초임계 이산화탄소내에서 이소부틸아클레이트와 이소부틸메타클레이트에 대한 용해도 측정

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Solubility Measurement on the iso-Butyl Acrylate and iso-Butyl Methacrylate with Supercritical Carbon Dioxide

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Introduction

Thermodynamic knowledge of high-pressure phase behavior experimental data of solutes 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 [1,2,3,4]. 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[5].

In this paper, a static-type experimental apparatus was designed for the present study and measurement of the phase behavior experimental data for carbon dioxide + iso-butyl acrylate and carbon dioxide + iso-butyl methacrylate systems.

The isothermal phase behavior experimental data of the binary mixture carbon dioxide + iso-butyl acrylate and carbon dioxide + iso-butyl methacrylate systems have been measured in the temperature range from 40 to 120℃ and pressure up to 160 bar. Therefore, the purpose of this study was to determine the bubble-, critical- and dew-points experimentally for binary mixtures of carbon dioxide + iso-butyl acrylate and carbon dioxide + iso-butyl 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-that has a 1.59 cm i. d., an o. d. of 7.0 cm and a working volume of 28 cm2, equipped with a window for visual observation and a movable piston. The experimental apparatus and procedure have been described in detail elsewhere [6,7]. 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 to within 0.005%). It contains an efficient magnetic stirrer to ensure fast equilibrium. The pressure was measured by means 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 mole fraction for both vapor and liquid phases was estimated to be within <1.0%. The solution in the cell is compressed to the desired operation 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 30-40 minutes. 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 phases 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 0.4 bar.

Carbon dioxide was provided by Deasung Oxygen Co.(Korea) with a certified purity of 99.9%. The iso-butyl acrylate (99 % purity), iso-butyl methacrylate (97 % purity) used in this work are obtained from Polysciences Inc and Aldrich chemical Inc. The chemicals were used without further purification.

Results and discussion

Bubble-, dew- and critical-point data for carbon dioxide + iso-butyl acrylate and carbon dioxide + iso-butyl 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 + iso-butyl acylate systems are obtained in this work. The mole fractions are accurate to within 0.002. The mole fractions for the solubility isotherms from 40 to 120℃ 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 ℃, and the range of pressures of 24 ~ 148 bar for the carbon dioxide + iso-butyl acrylate system. Three 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-I system [8] where a maximum occurs in the critical mixture curve.

Figure 2 shows the experi- mental P-x isotherms at 40, 60, 80, 100 and 120 ℃, and the range of 21 to 160 bar for the carbon dioxide + iso-butyl methacrylate system. Also, the type-I phase behavior is observed for carbon dioxide + iso-butyl methacrylate system.

The isothermal 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 [9.10] with the following mixing rules.

The properties of iso-butyl acrylate and iso-butyl methacrylate were calculated by group-contribution method [9,10] . The boiling point of iso-butyl acrylate and iso-butyl methacrylate obtained. The expression for the fugacity coefficient using these mixing rules is given by Peng and Robison [9,10] and is not reproduced here.

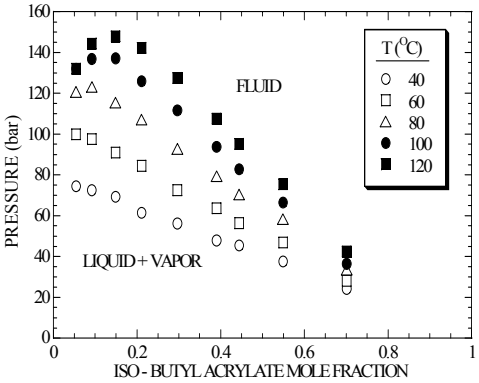

Figure1.Pressure-composition experimental data Carbon dioxide + iso butyl acrylatesystem.

