Interfacial Tensions of (CO₂ + N₂ + H₂O) System at Temperatures of (298 to 448) K and Pressures up to 40 MPa

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Abstract

Interfacial tension measurements of the (CO₂ + N₂ + H₂O) and (N₂ + H₂O) systems are reported at pressures of (2 to 40) MPa, and temperatures of (298.15 to 448.15) K. The pendant drop method was used in which it is necessary to know the density difference between the two phases. To permit calculation of this difference, the compositions of the coexisting phases were first computed from a combination of the Peng-Robinson equation of state (applied to the non-aqueous phase) and the NRTL model (applied to the aqueous phase). Densities of the non-aqueous phase were computed from the GERG-2008 equation of state, while those of the aqueous phase were calculated knowing the partial molar volumes of the solutes. The expanded uncertainties at 95% confidence are 0.05 K for temperature, 0.07 MPa for pressure, 0.019-γ for interfacial tension in the binary (N₂ + H₂O) system; and 0.032γ for interfacial tension in the ternary (CO₂ + N₂ + H₂O) system. The interfacial tensions in both systems were found to decrease with both increasing pressure and increasing temperature. An empirical correlation has been developed for the interfacial tension of the (N₂ + H₂O) system in the full range of conditions investigated, with an average absolute deviation of 0.20 mN·m⁻¹, and this is used to facilitate a comparison with literature values. Estimates of the interfacial tension for the (CO₂ + N₂ + H₂O) ternary system, by means of empirical combining rules based on the coexisting phase compositions and the interfacial tensions of the binary sub-systems, (N₂ + H₂O) and (CO₂ + H₂O), were found to be somewhat inadequate at low temperatures, with an average absolute deviation of 1.9 mN·m⁻¹ for all the conditions investigated. To enable this analysis, selected literature data for the interfacial tensions of the (CO₂ + H₂O) binary system have been re-analysed, allowing for improved estimates of the density difference between the two phases. The revised result on eleven isotherms were fitted with empirical models that generally represent the data to within 1 mN·m⁻¹.

Keywords: carbon dioxide; carbon storage; density; high pressure; interfacial tension; nitrogen; water.

Introduction

Carbon abatement by carbon dioxide capture and storage (CCS) is one of the transitional technologies that can be used to ensure energy security and diversity whilst mitigating climate change effects, by reducing CO₂ emissions into the atmosphere. CCS may contribute up to one fifth of the planned reduction in CO₂ emissions by 2050 [1]. Carbon dioxide released during the combustion of fossil fuels in power plant and other industrial processes can be captured by various techniques, compressed, transported to the storage site by pipeline, and finally injected into the underground storage site. Suitable storage sites include deep saline aquifers, which have the greatest estimated storage capacity, depleted oil and gas reservoirs, and unmineable coal seams. In the case of oil fields, CO₂ may be used for enhanced oil recovery (EOR) prior to final storage. There exists a wealth of experience in CO₂-EOR using high purity CO₂ from natural sources; however, the impact of the higher levels of impurities expected with industrially-captured CO₂ streams requires further investigation in relation to both EOR and long-term storage. Potential impurities include N₂, H₂, O₂, Ar, H₂S, SO₂, NO_x, CO and CH₄ [2]. The composition the CO₂ stream for storage will depend upon the various CO₂ sources feeding the storage site, the capture methods used, the safety and corrosion constraints associated with pipeline transport, and any identified storage constraints.

In carbon storage, CO₂ is expected to be injected into sedimentary formations at depths of greater than 800 m, corresponding to temperatures above 310 K and pressures above 8 MPa, in a supercritical state with density greater than 300 kg·m⁻³ [3]. To ensure an adequate flow, the CO₂ must be injected at a pressure higher than that of the existing reservoir fluids [4]. Envisioned CO₂ storage conditions involve temperatures up to 423 K with pressures up to 50 MPa [2]. The principal storage mechanisms in order of increasing time scale are: (a) structural trapping, where buoyant CO₂ is retained below impermeable caprocks; (b) capillary trapping, whereby CO₂ is immobilised in the pore space by means of interfacial forces; (c) solubility trapping, whereby the CO₂ dissolves in the reservoir fluids; and (d) mineralization, in which the CO₂ reacts to form carbonate minerals [5]. Each of these processes is strongly influenced by the thermophysical properties of CO₂ and its mixtures with reservoir fluids (oils and brines) at reservoir conditions. Knowledge of the fundamental thermophysical properties of relevant fluid mixtures under these extreme conditions is therefore crucial for modelling the long-term performance of the storage project. In particular, interfacial properties, especially interfacial tension between CO₂ and reservoir fluids in the presence of impurities, are fundamental for predicting the storage capacity of sedimentary formations and for estimating safe injection pressures that avoid fracturing [6]. The present paper is a contribution to the underpinning science in this area.

