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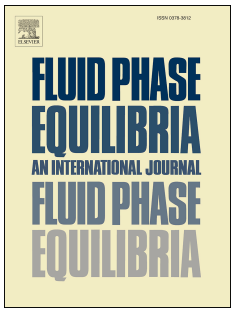

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A New Approach to Model Mixed Hydrates

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Keywords: gas hydrate; mixed hydrate; Carbon Captures and Storage; phase equilibrium algorithm; reference equation of state

Abstract

A new model for mixed hydrates is proposed, which is intended for modeling the formation of mixed hydrates in carbon capture and storage (CCS)-relevant mixtures. The model is based on the model developed by Ballard and Sloan [A.L. Ballard, E.D. Sloan Jr., Fluid Phase Equilib. 194 (2002) 371–383], which itself is based on the statistical approach by van der Waals and Platteeuw [J.H. van der Waals, J.C. Platteeuw, Adv. Chem. Phys. 2 (1959) 1–57]. The model of Ballard and Sloan contains a considerable amount of adjustable parameters for mixed hydrates and comparatively complex mixing rules, especially for the molar volume of mixed hydrates. For the newly developed mixed hydrate model, a simple mixing rule for the volume is used, which does not contain any adjustable parameters. Comparisons of the new model with experimental data for mixed hydrates in the ternary system carbon dioxide + methane + water show better results than the model by Ballard and Sloan. Results for the quaternary system nitrogen + oxygen + argon + water are in good agreement with the available experimental data. Furthermore, as in our previous work focused on modeling hydrates of pure gases [Fluid Phase Equilib. 427 (2016) 268] and contrary to other published hydrate models, reference equations of state are used in order to model phases in equilibrium with hydrates. A comprehensive study on phase equilibria with up to four phases in equilibrium for ternary mixtures forming gas hydrates and other solid phases was carried out in this work. The obtained results demonstrate the capabilities of the proposed mixed hydrate model and developed phase equilibrium algorithms.

1 Introduction

It was already discovered in 1934 by Hammerschmidt [1] that under unfavorable conditions natural gas hydrates might form in transportation pipelines, which could eventually lead to blockage of the pipelines. Since then, the gas hydrate related research increased and it was discovered that many substances in combination with water form gas hydrates under certain temperature and pressure conditions [2]. Many models for gas hydrates have been proposed since then; most of them are based on the statistical model suggested by van der Waals and Platteeuw [3]. One of the most sophisticated models for natural gas hydrates was developed by Ballard and Sloan and published in a series of articles [2,4–9]. Unlike the models that describe