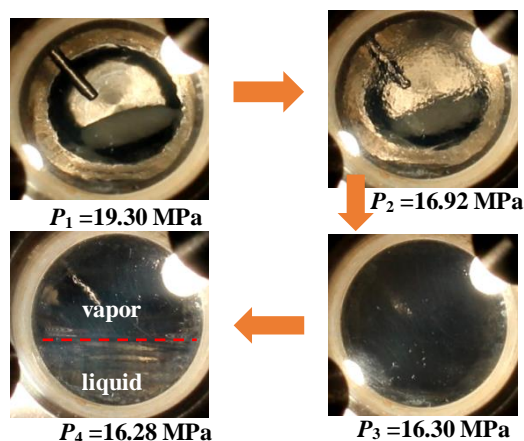

Fig. 2. Images of critical point phase transition for CO_2 (1) + dimethyl glutarate (DMG) solution (2) at 373.15 K and x_{CO2} = 0.8885.

4. Conclusions

The vapor-liquid phase transitions boundaries have been determined experimentally for CO_2 (1) + DMS (2), CO_2 (1) + DMG (2), CO_2 (1) + DMA (2) and CO_2 (1) + MMA (2) in a temperature range 313.15 K to 413.15 K and pressures up to near critical region by using a phase equilibrium analyzer (PEA). A polynomial function succeeds to determine the critical point for each isotherm. A comparison of the solubility of different esters compound in CO_2 was made in the following order: MMA < DMA< DMS < DMG. The optimal values of the adjustable binary interaction parameters have obtained from the data correlation. Those values are useful for the process development for DBEs separation using supercritical carbon dioxide as an auxiliary agent. The videos of the vapor-liquid phase transitions crossing the bubble-point, dew-point, and near critical point have also been taken in this study. These visualized materials can be served as an illustrative teaching-aided tool in the related classes, such as Thermodynamics or Supercritical Fluid Technology.

References

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