Interfacial tension (IFT) measurements of the (N₂ + H₂O) [7; 8; 9], (N₂ + n-alkane) [10; 11], (CO₂ + H₂O) [3; 12; 13; 14; 15; 16], (CO₂ + n-alkane) [10; 17; 18; 19], (CO₂ + brine) [12; 14; 16; 20; 21; 22; 23; 24], and (CO₂ + N₂ + H₂O) [8] systems under the elevated pressures and temperatures of interest have been studied by various authors. The effects of surfactants on (CO₂ + H₂O) system IFTs have also been investigated [15; 25; 26].

Wiegand and Franck [7] measured the IFT of water and various non-polar fluids including nitrogen, from pressures of (c.a. 20 to 280) MPa, at temperatures of (298 to 573) K. Lower pressure points are only available at $T = 298$ K, creating difficulty at higher temperatures in extrapolating back to compare with the

surface tension of water [27]. Wiegand and Franck provide data at only two pressures, approximately 20 MPa and 40 MPa, in the range applicable for CO₂ storage. Interfacial tensions of the (N₂ + H₂O) system measured at or above 373 K, was found initially to decrease with pressure until about 75 MPa, after which the IFT reached a pseudo-plateau, before increasing gradually with pressure. Tian et al. [9] measured the IFT of water and nitrogen, from pressures of (10 to 100) MPa, at temperatures of (298 to 473) K. Measurements at $p = 0.1$ MPa were made at $T = 298$ K only. Yan et al. [8] also measured this system, from pressures of (1 to 30) MPa, at temperatures of (298 to 373 K). These three data sets are in general agreement with each other, but with noticeable deviations at the lowest pressures reported by Tian et al.

The IFT of the (CO₂ + H₂O) system have been measured by Georgiadis et al. from (298 to 374) K and (1 to 60) MPa [3]. In that work, the results were fitted with dual linear correlations at lower temperatures, to reflect the existence of two distinct regions separated by an abrupt change in the pressure derivative of the IFT. At the two higher temperatures of 343.3 K and 374.3 K, the IFT was fitted with a rational function, reflecting the more gradual and steady decline of the IFT with increasing pressure at temperatures well above the upper critical end point of the (CO₂ + H₂O) system. Georgiadis et al. also discussed the factors that affect the accuracy of IFT measurements by the pendant drop method, including the time dependence arising from interfacial mass transfer, the effects of contamination by surface-active impurities, and sensitivity to erroneous temperature measurements. These factors were invoked to explain the scatter and partial inconsistency of the available literature data.

Duchateau and Broseta showed that the IFT of (gas + brine) systems is simply related to the surface tension of the brine and the (gas + H₂O) interfacial tensions at the same pressure and temperature [27]. Along an isotherm, they found that increasing the salinity shifted the (gas + brine) IFT to higher values. Li et al. measured (CO₂ + brine) IFT for various salts over wide ranges of pressure, temperature and molality, and provided a simple empirical correlation that can be used to predict IFTs of other brine systems [24] at high pressures.

The interfacial tension for various compositions of the ternary mixture (CO₂ + N₂ + H₂O) have been measured by Yan et al. [8] at pressures of (1 to 30) MPa and temperatures of (298 to 373) K. The interfacial tension of the ternary mixture (CO₂ + H₂S + H₂O), with 70 mol% CO₂ and 30 mol% H₂S in the initial gas mixture, have been studied by Shah et al. [6] at $T = 350$ K and at pressures up to 15.6 MPa. They found that the IFT is approximately equal to the molar average IFT of the binary systems of (H₂S + H₂O) and (CO₂ + H₂O) at the same temperature and pressure.

A number of theoretical approaches have been reported in the literature that provide either predictive or correlative descriptions of the interfacial properties of binary and multicomponent systems. Applications of density functional theory (DFT) coupled with a molecular equation of state have been reported by both Llovel et al. [28] for (CO₂ + hydrocarbon) systems and by Georgiadis et al. [18] for (CO₂ + H₂O) and (CO₂ + hydrocarbon) systems. This method is fully predictive and was shown to provide a generally good account of the available experimental data. Unfortunately, DFT is computationally demanding and unsuitable for routine application. Much simpler gradient-theory (GT) approaches have been successful when combined with either cubic or molecular equations of state. These methods involve binary ‘influence’ parameters specifically related to the interfacial properties; the like-like influence parameters being fitted to surface

