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Modeling the solubilities of high molecular weight *n*-alkanes in supercritical carbon dioxide

Sujit Kumar Jha, Giridhar Madras*

Department of Chemical Engineering, Indian Institute of Science, Bangalore-560012, India

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Abstract

The Peng-Robinson equation of state with quadratic mixing rules and a single adjustable parameter was used to model the solubilities of various high molecular weight solid *n*-alkanes in supercritical carbon dioxide. The key conclusion of the study is that the adjustable parameter, k_{ij}, varies linearly with the number of carbon atoms in the main chain of the *n*-alkane. Thus, the model can be used to predict the solubilities of various high molecular weight solid *n*-alkanes in supercritical carbon dioxide.

Keywords: Supercritical fluids; Solubility; Model; Alkane; Equation of state

1. Introduction

Fluids at temperature and pressure higher than their critical temperature and pressure are called supercritical fluids (ScFs). ScFs are used in the food [1], pharmaceutical [2] and petroleum [3] industries related applications. A significant amount of research has been devoted to their use as alternative environmentally friendly solvents [4]. Whenever a solid or a liquid is contacted by a supercritical fluid, phase equilibrium exists. Thus, it becomes important to study the phase behavior involved. The experimental methods and systems investigated in high-pressure fluid phase equilibria have been reviewed [5,6] and an exhaustive account on the experimental data on the solubilities of various organics in a variety of ScFs is available [7]. Since the experimental determination of the solubilities of various solutes in ScFs at various temperature and pressure is time consuming and expensive, modeling and prediction of the solubilities is important.

The solubility of high molecular weight *n*-alkanes in supercritical carbon dioxide (ScCO2) is of interest in the design of hydrocarbon processing systems [8,9]. Peters et al. [10] postulated a relationship between the solubility of liquid, i.e., relatively lower molecular weight, *n*-alkanes in supercritical solvents and the carbon number of the solute. The logarithm of the mole fraction of the solute was found to vary linearly with the carbon number. However, the formulation breaks down at near criticality of a solvent–*n*-alkane mixture. Reverchon et al. [9] correlated the solubility of solid *n*-octacosane ($C_{28}H_{58}$) and *n*-triacontane ($C_{30}H_{62}$) using the linear relationship between the logarithm of the solubility and the logarithm of the density of the pure solvent. Furuya and Teja [8] correlated their experimental data using an extension of the theory of dilute solution proposed by Mendez-Santiago and Teja [11]. The Krichevskii parameters were calculated based on the solubility of heavy *n*-alkanes in supercritical carbon dioxide and the results show that the variation of the Krichevskii parameter with the carbon number of the *n*-alkane is linear [12].

In this study, the Peng-Robinson equation of state (PR-EOS) with quadratic mixing rules has been used to calculate the solubilities of the solid *n*-alkanes in supercritical carbon dioxide. The adjustable binary interaction parameter in the model is found to vary linearly with the chain length of the *n*-alkanes. Based on this key observation, the binary interaction

* Corresponding author. Tel.: +91 80 22932321; fax: +91 80 3600683.
E-mail address: giridhar@chemeng.iisc.ernet.in (G. Madras).

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