이산화탄소-n-Pentyl Acrylate, 이산화탄소-n-Pentyl Methacrylate 계의 기-액
상평형에 대한 모델링

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**Vapor - Liquid Phase Equilibria and Modeling of Carbon Dioxide – n-Pentyl Acrylate and
Carbon Dioxide – n-Pentyl Methacrylate Systems**

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Introduction

Thermodynamic knowledge of high-pressure phase behavior experimental data of solute and supercritical carbon dioxide mixtures plays an essential role in the basic design of various separation processes and fine chemical industries. As a result, the attention has been placed on the thermodynamic understanding of supercritical fluid systems[1.2]. The information on the high-pressure behavior of fluids at supercritical states has been valuable in the design of new separation processes in various fields such as food, pharmaceutical and related industries[3]. The of high-pressure phase equilibrium information of mixtures composed of CO_2 and amides is of importance and has been actively studied for various utilities.

The isothermal phase behavior experimental data of the binary mixture carbon dioxide-n-pentyl acrylate and carbon dioxide-n-pentyl methacrylate systems have been measured in the temperature range 40 ^{o}C to 120°C and pressure up to 175 bar. Therefore the purpose of this study was to determine the bubble-,critical- and dew-points experimentally for binary mixtures carbon dioxide-n-pentyl acrylate and carbon dioxide-n-pentyl methacrylate systems. Also, the pressure-composition isotherms experimental data were modeled using the Peng-Robinson equation of state with two adjustable binary interaction parameters.

Experimental section

Bubble- dew- and critical curves are obtained using a high-pressure variable-volume that has a 1.59 cm i. d., an o. d. of 7.0 cm and a working volume of 28 cm^3, equipped with a window for visual observation and a movable piston. The experimental apparatus and procedure have been described in

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detail elsewhere[4.5]. The temperature was measured using a thermocouple placed inside wells drilled directly into the body of the equilibrium cell. The temperature of the cell is measured using a platinum resistance thermometer (Thermometrics Corp., Class A) and a digital multimeter (Yokogawa, Model 7563, accurate o within 0.005%). It contains an efficient magnetic stirrer to ensure fast equilibrium. The pressure was measured by means of a pressure transducer (Dresser Ind., Model CM-130163, 340bar) for which the accuracy of pressure readings was found to be better than 0.1 bar. The mixture inside the cell is viewed on a video monitor using a camera coupled to a borescope (Olympus Corp., Model F100-038-000-50) placed against the outside of the sapphire window.

The empty cell is purged several times with nitrogen followed by carbon dioxide to ensure that all of the chemicals is removed. The liquid solute is loaded into the cell to within 0.002g using a syringe and carbon dioxide is transferred into the cell gravimetrically to within 0.004g using a high-pressure bomb. In this work, the uncertainty was reported for the analysis of the composition in model fraction for both vapor and liquid phases was estimated to be within <1.0%. The solution in the cell is compressed to the desired operating pressure by displacing a movable piston using water pressurized by a high pressure generator (HIP Inc., Model 37-5.75-60). The equilibrium cell is maintained at the desired working temperature, controlled to within 0.1K. The solution in the cell is stirred by a magnetic stir bar, which is activated by an external magnet beneath the cell.

To reach thermal equilibrium, the cell is maintained at the temperature for at least 30-40minutes. When equilibrium was reached, the mixture in the cell is compressed to a single phase and the pressure is then slowly decreased until a second phase appeared at a fixed temperature. A bubble point is obtained if a small bubble appears in the cell, and a dew point is obtained if a fine mist appears in the cell. The transition occurs in the mixture-critical point if critical opalescence is observed during the transition process and if two phase of equal volume are present when the mixture phase separates. After this pressure has been determined at a given temperature, the procedure is repeated at a new temperature, until a pressure-temperature isopleth for the solution has been obtained. The estimated accuracy of the pressure measurements is 0.4bar.

Carbon dioxide was provided by Daesung Oxygen Co.(Korea) with a certified purity of 99.9%. The n-pentyl acrylate(97% purity), n-pentyl methacrylate(98% purity) used in this work are obtained from Aldrich Inc. The chemicals were used without further purification.

Results and discussion

Bubble-, dew- and critical-point data for carbon dioxide – n-pentyl acrylate and carbon dioxide – n-pentyl methacrylate systems are reproduced to within 0.3 bar at least twice for a given loading of the cell. Figure 1 and Figure 2 present the data of the carbon dioxide- n-pentyl acrylate and carbon dioxide – n-pentyl methacrylate systems are obtained in this work. The mole fractions are accurate to within 0.002. The mole fraction for the solubility isotherms from 40°C to 120°C are arranged according to

the value at least two independent data points which have an accumulated error of less than 1.0%.