tension data for the pure components and the unlike influence parameter being either estimated from a combining rule or fitted to experimental data. Miqueu et al. [29] [30] combined GT with the Peng-Robinson equation of state and to describe the IFT of binary and multicomponent (CH_4 + hydrocarbon) and (CO_2 + hydrocarbon) systems without fitting the unlike influence parameters. Muller et al. [31] and Mejia et al. [32] also applied GT predictively for mixtures, in this case using SAFT equations of state, and obtained good results for (alcohol + water) and (CO_2 + hydrocarbon) systems. On the other hand, to adequately represent the IFT of the more challenging (CO_2 + H_2O) system by means of a GT, Lafitte et al. [33] resorted to fitting the unlike influence parameter. Yan et al. [8] tested a GT model against their experimental data for the (CO_2 + N_2 + H_2O) system but concluded that it was unsuitable. Khosharay and Varaminian [34] combined the cubic-plus-association equation of state (CPA EOS) with GT and applied this successfully to systems involving high concentrations of carbon dioxide in the vapour phase, using data from Georgiadis et al. [3] and Yan et al. [8]. The model predicted (N_2 + H_2O) interfacial tensions with average absolute relative deviations (AAD) of 0.5 %; (CO_2 + H_2O) interfacial tensions with AAD of 2.0 %; and (CO_2 + N_2 + H_2O) interfacial tensions with AAD of 1.8 %.

To summarise the literature, measurements of (CO_2 + H_2O) and (N_2 + H_2O) IFT under reservoir conditions have been carried out by several authors. (Gas + brine) IFT can be obtained from empirical correlations if the (gas + H_2O) IFT and the brine surface tension are both known. Only one source of literature data is available for the IFT of the (CO_2 + N_2 + H_2O) system up to 30 MPa and 373 K. Fully-theoretical approaches to predicting the IFT by DFT are cumbersome but the simpler GT methods may be only correlative for aqueous systems. The possibility of estimating the IFT in ternary systems from a simple molar average of binary data is appealing in an engineering context, but requires further investigation. Accordingly, the object of this research was to investigate IFT in the (CO_2 + N_2 + H_2O) ternary system and its dependence upon temperature and pressure at CO_2 storage conditions.

Experimental Section

Apparatus.

The apparatus for carrying out pendant drop IFT measurements in corrosive environments at high temperatures (up to 473 K) and high pressures (up to 50 MPa) is shown in figure 1; it has been described in detail elsewhere [20]. The axisymmetric drop shape analysis (ADSA), based on integration of the Young-Laplace equation, was performed by commercial software (Advanced DROPimage, Ramé-Hart Instrument Co.). The high pressure vessel was made from Hastelloy C-276 and was fitted with axially opposed Poulter-type sapphire windows. In order to regulate the temperature, the vessel was contained within an insulated aluminium jacket fitted with electric cartridge heaters and a temperature sensor, and operated with a PID temperature controller. Fluids were injected from high-pressure syringe pumps. The water was injected through a capillary tube entering the optical cell from the top, thereby forming pendant drops. A calibrated platinum resistance thermometer was inserted into the wall of the view cell for the purpose of measuring the temperature. A pressure transducer, located in the tubing external to the view cell, was used to measure the pressure. Standard uncertainties were 0.025 K for temperature and 35 kPa for pressure.

Materials.

The sources and purities of the chemicals used are summarised in table 1. Pure deionised and degassed water (electrical resistivity $> 18 \text{ M}\Omega\cdot\text{cm}$) was used. BOC supplied nitrogen with a specified mole fraction purity > 0.99998 and the mixture $[x \text{ CO}_2 + (1 - x) \text{ N}_2]$ with $x = 0.5120$, $U(x) = 0.0050$, and impurities (by mole fraction) of less than 0.00005, where, $U(x)$ is the expanded uncertainty of the mole fraction at 95 % confidence.

Validation.

The pendant drop method is well-established, and the surface tension of water was measured at $T = 298.44 \text{ K}$ for validation. The surface tension was measured to be $(71.9 \pm 0.1) \text{ mN}\cdot\text{m}^{-1}$, in close agreement with the value $(71.93 \pm 0.05) \text{ mN}\cdot\text{m}^{-1}$ obtained from the IAPWS recommended correlation by means of the REFPROP 9.1 database [35; 36; 37].

Data Analysis.

The interfacial tension was evaluated from the relation

$$\gamma = \Delta\rho g R_0^2 / \beta, \quad (1)$$

where $\Delta\rho$ is the density difference between the two fluid phases, g is the gravitational acceleration, R_0 is the radius of curvature at the apex of the drop, and β is a dimensionless shape parameter.

The measured o.d. of the capillary tube for creating the pendant drop was $(1.59 \pm 0.01) \text{ mm}$ and this was used as an *in-situ* calibration length scale.

The most suitable time for analysis after forming a pendant drop was estimated by considering the time required to establish diffusive equilibrium between the drop and surrounding fluid phase, as described by Georgiadis et al. [3]. The diffusion coefficient and solubility of N_2 in water [38] were considered in these calculations and, since the diffusion coefficient increases rapidly with temperature, estimated equilibration times fell from (200 to 500) s at $T = 298 \text{ K}$ to (100 to 300) s at higher temperatures. These times were also applied in the case of the $(\text{CO}_2 + \text{N}_2 + \text{H}_2\text{O})$ system.

