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Predicting the phase equilibria of CO_2 + hydrocarbon systems with the PPR78 model (PR EOS and k_{ij} calculated through a group contribution method)

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Abstract

In 2004, we started to develop a group contribution method aimed at estimating the temperature dependent binary interaction parameters ($k_{ij}(T)$) for the widely used Peng–Robinson equation of state (EOS). Because our model relies on the Peng–Robinson EOS as published by Peng and Robinson in 1978 and because the addition of a group contribution method to estimate the k_{ij} makes it predictive, this model was called PPR78 (predictive 1978, Peng Robinson EOS). In our previous papers eleven groups were defined: CH_3, CH_2, CH, C, CH_4 (methane), C_2H_6 (ethane), CH_{aro}, C_{aro}, $C_{fused\ aromatic\ rings}$, $CH_{2,cyclic}$ and $CH_{cyclic}=C_{cyclic}$. It was thus possible to estimate the k_{ij} for any mixture containing alkanes, aromatics and naphthenes at any temperature. In this study, the PPR78 model is extended to systems containing carbon dioxide. To do so, the group CO_2 was added. The results obtained in this study are in many cases accurate.

Keywords: Equation of state; Vapor–liquid equilibrium; Predictive model; Binary interaction parameters; Critical locus; Carbon dioxide

1. Introduction

Carbon dioxide is an extremely important product of the chemical, pharmaceutical and petrochemical industries. Its main applications are production of coal liquids, petroleum processes [1–4], enhanced oil recovery [5–13], separation [14–18], supercritical fluid extraction, etc. Moreover, CO_2 is a greenhouse gas that affects the Earth's temperature and many efforts are devoted to the reduction of CO_2 emissions. In order to simulate and design the processes involving CO_2, it is necessary to predict the phase equilibrium of mixtures containing this molecule in both the sub-critical and critical regions. Simultaneous fulfillment of these objectives is a very difficult and challenging task for an equation of state (EOS). In order to meet these requirements, Jaubert and coworkers [19–23] developed a group contribution method allowing the estimation of the temperature dependent binary interaction parameters ($k_{ij}(T)$) for the widely used Peng–Robinson equation of state. A key point in this approach is that the k_{ij} between two components i and j is a function of temperature (T) and of the pure component critical temperatures (T_{ci} and T_{cj}), critical pressures (P_{ci}, P_{cj}) and acentric factors (ω_i, ω_j). This means that no additional properties besides those required by the EOS itself (T_c, P_c, ω) are needed. Because our model relies on the Peng–Robinson EOS as published by Peng and Robinson in 1978 and because the addition of a group contribution method to estimate the k_{ij} makes it predictive, we decided to call this new model PPR78 (predictive 1978, Peng Robinson EOS).

In our previous papers [19–21], eleven groups were defined: CH_3, CH_2, CH, C, CH_4 (methane), C_2H_6 (ethane), CH_{aro}, C_{aro}, $C_{fused\ aromatic\ rings}$, $CH_{2,cyclic}$ and $CH_{cyclic}=C_{cyclic}$. It was thus possible to estimate the k_{ij} for any mixture containing saturated hydrocarbons (n-alkanes and branched alkanes), aromatic hydrocarbons and cyclic hydrocarbons (naphthenes) at any temperature. In this study, the PPR78 model is extended to systems containing carbon dioxide. To do so, the CO_2 group was added. The interactions between this new group and the eleven ones previously defined (a total of 22 parameters) are determined. Today, it is thus possible to estimate, at any temperature, the k_{ij} between two components in any mixture containing paraffins, naphthenes, aromatics and CO_2.