



Densities and dielectric permittivities for (carbon monoxide + carbon dioxide) mixtures determined with a microwave re-entrant cavity resonator



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ABSTRACT

A microwave re-entrant cavity resonator apparatus was used for the determination of dielectric permittivity, mole fraction composition and molar density of two binary (CO + CO₂) mixtures, with CO₂ mole fractions of approximately 0.25 and 0.50. The dielectric permittivity was measured with a relative combined expanded uncertainty ($k = 2$) less than or equal to 0.13% over the temperature range from $T = (255.05 \text{ to } 313.28) \text{ K}$ at pressures up to 8 MPa. The new dielectric permittivity data were used together with the pure fluid polarizability correlations to reduce the uncertainty in the mixture's mole fraction composition by factor of 15 relative to that provided by the supplier. Moreover, by applying the Harvey-Prausnitz mixing rule, we determined the mixture molar densities from measured permittivities to within 0.53% ($k = 2$) in a previously unstudied region. The new mixture density data near 6 MPa agree within 1.4% of predictions made with the multi-parameter equation of state optimized for combustion gases (EOS-CG). Comparison of these data with the EOS-CG and literature density values show that mixture density determinations based on dielectric permittivity measurements and the Harvey-Prausnitz mixing rule can also be accurate for gas mixtures containing appreciable amounts of a polar substance.

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1. Introduction

Accurate knowledge of the thermodynamic properties of carbon dioxide-rich mixtures is a prerequisite for the carbon capture and storage (CCS) technology, which is often discussed for reducing CO₂ emissions of power plants fired by fossil fuels. The fundamental properties of mixtures involved in CCS-processes are of great importance for the development and validation of different engineering models. The performance of currently established models in predicting such thermodynamic properties, such as the multi-parameter Helmholtz Equation of State for Combustion Gases and Combustion-Gas-like Mixtures (EOS-CG) of Gernert and Span [1] and the GERG-2008 equation of state for natural gases and similar mixtures developed by Kunz and Wagner [2], is limited by the quality and quantity of the underlying data. This is particularly pertinent for mixtures containing compounds such as carbon monoxide, which are less frequently studied due to their toxicity and/or reactivity.

Carbon monoxide (CO) is considered as a secondary combustion gas component in CCS-related processes. Because of the hazardous and toxic nature of the pure CO and its fluid mixtures as well as its capacity to react with metals (Mond reaction [3]) at high pressures, experimental data for mixtures containing CO are very sparse and the available data are of limited accuracy. For the binary (CO + CO₂) system only three (p, ρ, T, x)-data sets [4–6] are available in the literature. Mallu *et al.* [4,5] reported densities for three binary (CO + CO₂) mixtures over a temperature range from (323 to 423) K and at pressures up to 6.5 MPa, and Cipollina *et al.* [6] published values in the supercritical region at very high pressures (>22.5 MPa).

To reduce the difficulties of conducting measurements in fluid mixtures, it is helpful to use robust experimental apparatus that require relatively small sample volumes. Instruments based on microwave re-entrant cavities have shown their applicability to the determination of thermodynamic properties for aggressive and hard-to-measure substances. For instance, Rogers *et al.* [7] and May *et al.* [8,9] have shown the power of the microwave techniques by phase behaviour measurements on acid-gas/heavy oil systems and multi-component gas condensate mixtures, respectively. Moreover, Tsankova *et al.* [10] recently used a microwave

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re-entrant cavity resonator to accurately measure the dielectric permittivity, electric dipole moment and molecular polarizability of pure gaseous CO over a wide range of temperature and pressure.

In the present work, we have used the same microwave re-entrant cavity resonator described by Tsankova *et al.* [10–12] to determine key properties of mixtures relevant to CCS-processes. We measured the dielectric permittivities of (0.7493 CO + 0.2507 CO₂) and (0.4959 CO + 0.5041 CO₂) mixtures over the temperature range from $T = (255.05 \text{ to } 313.28) \text{ K}$ and at pressures up to 8.0 MPa. The dielectric permittivity data were combined with the pure fluid polarizabilities to first improve the uncertainty in the supplier's mole fraction composition. Then the polarizability mixing rule of Harvey and Prausnitz [13] was used to determine molar mixture densities from the dielectric permittivity data. Such an approach was previously demonstrated to be effective with gas mixtures of non-polar compounds [12]; in this work we applied the technique for the first time to a gaseous mixture containing a polar compound. These results show how the use of microwave re-entrant cavity resonators can be further extended to the determination of properties in difficult to handle fluid mixtures and deliver new data relevant to the development of thermodynamic models for CCS applications.

2. Theory

The dielectric permittivity ϵ_r and the molar density ρ of a polar fluid, such as carbon monoxide, are related to its molar polarizability P by the expression of Kirkwood:

$$P = \frac{1}{\rho} \frac{(\epsilon_r - 1)(2\epsilon_r + 1)}{9\epsilon_r} \quad (1)$$

The molar polarizability is generally a weak function of density, and the dependence of a pure fluid's polarizability is often represented using the dielectric virial expansion:

$$P = A_\epsilon(1 + b_\epsilon\rho + \dots) \quad (2)$$

Here A_ϵ and b_ϵ are the first and the second dielectric virial coefficients, respectively. The term A_ϵ contains information about the isolated molecule's properties, namely the molecular polarizability α_e and electric dipole moment μ_e :

$$A_\epsilon = \frac{N_A}{3\epsilon_0} \left(\alpha_e + \frac{\mu_e^2}{3k_B T} \right) = A'_\epsilon + \frac{A_\mu}{T}, \quad (3)$$

where $N_A = 6.0220 \cdot 10^{23} \text{ mol}^{-1}$ is the Avogadro constant, $\epsilon_0 = 8.8542 \cdot 10^{-12} \text{ F m}^{-1}$ is the dielectric permittivity in vacuum, and $k_B = 1.3806 \cdot 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant. The second dielectric virial coefficient is usually a reasonably weak function of temperature, except for the CO₂ molecule, whose large quadrupole moment is the reason for the relatively large temperature dependence in b_ϵ [14].

