이성분 이산화탄소-싸이클로헥실 아클레이트와 이산화탄소-싸이클로헥실 메타클레이트 혼합물에 대한 고압상거동

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High Pressure Phase Behavior for Binary CO_2-Cyclohexyl Acrylate and CO_2-Cyclohexyl Methacrylate Mixtures

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Introduction

Phase behavior information for mixtures containing supercritical fluids is required for practical uses such as plant design and operation of separation process in the petroleum, natural gas and related fields. The advance of supercritical fluid extraction development is often dependent on new thermodynamics data on vapor-liquid , liquid-liquid-vapor, and liquid-liquid equilibria. Phase behavior data with the carbon dioxide + alkyl (meth)acrylate system were reported by McHugh et al.[5,6,8], and Byun[7]. These data of miscibility for supercritical carbon dioxide + monomer system have important condition needed for polymer synthesis and polymerization process.

The first part of this work is the high-pressure experimental data for carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate mixtures by investigating mixtures of carbon dioxide with two components. Also, the pressure-temperature (*P* - *T*) diagrams of the mixture critical curve are presented for the carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate systems in the vicinity of the critical point of pure carbon dioxide. Also, to provide phase behavior information for high pressure process design purposes the measured bubble-, critical- and dew-point data of binary systems is modeled using the Peng-Robinson equation of state. These results can provide valuable information for rational design and operation of the supercritical region.

Experimental Section

The main component of the experimental apparatus is a high pressure, variable-volume cell which is constructed of a high-nickel-content austenitic steel (Nitronic 50®, 5.7 cm O.D., 1.59

cm I.D., a working volume of ~28 cm^3) and is capable of operating up to pressure of 100 MPa. A 1.9 cm thick sapphire window is fitted in the front part of the cell to allow observation of the phases. Typically, a quantity of liquid cyclohexyl acrylate or cyclohexyl methacrylate was loaded into the cell to within an accuracy of ±0.002 g by using a syringe, after the empty cell was purged several times with carbon dioxide to remove air. Carbon dioxide was then added to the cell to within an accuracy of ±0.004 g by using a high pressure bomb.

Materials Carbon dioxide was obtained from Daesung Oxygen Co.(99.9 % minimum purity) and was used as received. The cyclohexyl acrylate (min 85 mass % purity) and cyclohexyl methacrylate (~98.0 mass % purity) used in this work were obtained from Polysciences Inc. Both components were used without further purification in the experiments.

Experimental Results and Discussion

Bubble, critical, and dew point curves for both the carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate systems are measured and reproduced at least twice to within ±0.03 MPa and 0.2 K for a given loading of the cell. The mole fractions are accurate to within ±0.002. The carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate mixtures for the solubility isotherms at 313.2 to 393.2 K are arranged according to the value at least two independent data points that have an estimated accumulated error of less than ±1.0%.

Figure 1 shows the experimental pressure-composition (P - x) isotherms at 313.2, 333.2, 353.2, 373.2 and 393.2 K, and the range of pressures of 1.7 to 20.0 MPa for the carbon dioxide + cyclohexyl acrylate system. As shown in Figure 1, three phases were not observed at any of the five temperatures studied. Although the characteristics of the P - x isotherms appear to be consistent with those expected for a type-I system, the lowest temperature isotherm is too far away from the critical point of pure carbon dioxide to make any definitive statement concerning whether this mixture indeed exhibits type-I behavior.[11,12]

Figure 2 shows the experimental phase behavior of P - x isotherms at 313.2, 333.2, 353.2, 373.2 and 393.2 K for the carbon dioxide + cyclohexyl methacrylate system. The P - x isotherms shown in Figure 2 are consistent with the characteristics expected for a type-I system where a maximum occurs in the critical mixture curve at (313.2, 333.2, 353.2, 373.2 and 393.2) K. As shown in Figure 2, the solubility of carbon dioxide for carbon dioxide + cyclohexyl methacrylate system decreases as the temperature increases at constant pressure. Also, the mixture-critical points (8.64 MPa at 313.2 K; 12.21 MPa at 333.2 K; 15.45 MPa at 353.2 K; 18.21 MPa at 373.2K; and 20.59 MPa at 393.2K) for the carbon dioxide + cyclohexyl methacrylate system increases as the temperature increases.

