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High-Pressure Vapor-Liquid and Vapor-Liquid-Liquid Equilibria in the Carbon Dioxide + 1-Pentadecane System

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INTRODUCTION

Investigation of fluid multiphase behavior is of considerable interest to experimental and theoretical applications. In this work high-pressure phase equilibria of binary mixtures containing carbon dioxide, and pentadecane have been investigated. The Soave-Redlich-Kwong (SRK) equation of state coupled with classical van der Waals mixing rules (two-parameters conventional mixing rule - 2PCMR) was used to predict the complex phase behavior (critical curve, LLV line, isothermal VLE, and VLLE) of the carbon dioxide + 1-pentadecane binary mixture.

EXPERIMENTAL WORK

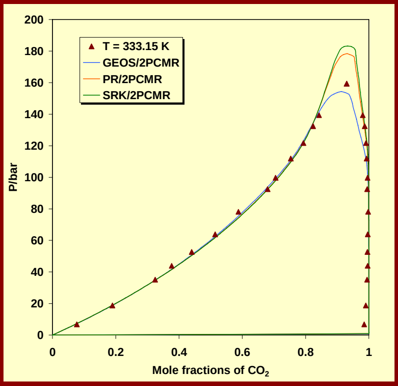
Phase equilibria measurements were made in a high-pressure visual cell with variable volume based on the static-analytical method. A detailed description of the apparatus and experimental procedure was presented in our previous papers [1-2]. In this study we present new phase equilibrium data obtained using a static-analytical method, in a high-pressure visual cell, for carbon dioxide + 1-pentadecane binary system. New vapor–liquid (VLE), liquid-liquid (LL), and vapor–liquid–liquid equilibria (VLLE) data for the carbon dioxide + 1-pentadecane system at 293.15, 303.15, 313.15, 333.15 and 353.15K up to 17.5 MPa, and phase compositions of the two liquid phases and vapor phase as a function of temperature along the liquid–liquid–vapor (LLV) line were measured.

MODELLING

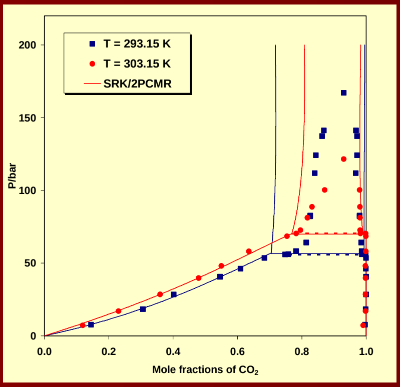
Measured and literature data were correlated with Soave-Redlich-Kwong (SRK), the General Equation of State (GEOS), and Peng-Robinson (PR) equations of state coupled with classical van der Waals mixing rules. As shown in recent papers [3-6], this approach fails to reproduce correctly the phase behavior, particularly the UCEP, the LLE and the critical lines, even the errors in bubble-points pressure are small. Therefore, a semi-predictive approach was used, in order to reproduce the type III phase behavior. In this work only the results obtained with the SRK/2PCMR equation of state are presented. One set of parameters (k_{12} = 0.096, l_{12} = 0.070) was used to predict VLE, VLLE, critical curve and LLV line [6]. The parameters set was obtained by a trial and error method in order to reproduce reasonably the minimum pressure of the critical curve and the minimum temperature of the liquid-liquid part of the critical curve.

RESULTS

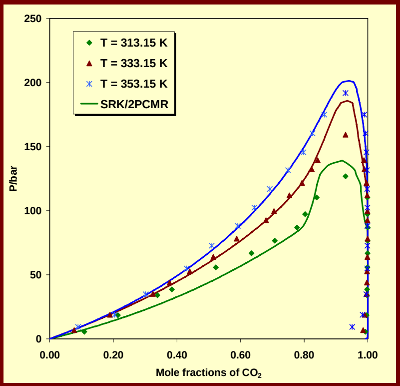
Some experimental results are shown in the figures below. The correlations and the predictions for binary system are included.



