

Molar Volumes of mixtures of organics solvent (EtOH, DMSO, acetone, acetonitrile) and CO₂ in the vicinity of the mixture critical pressure for 308 K, 313 K 323 K and 333 K: Measurement and modelling using the NRHB-Model

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Volumetric properties are crucial for modeling the extraction of organic solvents with CO₂ from porous media, a process that takes place but is by far not limited to the production of aerogels. These processes are typically isobar and isotherm and the fraction of CO₂ inside the pores varies from $x_{\text{CO}_2}=0$ at the beginning of the extraction to $x_{\text{CO}_2}=1$ after completion. Unfortunately, besides the well-known binary system of EtOH/CO₂, comprehensive mixture volume data spanning the whole composition range is absolutely scarce. One reason for this is that most molar volume data for organic-solvent/CO₂ systems are published for saturated phases.

In this work, we report comprehensive mixture volume measurements for the binary systems consisting of ethanol (EtOH), dimethyl sulfoxide (DMSO), acetone and acetonitrile with CO₂ from 308 K to 333 K in 5 K increments and 6 MPa to 12 MPa in 1 MPa increments over the whole composition range in the single phasic regions in 0.05 mole fraction increments.

Measurements are carried out in a custom-built dynamic flow type setup, where two high precision syringe pumps dispense known molar flows of organic solvent and CO₂ into a capillary mixing section that leads to a Coriolis density meter where the mixture density is recorded and converted in molar volumes. Pressure regulation is achieved by a third back pressure syringe pump. Main advantages of this setup are the precise adjustment of single-phase compositions and the extraordinarily high acquisition rate of new molar volume data.

Measured mixture volume data showed very good agreement with published values for EtOH/CO₂ and acetone/CO₂. For DMSO and acetonitrile, we were not able to find published liquid phase mixture volumes from non-saturated mixtures. Modeling of mixture molar volumes was achieved with the Non-Random Hydrogen Bonding (NRHB) Model with one single temperature independent binary mixture parameter. Average relative deviation between measurements and model was found to be smaller than 2 % for each of the four systems. Besides the mixture molar volume data, the here presented measurements further allow to determine the vapor-liquid equilibrium within a 0.05 mole fraction interval.

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