Density Corrections

In this study, we present new experimental measurements for the IFT of $(\text{N}_2 + \text{H}_2\text{O})$ and $(\text{CO}_2 + \text{N}_2 + \text{H}_2\text{O})$. We also reappraise some of the available literature for the IFT of $(\text{CO}_2 + \text{H}_2\text{O})$. For each system, it is necessary to know the difference $\Delta\rho$ between the densities of the aqueous and non-aqueous phases. We argue below that it is sufficient, for purposes of estimating the non-aqueous-phase density, to ignore the presence of H_2O under the conditions investigated here. As highlighted by Cumicheo et al. [39], and despite the limited mutual solubility of the aqueous and non-aqueous components studied in this work, the approximation of using pure bulk phase densities instead of the equilibrium phase densities of the mixture can affect the accuracy of the calculated IF, especially for conditions near to a barotropic transition. Therefore, we account for the presence of CO_2 and/or N_2 in the aqueous phase and estimate

the densities from available phase-equilibrium models and partial molar volumes; non-aqueous-phase densities are determined from reference equations of state.

(CO₂ + H₂O) System Density Difference.

The interfacial tension measurements reported by Georgiadis et al. [3] were based on the assumption that the density differences $\Delta\rho$ could be approximated by the difference between the pure component densities of H₂O and CO₂. In this work, we apply corrections to the bulk-liquid phase densities to account for CO₂ solubility in water, using the solubility model reported recently by Hou et al. [40], the equation of state of pure water [36], and the model of Sedlbauer et al. [41] for the partial molar volumes of CO₂ in aqueous solution. As detailed in tables 2 and 3 and ref. [40], the solubility model of Hou et al. was of the asymmetric type with the Peng-Robinson (PR) equation of state to describe the CO₂-rich phase and an extended form of Henry's law combined with the NRTL activity-coefficient model to describe the aqueous phase. The parameters of this PR-NRTL model were regressed against experimental measurements at temperatures from (298.15 to 448.15) K and pressures from (1.5 to 18.0) MPa. We have validated this model for application at pressures of up to 200 MPa and temperatures below 448 K by comparison with the CO₂-H₂O solubility model of Duan and Sun [42], with average absolute deviations of 2 %. At higher temperatures, there are noticeable differences between the two models but these have negligible effects on the calculated liquid density. Having found the composition of the liquid phase, the molar volume V_{mix} , and hence the density, was determined from the partial molar volumes V_i of the components as follows:

$$V_{\text{mix}} = \sum_{i=1}^N V_i x_i , \quad (2)$$

where N is the number of components. The partial molar volume of water was taken to be that of pure water at the same temperature and pressure, while that of CO₂ was obtained from the model of Sedlbauer et al. [41].

A comprehensive study of the density of H₂O-saturated CO₂, covering the whole range of temperatures and pressures of interest in this work, has recently been completed [43]. According to this, the differences between the density of H₂O-saturated CO₂ and pure CO₂ reach a maximum of (5 to 8) kg·m⁻³ at densities of around 500 kg·m⁻³, depending upon temperature, but decay rapidly at higher densities. The consequence of this is that the estimated relative effect of the H₂O present in the CO₂-rich phase upon the difference $\Delta\rho$ is always smaller than about 1 %. Given the smallness of this difference and the lack of a thermodynamic model that accurately captures the experimental results, we follow Georgiadis et al. in calculating the density of the CO₂-rich phase from the CO₂ equation of state of Span and Wagner [44] as implemented in REFPROP 9.1 [35]. However, we expand the uncertainty of $\Delta\rho$ to allow for the neglect of the H₂O in the CO₂-rich phase.

To illustrate the importance of accurate phase densities for this system, the calculated densities at two temperature are plotted in figure 2 (a) and (b) for the aqueous and non-aqueous phases respectively. The densities of the aqueous phase are seen to increase with pressure as expected. For the (CO₂ + H₂O) system, this increase is in part due to the increasing mole fraction of dissolved CO₂. At $T = 298.15$ K, a change of slope can be discerned at the three-phase equilibrium pressure where the phase behaviour of the system

changes for gas-liquid to liquid-liquid equilibrium. Looking at the non-aqueous phase, the step change in density, which occurs when the three-phase line is crossed, is also clear. As the pressure is further increased the density of the CO₂-rich phase starts to approach that of the aqueous phase. Consequently, small changes in the calculated phase densities, such as the difference between including or neglecting CO₂ dissolution in the liquid phase, can have a much larger relative effect on $\Delta\rho$ and hence on the IFT. In figure 3, we plot the difference between the calculated densities of CO₂-saturated water and of pure water along the isotherms studied by Georgiadis et al. As expected, this shows that the effect of CO₂ saturation is greatest at low temperatures and high pressures where $\Delta\rho$ is small and sensitive to small changes in the density of either phase.

