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Evaluation of the CO_2 behavior in binary mixtures with alkanes, alcohols, acids and esters using the Cubic-Plus-Association Equation of State

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ABSTRACT

Knowledge regarding the high pressure phase behavior of CO_2 mixtures is of primary importance for designing, operating and optimizing many industrial processes, such as supercritical fluid extraction for pharmaceutical, food and biodiesel industries and oil recovery enhancement through CO_2 flooding.

In the present work, it is investigated how the CPA EoS (Cubic-Plus-Association equation of state) can be used for an adequate description of the VLE of an extensive series of CO_2 binary systems containing *n*-alkanes, *n*-alcohols, esters and *n*-acids, in a broad range of temperatures and pressures. These families constitute a series of non-self associating, associating and cross-associating components whose potential associative interactions with CO_2 are evaluated here.

A detailed investigation regarding the differing behavior of CO_2 depending on the nature of the second component and how the CPA EoS can best describe them is presented here, namely explicitly considering the CO_2 association and also evaluating also its different association schemes.

It will be shown that it is important to consider CO_2 self- and cross-association to describe the VLE of *n*-alkane and small alcohol/CO_2 systems. However, it is not necessary to consider CO_2 association when dealing with systems of heavy alcohols, esters or acids.

The CPA EoS provides very good results for the extensive range of CO_2 binary systems considered here using, for most of them, single, small, temperature independent, positive and chain length dependent binary interaction parameters.

1. Introduction

Binary systems consisting of CO_2 and alkanes, alcohols, acids and esters are of highly relevance for several technological applications. CO_2, being easily available in high purity, cheap, non-toxic and non-flammable [1], is currently considered as an important solvent for supercritical separation processes. Supercritical extraction can replace commonly used separation processes, such as distillation and liquid–liquid extraction, with the advantages of lower extraction times, increased flexibility and no degradation of extracts [2]. CO_2/hydrocarbons and CO_2/alcohols systems have been a focus of great attention due to their importance as supercritical fluid/cosolvent pairs [3]. It is known that short alkanes and alcohols are the best co-solvents for the extraction of biomaterials and drugs of relevance for the cosmetic, pharmaceutical, surfactant, and food industries [4].

CO_2/hydrocarbons and CO_2/alcohols mixtures are also present in the oil and gas industries. Petroleum fuel has played a vital role in human life, and mankind is almost totally dependent on it for transportation as well as in other sectors of the economy. However, increased oil consumption in developing economies, along with the uncertainty concerning petroleum availability, increases the need to optimize oil recovery processes [5].

One of the enhanced oil recovery methods is CO_2 flooding. High pressure CO_2 is injected in to the oil reservoir forming a low viscosity and surface tension fluid that is easily displaced [6].

Being able to accurately describe the phase behaviour of CO_2/hydrocarbons systems, in wide ranges of temperatures and pressures, is thus essential to understand an efficient oil displacement by CO_2 [7–8]. Additionally, CO_2/hydrocarbons phase equilibria are also important for plants processing oil and gas produced by CO_2 flooding that have high CO_2 concentrations. Data for CO_2/short alcohols is necessary for choosing the best alcohol to be injected in pipelines in order to prevent the formation of hydrates in oil and natural gas facilities [3].

Moreover, CO_2 and alcohol-containing systems are of relevance for methanol to hexanol synthesis through the syngas reaction, as

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