Recently, we used a re-entrant cavity resonator to measure the dielectric permittivity of pure CO from (255 to 313) K at pressures from (2 to 8) MPa for the first time with a combined expanded uncertainty ($k = 2$) of less than $52 \cdot 10^{-6}$ [10]. By combining these dielectric permittivity data with molar densities calculated from the measured temperature and pressure using the reference equation of state for CO of Lemmon and Span [15] (as implemented in [16]), Tsankova *et al.* [10] determined experimental values of $\alpha_e = 2.176 \cdot 10^{-40} \text{ C}^2 \cdot \text{m}^2 \cdot \text{J}^{-1}$ and $\mu_e = 3.584 \cdot 10^{-31} \text{ C} \cdot \text{m} \approx 0.107 \text{ D}$ ($1 \text{ D} \approx 3.335641 \cdot 10^{-30} \text{ C} \cdot \text{m}$), both with relative combined standard uncertainties of around 1.0%. The second dielectric virial coefficient was determined to be $b_\epsilon = (1.015 \pm 0.044) \text{ cm}^3 \cdot \text{mol}^{-1}$; the variation of b_ϵ over this temperature range was not measurable within the estimated experimental uncertainty.

For many fluids, such as CO₂ and other components of natural gas, which have been characterised extensively, Harvey and Lemmon [14] provided wide-ranging correlations for their polarizability with the following functional form based on a generalised version of Eqs. (2) and (3):

$$P = A'_\epsilon + \frac{A_\mu}{T} + B_\epsilon\rho + C\rho^D. \quad (4)$$

Here, the symbol P refers to the molar polarizability whereas in reference [14] it refers to the electric polarization, which is given by ρP in our notation. In this formulation, the first dielectric virial coefficient A_ϵ is separated into a non-polar part, A'_ϵ , and a polar part, A_μ . The latter term is temperature independent and only non-zero for fluids with electric dipole moments. The quantities A'_ϵ , B_ϵ and C in Eq. (4) are in general, temperature-dependent parameters defined by the auxiliary equations given by Harvey and Lemmon [14]. The exponent parameter D is temperature independent. In this work, the molar polarizability of CO₂ was calculated using Eq. (4) with the parameters given by Harvey and Lemmon [14]; as CO₂ is non-polar, $A_\mu = 0$.

In the limit of zero density, the polarizability of a gas mixture can be rigorously calculated via a simple mole-fraction average of the first dielectric virial coefficients of the component pure fluids, $A_{\epsilon,i}$. Thus, measurements of a binary mixture's molar polarizability obtained at low to moderate pressures can be used together with the component $A_{\epsilon,i}$, to determine the mixture's mole fraction composition, x_i , through the relationship

$$\lim_{\rho \rightarrow 0} \left(P_{\text{mix}} - \sum_i x_i A_{\epsilon,i} \right) = 0. \quad (5)$$

This procedure, which is analogous to several others that make use of the ideal gas limit to constrain binary mixture compositions [17], does not require accurate knowledge of the gas mixture molar density because $\lim_{\rho \rightarrow 0} (\rho - p/RT) = 0$. It only requires that the mixture polarizability measurements be made along isothermal pathways at pressures where the extrapolation to zero density can be done accurately. The uncertainty with which the binary mixture composition can be determined is essentially set by the statistical uncertainty in the extrapolated value of P_{mix} at $\rho = 0$.

At finite pressures, Tsankova *et al.* [12] have demonstrated how measured values of the mixture dielectric permittivity, $\epsilon_{r,\text{mix}}$, can be used to estimate the mixture molar density, ρ_{mix} , at the experimental temperature, pressure and composition. The procedure involves inverting the corresponding states method of predicting the polarizability of the mixture from those of the component fluids using the dielectric mixing rule developed by Harvey and Prausnitz [13]. To predict the molar polarizability of a mixture, Harvey and Prausnitz proposed mixing the pure-component electric polarizations at constant temperature T and reduced molar mixture density $\rho_{r,\text{mix}} = \rho_{\text{mix}} \sum_i x_i v_i^*$, where x_i is the mole fraction and v_i^* is the critical volume of the pure component i , according to:

$$\rho_{\text{mix}} P_{\text{mix}} = \sum_i \Phi_i^* \cdot \frac{\rho_{r,\text{mix}}}{v_i^*} \cdot P_i \left(T, \frac{\rho_{r,\text{mix}}}{v_i^*} \right). \quad (6)$$

Here, the volume fraction of each component is defined as $\Phi_i^* = x_i v_i^* / \sum_j x_j v_j^*$, the quantity $\rho_{r,\text{mix}} / v_i^*$ is the equivalent molar density of the pure component i at the same reduced density as the mixture. We note that eq. (6) is the correct version of the mixing rule; Eq. (7) of Ref. [12] was written incorrectly. Evaluating the polarizability of each pure component at the same temperature and reduced density and combining them according to the right hand side of Eq. (6) provides an estimate of the measurable quantity $(\epsilon_{r,\text{mix}} - 1)(2\epsilon_{r,\text{mix}} + 1)/(9\epsilon_{r,\text{mix}})$.

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