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Global phase behaviour in carbon dioxide plus *n*-alkanes binary mixturesHéctor Quinteros-Lama^{a,*}, Fèlix Llovell^b^a*Department of Industrial Engineering, Universidad de Talca. Merced 437, 3341717, Curicó, Chile*^b*Department of Chemical Engineering and Materials Science, IQS School of Engineering, Universitat Ramon Llull, Via Augusta 390, 08017, Barcelona, Spain*

Abstract

The family of carbon dioxide (CO₂) plus linear alkanes is one of the most common type of mixtures found in supercritical CO₂ separation and extraction. Consequently, an accurate thermodynamic representation is a key element for a proper process design. In this contribution, the PPC-SAFT equation of state is applied to the construction of the *serial-prediction-domain global phase diagram* (spd-GPD) of the CO₂ plus *n*-alkanes series to carefully analyse the presence of different thermodynamic phenomena. The goal is to address the capability of the equation to predict the global behaviour of these mixtures, with emphasis in accurately reproducing their mechanisms and topology. The results obtained reveal quantitative agreement with the available experimental data, including a complete description of the emergence of different phenomena as a function of the hydrocarbon chain length, such as azeotropy, double retrograde behaviour, critical transitions, mass and molar density inversions and critical pressure step points.

Keywords: Carbon dioxide; Alkanes; Equation of state (EoS); Global Phase Diagram (GPD); Critical transitions; double retrograde behaviour; PPC-SAFT

1. Introduction

The use of carbon dioxide (CO₂) as a supercritical fluid for a variety of applications related to extraction processes has become one of the most versatile technologies in the industry. Carbon dioxide is chosen because it is readily available, cheap, non-toxic and non-flammable, resulting into an ideal solvent to be used in this kind of processes. In addition, its relatively low critical temperature and pressure allow reaching supercritical conditions with a modest energy investment.

One of the most important applications of this compound is the use of supercritical CO₂ for the enhanced oil recovery (EOR) process. Nowadays, natural and industrial sources of CO₂ are used to enhance production of oil from older wells by injecting CO₂ into appropriate underground formations. Carbon dioxide is used selectively, primarily in wells which will benefit not only from repressurisation, but also from a reduction in viscosity of the

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