(N₂ + H₂O) System Density Difference.

For the solubility of N₂ in H₂O we use the same PR-NRTL model with a correlation for the Henry's law constant from Fernández-Prini et al. [45] and NRTL interaction parameters set to zero. The binary interaction parameter in the PR equation for N₂-H₂O was taken from Abudour et al. [46] and the partial molar volume of N₂ in aqueous solution was obtained from Mao and Duan [47]. The solubility model was compared with that of Mao and Duan [47], applicable at pressures from (1 to 60) MPa and temperatures from (273 to 590) K, and absolute differences in the mole fraction of N₂ were found to be less than 3.2 %. The calculated densities of N₂-saturated H₂O were found to differ from those of pure H₂O by less than 2 kg·m⁻³. The N₂-rich phase was treated as pure N₂ and its density was calculated from the equation of state of Span et al. [48]. The calculated phase densities at two temperatures are illustrated in figure 2. In this case, $\Delta\rho > 670$ kg·m⁻³ and the limited mutual solubility of the system has a negligible effect on the calculated density difference.

(N₂ + CO₂ + H₂O) System Density Difference.

For the ternary system, determining the phase compositions requires knowledge of the overall system composition which, in the present work, was estimated from the approximately-known amounts of gas and liquid injected into the known volume of the view cell. The phase compositions were then determined by means of isochoric flash calculations using the models detailed above for phase-equilibrium and phase-density calculations together with the overall system composition. In fact, with the vessel never more than half full of water, the calculated ratio of the mole fractions of N₂ and CO₂ in the gas phase was found to be within 1 % of that in the feed gas. Having found the phase compositions, the liquid density was determined from Equation (2), with partial molar volumes as before, and the gas-phase density was calculated from the mixture model available in the REFPROP 9.1 database incorporating the equations of state of the pure components [35; 36; 44; 48; 49]. Again, we plot the calculated phase densities at two temperatures in figure 2. In this case the results are intermediate between the (CO₂ + H₂O) and (N₂ + H₂O) binary systems but $\Delta\rho > 390$ kg·m⁻³ and the mutual solubility has only a marginal effect on the density difference.

Results

(CO₂ + H₂O) system.

Applying the density correction to the raw data of Georgiadis et al. [3], we obtained the revised interfacial tension values given in table 4 at temperatures between (297.9 and 374.3) K and pressures up to 60 MPa. The corresponding phases in equilibrium for the (CO₂ + H₂O) mixture are indicated in the table as liquid + gas (L-G), liquid + liquid (L-L) or liquid + supercritical fluid (L-SC). Here, the CO₂-rich phase is designated according the relation between the state in question, the three-phase line and the temperature T_c and pressure p_c at the upper critical end point (UCEP). For $T < T_c$, the state is gas below the three phase pressure and liquid above, while for $T \geq T_c$ the state is gas at $p \leq p_c$ and supercritical at $p > p_c$.

The standard relative uncertainties $u_r(\gamma)$ of the corrected values were estimated from the relation:

$$u_r(\gamma)^2 = \left[\frac{1}{\gamma} \left(\frac{\partial \gamma}{\partial T} \right)_p u(T) \right]^2 + \left[\frac{1}{\gamma} \left(\frac{\partial \gamma}{\partial p} \right)_T u(p) \right]^2 + \left[\frac{u(\Delta \rho)}{\Delta \rho} \right]^2 + \left[\frac{\sigma(\gamma)}{\gamma} \right]^2 \quad (3)$$

This differs from the analysis of Georgiadis et al. [3] because of the inclusion of the uncertainty $u(\Delta \rho)$ of the density difference. The magnitude of this uncertainty is estimated from measurements of the liquid and gas phase densities of the (CO₂ + H₂O) system reported by Efika et al. [43]; $u(\Delta \rho)/\Delta \rho$ has an average of about 1%, with a maximum of 3% at high pressures and low temperatures where the densities of the two phases become more similar.

The revised interfacial tension data for the (CO₂ + H₂O) system are shown in figures 4 and 5. The changes in Georgiadis et al.'s interfacial tension values arising from the density corrections are significant at low temperatures and high pressures, with maximum absolute relative differences of 15 % at $T = 297.9$ K and 28% at $T = 333.5$ K.

The same analysis was applied to the (CO₂ + brine) data of Li et al. [20; 24], for the brine composition of (0.864 NaCl + 0.136 KCl) measured at various brine salinities, from 1 to 5 mol·kg⁻¹. The interfacial tension values were extrapolated back to zero salt molality, and a density value was calculated using the same method described in their paper, at the zero salt molality condition. Density correction was then applied to the extrapolated interfacial tension values. The results are presented in table 5 at temperatures between (323.15 and 448.15) K and pressures up to 50 MPa. In this case, the estimated standard relative uncertainty was taken to be that of the original CO₂-brine IFT data.