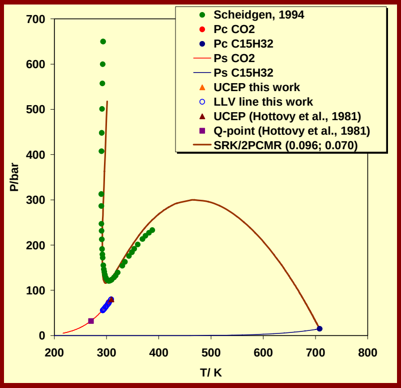
Comparison of experimental phase equilibrium data with correlations results by the GEOS, PR, SRK/2PCMR EoS for the carbon dioxide (1) + 1-pentadecane (2) system at 333.15 K.



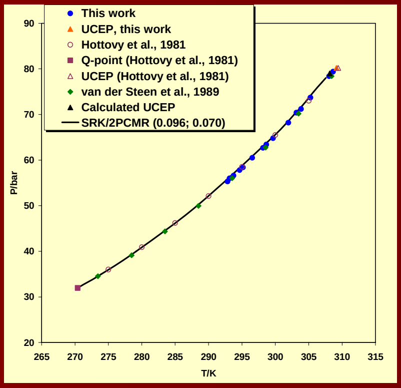
Comparison of experimental phase equilibrium data with correlations results by the SRK/2PCMR EoS for the carbon dioxide (1) + 1-pentadecane (2) system at 293.15 K and 303.15 K.



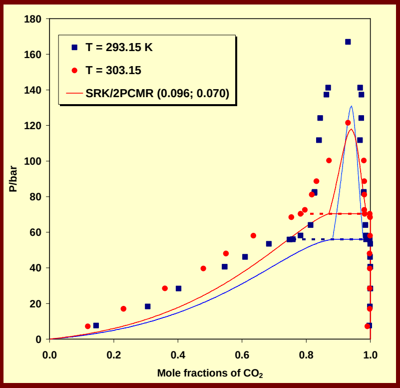
Comparison of experimental equilibrium data with correlations results by the SRK/2PCMR equations of state for the carbon dioxide + 1-pentadecane system at 313.15 K, 333.15 K, and 353.15 K.



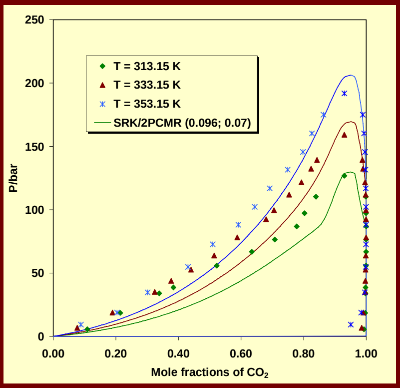
P-T fluid phase diagram of phase carbon dioxide + 1-pentadecane system.



P-T projection of the three phase curve, comparing experimental results and predictions with SRK/2PCMR (k_{12} = 0.096; l_{12} = 0.070).



Experimental results and predictions with SRK/2PCMR at 293.15 and 303.15 K.



Experimental results and predictions with SRK/2PCMR at 313.15, 333.15 and 353.15 K.

CONCLUSIONS

A visual high-pressure variable volume static-analytic apparatus was used to obtain VLE, VLLE data and critical points for carbon dioxide + 1-pentadecane system. New experimental data were measured at 293.15, 303.15, 313.15, 333.15 and 353.15 K. It was found that the new data agree well with those reported earlier. The three-phase LLV equilibrium data from 292.85 K up to the upper critical endpoint (309.15 K) were measured. The compositions of the two liquid phases as function of temperature are determined for this mixture. The SRK/2PCMR model is applied in a semi-predictive approach for the mixture under study. The simple model used is reasonably in representing the complicated topology of the phase behavior of the carbon dioxide + 1-pentadecane system.

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