VLE Measurements of Polar Binary Mixtures with Microwave Resonators

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The Kigali amendment to the Montreal protocol aims to phase out the production and use of high global warming potential (GWP) refrigerants. Fourth generation refrigerants, hydrofluoroolefins, have low global warming potential but can be flammable and may have poorer efficiency compared to third generation refrigerants, hydrofluorocarbons. Blends of third or fourth generation refrigerants with carbon dioxide can make an effective compromise, with lower GWP, low flammability, and higher efficiencies. Accurate predictions of the mixture phase behaviour are required for industry to design refrigeration processes. These predictions are made with equations of state, which require measurements of density, composition, and quality of coexisting phases as a function of temperature, to tune the binary interaction parameters affecting phase behaviour.

In this work, a microwave resonator designed for in situ measurements of composition, density, and vapour quality in vapour-liquid equilibrium (VLE) is used to characterise phase behaviour of non-polar and polar binary refrigerant mixtures. Microwave resonators operate by measuring the dielectric permittivity of a sample fluid contained within the cavity. This cavity is designed with three modes that measure the dielectric permittivity of the vapour phase, liquid phase, and the liquid volume fraction. Dielectric mixing rules are then used to determine the density, composition, and vapour quality of the co-existing phases.

Here, we apply this apparatus to binary mixtures of non-polar carbon dioxide (CO_2) and polar difluoromethane (R32). Binary mixtures were studied in the range of 0.2 to 0.8 mole fraction of CO_2, for temperatures between (203 and 353) K and pressures up to 10 MPa. Mixing rules for the dielectric permittivity of polar fluids have been proposed in literature but have not been measured to our knowledge. We explore the challenges of measuring polar-fluid mixtures with microwave resonators and suggest methods of improvement. Our results are based on a new pure fluid polarization model for R32 and the existing polarization model of CO_2. Presented are results of VLE measurements on the binary refrigerant mixtures for dielectric permittivity, composition, and density of the co-existing phases, as well as liquid volume fraction and vapour quality.