For Li et al.'s data, the changes in interfacial tension values after density corrections are significant at high pressures, with maximum absolute relative difference of 7 % at $T = 448.15$ K and $p = 50$ MPa. Li et al.'s original liquid phase density calculation already incorporates the density increase due to dissolved CO₂. The liquid phase density is evaluated from the solubility model of Duan and Sun [42], and has been mentioned previously to agree within AAD of 2%. The differences observed in the two density calculation methods result from the evaluation of the partial molar volumes of CO₂ in aqueous solution. In the present paper, the partial molar volumes of CO₂ in aqueous solution is evaluated from the model of Sedlbauer et

al. [41], whereas the one used in Li et al.'s paper has been assumed constant for all pressure and temperature conditions.

In order to permit interpolation with respect to pressure, the experimental data have been fitted along isotherms with two different equations. The first, was a dual linear correlation applied for temperatures between (297.9 and 333.5) K as follows:

$$\gamma_{\text{CO}_2\text{-H}_2\text{O}} / (\text{mN} \cdot \text{m}^{-1}) = a_1 - b_1 (p / \text{MPa}). \quad (4)$$

In this correlation, two sets of parameters are used above and below an apparent point of intersection. In this way, the model accommodates the sharp change in slope exhibited by the experimental data along the isotherms in question.

The second correlation was a rational function chosen to represent the smooth dependence of γ upon p observed at higher temperatures:

$$\gamma_{\text{CO}_2\text{-H}_2\text{O}} / (\text{mN} \cdot \text{m}^{-1}) = \frac{a_2 b_2 + c_2 (p / \text{MPa})^{d_2}}{b_2 + (p / \text{MPa})^{d_2}}. \quad (5)$$

The parameters a_i , b_i , c_i and d_i , ($i = 1, 2$) are listed in table 6. As shown in figure 5, the models are generally within the expanded uncertainties of the experimental data, with some outliers at pressures below 10 MPa.

As pointed out by Müller and Mejía [50], at temperatures below the UCEP, approximately 304.6 K for ($\text{CO}_2 + \text{H}_2\text{O}$) [51], the interfacial tension is not a continuous function of pressure along an isotherm. For pressures below the three-phase equilibrium pressure p_t , one has gas-liquid equilibrium characterised by interfacial tension $\gamma_{\text{GL}_1}(p)$, while at higher pressures one has liquid-liquid equilibrium characterised by interfacial tension $\gamma_{\text{L}_1\text{L}_2}(p)$, where L_1 denotes water-rich liquid and L_2 denotes CO_2 -rich liquid. At $p = p_t$, three phases may coexist with interfacial tensions $\gamma_{\text{L}_1\text{L}_2} + \gamma_{\text{GL}_2} \geq \gamma_{\text{GL}_1}$, where γ_{GL_2} is the interfacial tension between gas and CO_2 -rich liquid. According to the computer simulations of Müller and Mejía [50], $\gamma_{\text{GL}_2} = 1.75 \text{ mN} \cdot \text{m}^{-1}$ at $T = 298.15$, diminishing to zero as $T \rightarrow T_c$. The experimental data considered in this work were measured either below p_t in the G- L_1 region, or above p_t in the L_1 - L_2 region and there is no ambiguity about these designations. However, when plotted together along an isotherm and extrapolated to $p = p_t$ from both above and below, there should exist a small discontinuity such that $\gamma_{\text{GL}_2} > \gamma_{\text{GL}_1}$. This is in fact found to be the case when we examine the one sub-critical isotherm, that of Georgiadis et al. at $T = 297.90$ K. The three-phase equilibrium pressure at that temperature, interpolated from the experimental data of Wendland et al. [51] is 6.37 MPa, at which pressure equation (4) with the parameters from table 6 gives $\gamma_{\text{GL}_1} = 34.0 \text{ mPa} \cdot \text{s}$ and $\gamma_{\text{L}_1\text{L}_2} = 32.2 \text{ mPa} \cdot \text{s}$. The difference between these values is remarkable consistent with the estimated reported by Müller and Mejía [50].

One notable feature of the IFT data for the ($\text{CO}_2 + \text{H}_2\text{O}$) system is the crossing of isotherms, *e.g.* the isotherms at $T = (312.9 \text{ and } 343.3) \text{ K}$ in the data of Georgiadis et al. which cross at a pressure of about 15 MPa. We attribute this behaviour to a gradual transition between the bi-linear behaviour observed at low temperature and the smooth and continuous isotherms observed at higher temperatures.

(N₂ + H₂O) system.