The experimental data obtained in this work were correlated with Peng-Robinson equation of

state using van der Waals one fluid mixing rules including two binary interaction parameters. This equation of state is briefly described here. The Peng-Robinson equation [15] of state is used with the mixing rules given by,

$$a_{\mathrm{mix}} = \sum_{\mathrm{i}} \sum_{\mathrm{j}} x_{\mathrm{i}} x_{\mathrm{j}} a_{\mathrm{ij}} \quad , \qquad a_{\mathrm{ij}} = \left(a_{\mathrm{ii}} a_{\mathrm{jj}}\right)^{1/2} \left(1 - k_{\mathrm{ij}}\right)$$

$$b_{\mathrm{mix}} = \sum_{\mathrm{i}} \sum_{\mathrm{j}} x_{\mathrm{i}} x_{\mathrm{j}} b_{\mathrm{ij}} \quad , \qquad b_{\mathrm{ij}} = 0.5\left[\left(b_{\mathrm{ii}} + b_{\mathrm{jj}}\right)\right]\left(1 - \eta_{\mathrm{ij}}\right)$$

We compared experimental results with calculated *P* - *x* isotherms at temperatures of 313.2, 333.2, 373.2 and 393.2 K for the carbon dioxide + cyclohexyl acrylate system using the optimized values of k_{ij} and η_{ij} determined at 353.2 K. As shown in Figure 1, a good fit of the data are obtained with Peng-Robinson equation using an adjustable mixture parameters for the carbon dioxide + cyclohexyl acrylate system. The RMSD at five temperatures 313.2, 333.2, 353.2, 373.2 and 393.2 K for carbon dioxide + cyclohexyl acrylate system was 5.93 % of the 56 bubble points.

Figure 2 shows a comparison of experimental with calculated *P* - *x* isotherms at temperature of 313.2, 333.2, 353.2, 373.2 and 393.2 K for the carbon dioxide + cyclohexyl methacrylate system. These isotherms are calculated using the optimized values bubble-point data = 10, RMSD = 1.82 % of k_{ij} equal to 0.033 and η_{ij} equal to -0.013 determined at 353.2 K in the same way as above. The RMSD at five temperatures for carbon dioxide + cyclohexyl methacrylate system was 9.29 % of the 49 bubble points.

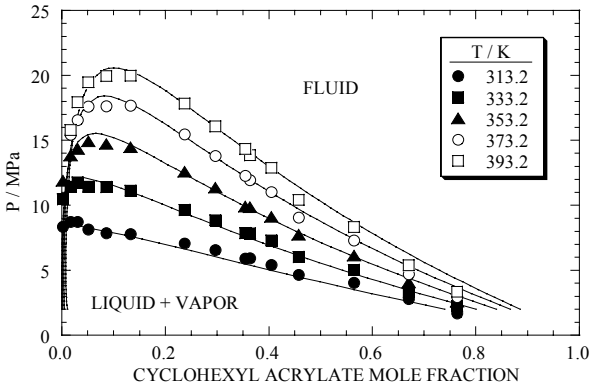

Figure 1. Comparison of the experimental data (symbols) for the carbon dioxide + cyclohexyl acrylate system with calculated data (solid lines) obtained with the Peng-Robinson equation of state with k_{ij} equal to 0.031 and η_{ij} equal to 0.006.

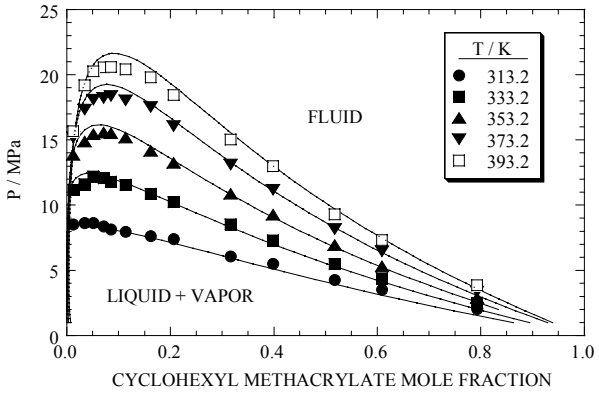

Figure 2. Comparison of the experimental data (symbols) for the carbon dioxide + cyclohexyl methacrylate system with calculated data (solid lines) obtained with the Peng-Robinson equation of state with $k_{ij} = 0.033$ and $\eta_{ij} = -0.013$.

Conclusions

High pressure phase behavior data of carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate systems are obtained at 313.2 to 393.2 K and pressure range of 1.7 to 20.6 MPa for binary mixtures. The Peng-Robinson equation of state models the pressure-composition isotherms for two carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate systems reasonably well using the independent-temperature mixture parameters

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