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Phase equilibria of (CO_2 + H_2O + NaCl) and (CO_2 + H_2O + KCl): Measurements and modeling

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We report experimental measurements of the phase behavior of (CO_2 + H_2O + NaCl) and (CO_2 + H_2O + KCl) at temperatures from 323.15 K to 423.15 K, pressure up to 18.0 MPa, and molalities of 2.5 and 4.0 mol kg^{-1}. The present study was made using an analytical apparatus and is the first in which coexisting vapor- and liquid-phase composition data are provided. The new measurements are compared with the available literature data for the solubility of CO_2 in brines, many of which were measured with the synthetic method. Some literature data show large deviations from our results.

The asymmetric (γ–φ) approach is used to model the phase behavior of the two systems, with the Peng–Robinson equation of state to describe the vapor phase, and the electrolyte NRTL solution model to describe the liquid phase. The model describes the mixtures in a way that preserves from our previous work on (CO_2 + H_2O) the values of the Henry's law constant and the partial molar volume of CO_2 at infinite dilution Hou et al. [22]. The activity coefficients of CO_2 in the aqueous phase are provided. Additionally, the correlation of Duan et al. [14] for the solubility of CO_2 in brines is tested against our liquid-phase data.

1. Introduction

In CO_2-enhanced oil recovery (EOR) and carbon storage, the fluid systems of interest are (CO_2 + hydrocarbons + aqueous brines) and to design effective processes it is necessary to know the phase behavior and thermophysical properties of these mixtures. A gap analysis indicates that the available thermophysical data are quite limited, especially for phase equilibria in multi-component systems and mixtures containing brines [1]. The phase behavior of the (CO_2 + brine/water) system is also of great interest in geological research [2].

Na^+, K^+ and Cl^- are among the most abundant ions in seawater and reservoir brines. A number of experimental studies have been made on the (CO_2 + H_2O + NaCl) system but, at pressures above ambient, the available data are limited. Among previous works, Malinin and Savelyeva [3] and Malinin and Kurovskaya [4] obtained the composition of CO_2-saturated brine by degassing the sample and absorbing the CO_2 with KOH(aq). Altogether, they provided 35 data points at temperatures from 323.15 K to 423.15 K at a fixed pressure of 4.9 MPa. Nighswander et al. [5] measured the CO_2 solubility in water and 1.0 wt.% NaCl(aq) using a variable volume vessel, and the degassed CO_2 was measured volumetrically by bubbling through sulfuric acid solution. They also measured dew points but only at T = 433 K and 473 K. Rumpf et al. [6] and Kiepe et al. [7] measured the solubility of CO_2 in NaCl(aq) at temperatures up to 373.15 K and pressures up to 10 MPa. Drummond [8] made measurements of CO_2 solubility over wide ranges of temperature and pressure, and reported 444 data points; however, the data quality are assessed to be low by Akinfiev and Diamond [9]. All the above measurements were made by the synthetic method, using slightly different experimental arrangements. In the work of Bando et al. [10], the solubility was quantified by degassing a known amount of saturated solution. They report measurements at pressures between 10 MPa and 20 MPa at temperature between 303.15 K and 393.15 K. Most recently, Koschel et al. [11] determined the solubility of CO_2 in NaCl(aq) from calorimetric measurements of the enthalpy of mixing.

When it comes to the system (CO_2 + H_2O + KCl), the only available data are those of Kiepe et al. [7], Kamps et al. [12] and Liu et al. [13]. All these were measured with the synthetic method. The data of Kiepe et al. [7] cover similar ranges of temperature and pressure as for their studies for (CO_2 + H_2O + NaCl). Kamps et al. [12] provided data at T = 313–433 K, and pressure from 0.3 MPa to 9.4 MPa, while Liu et al. [13] provided data at T = 318.15 K and brine molality of 1.49 mol kg^{-1}.

The temperature, pressure and molality ranges of the published studies are summarized in Table 1. It can be seen that very few data pertain to both T > 373 K and p > 10 MPa, and only Nighswander et al.

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