Four isotherms at temperatures between (298 and 448) K have been measured in the (N₂ + H₂O) system over a range of pressures from (2 to 40) MPa. The results are given in table 7 and figure 7. Based on the critical pressure of nitrogen [48], the phases in equilibrium at $p = 2$ MPa were classified as liquid + gas, while all others were classified as liquid + supercritical fluid. The relative standard deviation $\sigma(\gamma)/\gamma$ of the IFT data at each state point was evaluated from 3 to 5 repeated measurements and the average was found to be 0.2 %; in all cases it was < 0.7 %. The overall relative uncertainty $u_r(\gamma)$ was then calculated from Equation (3). Reliable measurements of the liquid and vapour phase densities under the conditions of interest are not available. To estimate the uncertainty $u(\Delta\rho)$ of the density difference we compared our values of $\Delta\rho$, obtained with the PR-NRTL model and the mixture model in the REFPROP 9.1 database incorporating the equations of state of the pure components [35; 36; 48; 49], with the density difference between the pure substances at the same temperature and pressure. The maximum difference in the density differences is 0.7 %, and the average absolute deviation is 0.2 %. Overall, the relative uncertainty of interfacial tension of all state points is 0.9 %, and the expanded relative uncertainty at 95 % confidence is 1.9 %.

As expected, the interfacial tensions of the (N₂ + H₂O) system are observed to decrease with increasing pressure and temperature. The interfacial tension data are compared with the density-corrected measurements of Wiegand and Franck [7], Tian et al. [9] and Yan et al. [8] under overlapping p - T conditions, and the agreement is within 3.0 mN·m⁻¹.

For the purpose of interpolating the interfacial tension of the (N₂ + H₂O) system, the following empirical equation was developed:

$$\gamma_{\text{N}_2\text{-H}_2\text{O}}/(\text{mN} \cdot \text{m}^{-1}) = \frac{1 + a_{31}(T/\text{K}) + a_{32}(p/\text{MPa})^{d_3}}{b_{31} + b_{32}(T/\text{K}) + c_3(p/\text{MPa})^{d_3}}. \quad (6)$$

This model is valid at $298.15 \leq T/\text{K} \leq 448.15$ K and $p \leq 40$ MPa, and the six parameters are listed in table 8. The absolute average deviation is 0.45 mN·m⁻¹ for the 84 measured data points; as shown in figure 8, all points are fitted within their uncertainties. The literature results of Wiegand and Franck, Tian et al. and Yan et al. are generally predicted by Equation (6) to within 1.5 mN·m⁻¹.

(CO₂ + N₂ + H₂O) System.

In the case of the (CO₂ + N₂ + H₂O) system, four isotherms were measured at temperatures between (298 and 448) K at pressures from (2 to 40) MPa. The results are given in table 9. Based on the reported critical locus of the (CO₂ + N₂) binary system [52; 53], the phases in equilibrium at $p \leq 10$ MPa were classified as liquid + gas, while all others were classified as liquid + supercritical fluid. In figure 9, the interfacial tension data are found to be similar to those of Yan et al., which relate to the gas phase mixture composition of $[x \text{ CO}_2 + (1 - x) \text{ N}_2]$ with $x = 0.5072$, at two overlapping temperature conditions of (298 and 373) K. The relative standard deviation $\sigma(\gamma)/\gamma$ of the IFT data at each state point was evaluated from 3 repeated measurements; the average was 0.3 %, and in all cases it was < 1.3 %. The overall relative uncertainty $u_r(\gamma)$ was calculated from relation (3). As discussed above, the coexisting phase compositions, and hence the density difference, depends to some extent upon the overall system composition. Given the known upper

and lower bounds on the amount of water in the cell, and the known composition of the feed gas, the standard relative uncertainty of the density difference was estimated to be 1 %. Finally, the overall standard relative uncertainty of interfacial tension of all state points was found to be 1.6 %.

As detailed in the introduction, thermoetical approaches based on equations of state in combination with gradient theory may be capable of describing ternary IFT data [54]. Such an analysis is beyond the scope of the present paper and we confine ourselves to testing an empirical connection between the interfacial tension of the ternary system and that of the constituent binary sub-systems. Shah et al. [6] proposed that a mole-fraction-weighted average may be used for this purpose and that approach was applied with some success for the (H₂S + CO₂ + H₂O) system. In the present work, we have tested a similar approach in which we allow also for the presence of water in the vapour phase as follows:

$$\gamma_{\text{N}_2\text{-CO}_2\text{-H}_2\text{O}} = (y_{\text{N}_2}\gamma_{\text{N}_2\text{-H}_2\text{O}} + y_{\text{CO}_2}\gamma_{\text{CO}_2\text{-H}_2\text{O}})/(y_{\text{N}_2} + y_{\text{CO}_2}) \quad (7)$$

The equilibrium vapour compositions were again calculated using the PR-NRTL model as described above and the interfacial tensions of the binary systems were evaluated from Equations (4) or (5) and (6). The predictions obtained with Equation (7) are compared with the experimental data in figure 10. It can be seen that the agreement is good at the two higher temperatures but that the model fails to follow the experimental data closely at lower temperatures and high pressures. The simple method produces predictions with AAD of 4.8 % for all temperatures and pressures measured. This is compared with the AAD of 1.8 % reported by Khosharay and Varaminian [34], using a linear-gradient model based on the CPA equation of state, with the experimental data of Yan et al. [8].