   Figure 1 shows the experimental pressure-composition (P-x) isotherms at 40, 60, 80, 100 and 120 °C, and the range of pressures of 22 – 168 bar for the carbon dioxide – n-pentyl acrylate system. The phases were not observed at any of the five temperatures. The P-x isotherms shown in Figure 1 are consistent with those expected for a type-1 system[6] where a maximum occurs in the critical mixture curve.
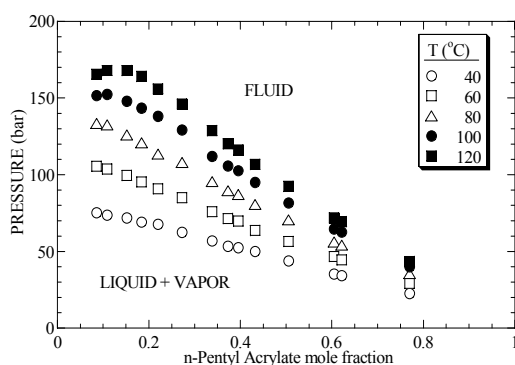

Figure 1. Pressure-composition experimental data of
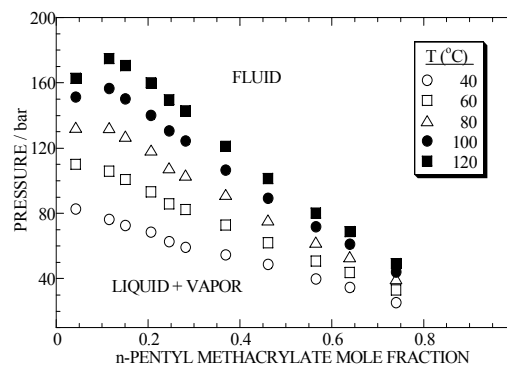   Carbon dioxide-n-pentyl acrylate system.

Figure 2. The phase behavior data of carbon
   dioxlde-n-pentyl methacrylate system.

   Figure 2 shows the experi-mental P-x isotherms at 40, 60, 80, 100 and 120 °C, and the range of pressure of 25 to 175 bar for the carbon dioxide – n-pentyl methacrylate system. Also, the type-1 phase   behavior is observed for carbon dioxide – n-pentyl methacrylate system.

   The isotherms phase equilibria experimental data in this work is modeled using the Peng-Robinson equation of state. The equation of state is briefly described here. For the correlation with the experimental data, we used the Peng-Robinson equation of state with the following mixing rules.

   The properties of n-pentyl acrylate and n-pentyl methacrylate were calculated by group-contribution method. The boiling point of n-pentyl acrylate and n-pentyl methacrylate obtained by Aldrich corp. are pure component parameters as defined by Peng and Robinson. The expression for the fugacity coefficient using these mixing rules is given by Peng and Robinson and is not reproduced here.

   Figure 3 shows a comparison of carbon dioxide- n-pentyl acrylate experimental results with calculations obtained using Peng-Robinson equation at a temperature 80 °C. The binary interaction parameters of the Peng-Robinson equation of state are fitted by the experimental data at 80 °C. The value of the adjusted parameters for the Peng-Robinson equation of state the carbon dioxide- n-pentyl acrylate system are $k_{ij} = 0.0293$ $n_{ij} = -0.0448$.

   A reasonable fit of the data is obtained over most of the composition range even if no mixture parameters are used. But if two mixture parameters, are used the fit of the experimental results is significantly better. As shown of Figure 4, these sets parameters are used to predict the vapor-liquid equilibria at other temperatures, namely, 40 - 120 °C.
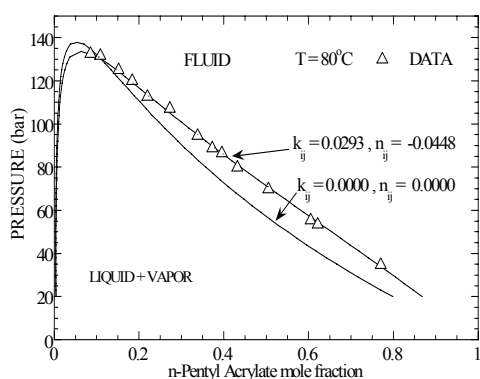
Figure 3. Comparison of the best fit of Peng-Robinson equation of state to the carbon dioxide-n-pentyl acrylate system at 80℃
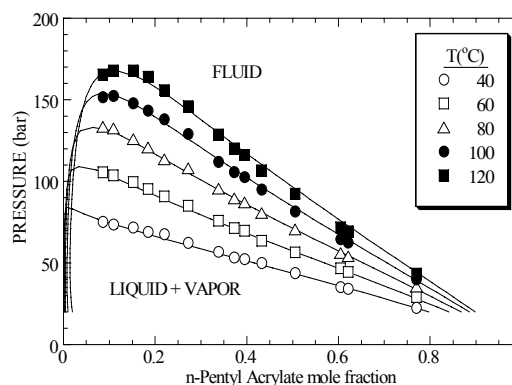
Figure 4. Comparison of the experimental data for the carbon dioxide-n-pentyl acrylate system wit with calculated values obtained with Peng -Robinson equation of state

Conclusion

　　Vapor-liquid phase Equilibria for the binary systems of carbon dioxide - n-pentyl acrylate and carbon dioxide n-pentyl methacrylate was measured at near critical points of carbon dioxide. Pressure-composition isotherms were obtained for carbon dioxide - n-pentyl acrylate and carbon dioxide - n-pentyl methacrylate systems at 40, 60, 80, 100 and 120℃ using a variable-volume view cell in static type. Also, the solubility of carbon dioxide for carbon dioxide - n-pentyl acrylate and carbon dioxide - n-pentyl methacrylate system decreases as the temperature increase at constant pressure. The experimental results were correlated with equation of state.

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