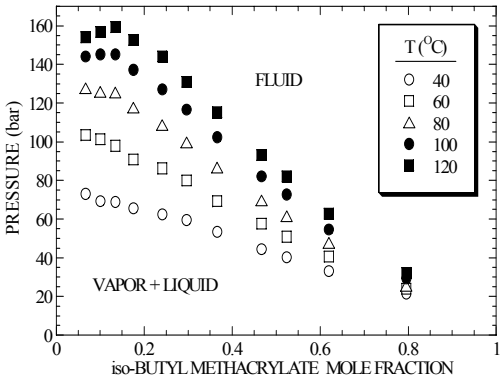

Figure2. The phase behavior data of carbon dioxide + iso butyl methacrylate system.

$$a_{mix} = \sum_i \sum_j x_i x_j a_{ij} \quad (1)$$

$$a_{ij} = (a_{ii} a_{jj})^{1/2} (1 - k_{ij}) \quad (2)$$

$$b_{mix} = \sum_i \sum_j x_i x_j b_{ij} \quad (3)$$

$$b_{ij} = 0.5[(b_{ii} + b_{jj})](1 - \eta_{ij}) \quad (4)$$

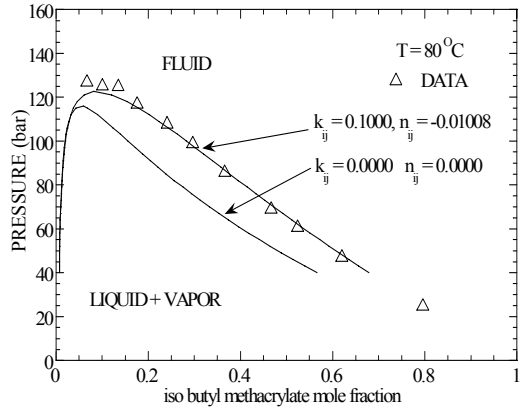

Figure3. Comparsion of the best fit of Prng-Robbison equation of state to the carbon dioxide + iso butyl methacrylate system at 80℃

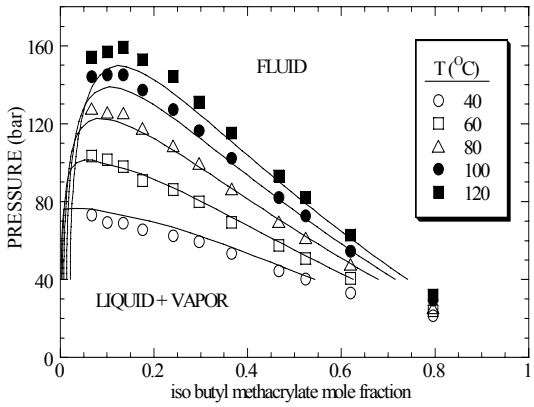

Figure4. Comparision of the experimental data for the carbon dioxide + iso butyl methacrylate system wit with calculated values obtained with Peng-Robbison equation of state

Figure 3 shows a comparison of carbon dioxide + iso butyl methacrylate experimental results with calculations obtained using Peng-Robison equation at a temperature of 80℃. The binary interaction parameters of the Peng-Robison equation of state are fitted by the experimental data at 80℃. The values of the adjusted parameters for the Peng-Robison equation of state of the carbon dioxide + iso-butyl methacrylate system are k_{ij} = 0.100 and n_{ij} = -0.0101. 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 of

parameters are used to predict the vapor-liquid equilibria at other temperatures, namely, 40 - 120℃.

Conclusion

High pressure phase behavior of the iso-butyl acrylate and iso-butyl methacrylate with supercritical carbon dioxide has been stuied. Pressure-composition isotherms are obtained for binary mixtures of carbon dioxide + iso-butyl acrylate system at 40, 60, 80, 100 and 120℃ and pressures to 150 bar and for of carbon dioxide + iso-butyl methacrylate pressure up to 160 bar. The solubility of iso-butyl acrylate and iso-butyl methacrylate for the carbon dioxide + iso-butyl acrylate and carbon dioxide + iso-butyl methacrylate systems increases as the temperatures increases at constant pressure. The carbon dioxide + iso-butyl acrylate and carbon dioxide + iso-butyl methacrylate system exhibits type-I phase behavior, characterized by a continuous critical line from pure carbon dioxide the second component with a maximum in pressure. The experimental results for the the carbon dioxide + iso-butyl acrylate and carbon dioxide + iso-butyl methacrylate systems have been modeling the Peng-Robinson equation of state.

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