

Phase Equilibria for $\text{CO}_2 + [(1 - x)\text{NaCl} + x\text{KCl}](\text{aq})$: Measurements and Modeling

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Vapor-liquid equilibria (VLE) is of fundamental importance in the oil industry. For CO_2 -EOR and carbon storage, the systems of interest are (CO_2 + hydrocarbons + brines) and a gap analysis indicates that the available experimental data are quite limited, especially for multi-component systems and mixtures containing brines.^[1] Moreover, most experimental data are for pressures below 10 MPa and lack a full composition analysis. The (CO_2 + brine) system is also of great interest in geological research.^[2] An analytical apparatus has been designed and built to study the VLE of representative fluids. The high-pressure cell is fitted with sapphire windows and a magnetic stirrer. Fluid phases are circulated by means of a dual-channel pump: one drawing from the top of the cell, and the other drawing through a special probe that may be rotated to sample fluid at a chosen height within the cell, thereby permitting the study of VLLE phenomenon. High-pressure sampling valves fitted in the recirculation loops permit aliquots to be withdrawn for analysis. The volatile components are flash vaporised in the sampling devices and analysed by GC. To validate the new apparatus, measurements have been made first on the binary system (CO_2 + H_2O) over a wide temperature and pressure range and the results compared with the literature published since 1937. VLE of CO_2 with both $\text{NaCl}(\text{aq})$, $\text{KCl}(\text{aq})$ and their mixtures have been measured at temperatures from 298.15 K to 448.15 K, pressure from 1 MPa to 20 MPa and various molalities of salt. VLLE data were also measured at low temperatures. Initial modelling was carried out with the Peng-Robinson EoS^[3] with the classical mixing rules and a temperature-dependent interaction parameter for the vapor phase, and the activity coefficient functions of Rumpf et al.^[4] and Duan and Sun^[5] for the liquid phase.