Conclusion

Interfacial tension measurements of the (CO₂ + N₂ + H₂O) and (N₂ + H₂O) systems are reported at pressures of (2 to 40) MPa and temperatures of (298.15 to 448.15) K. An accurate empirical correlation for interfacial tension has been developed for the (N₂ + H₂O) system in the range of conditions investigated. Interfacial tension data for the (CO₂ + H₂O) system reported in the literature have been revised to account for improved estimates of the coexisting phase densities, and the results along each isotherm have been fitted with empirical models. Finally, interfacial tension predictions of the (CO₂ + N₂ + H₂O) system, based on a simple combination of the interfacial tensions of the two binary system, (N₂ + H₂O) and (CO₂ + H₂O), have been considered. These were found to be favourable except at low temperatures and high pressures.

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Figures and Tables

Figure 1. Interfacial tension apparatus, where the gas cylinder provides pressurised pure N₂ or the equimolar (CO₂ + N₂) gas mixture to the view cell. C1: optical cell with stirrer; P1, P2, P3: high-pressure Quizix pumps; P4: vacuum pump; TT: platinum resistance thermometer (Pt100); PT: flow-through pressure transducer; N1, N2: injection ports; V1, V2: high-pressure valves; V3, V5, V6: three-way valves; V4: four-way switch; V7: relief valve; V8: rupture-disc safety head.

Figure 2. Densities calculated at phase equilibrium for the liquid phase (left) and vapour phase (right) at $T = 298.15 \text{ K}$ (solid lines) and $T = 323.15 \text{ K}$ (dashed lines) for the following systems (in order of ascending density): $(\text{N}_2 + \text{H}_2\text{O})$ (blue), $(\text{CO}_2 + \text{N}_2 + \text{H}_2\text{O})$ (green) and $(\text{CO}_2 + \text{H}_2\text{O})$ (red).

Figure 3. Density difference between (CO₂ + H₂O) bulk-liquid phase equilibrium densities calculated in PR-NRTL model of Hou et al. and pure water, at six isotherms: —, 297.9 K; — ·, 312.9 K; — —, 333.5 K; — · —, 343.3 K; ·····, 374.3 K; and — · · ·, 448.0 K.

Figure 4. Density corrected interfacial tensions of the ($\text{CO}_2 + \text{H}_2\text{O}$) system, data from Georgiadis et al., along five isotherms: $\triangle$, 297.9 K; $\circ$, 312.9 K; $\diamond$, 333.5 K; $\times$, 343.3 K; $\square$, 374.3 K; $---$, Eq. (4); and $---$, Eq. (5).

Figure 5. Density corrected interfacial tensions of the ($\text{CO}_2 + \text{H}_2\text{O}$) system, data from Li et al., along six isotherms: Δ , 323.15 K; $\circ$, 343.15 K; $\diamond$, 373.15 K; $\times$, 393.15 K; $\square$, 423.15 K; $*$, 448.15 K; $---$, Eq. (4); and $---$, Eq. (5).

Figure 6. Deviations of the density corrected interfacial tension results for the ($\text{CO}_2 + \text{H}_2\text{O}$) system, from the fitted models (4) and (5), along eleven isotherms: $\blacktriangle$, 297.9 K; $\bullet$, 312.9 K; $\triangle$, 323.15 K; $\blacklozenge$, 333.5 K; $\circ$, 343.15 K; $\times$, 343.3 K; $\square$, 373.15 K; $\blacksquare$, 374.3 K; $\diamond$, 393.15 K; $-$, 423.15 K; and $-$, 448.15 K. Error bars show the expanded uncertainty of data from Georgiadis et al. after density adjustment, and are not applicable for the zero molality extrapolated interfacial tension data of Li et al. Dashed lines show the absolute average deviation of all the models.

Figure 7. Interfacial tensions γ at various pressures p for the ($\text{N}_2 + \text{H}_2\text{O}$) system, along four isotherms: $\diamond$, 298 K; $\square$, 323 K; $\triangle$, 373 K; $\circ$, 448 K; —, Eq. (6). Interfacial tension measurements within the conditions studied in the present work, from Wiegand and Franck [7] at $+$, 298 K and $*$, 373 K; Tian et al. [9] at $\triangle$, 298 K and $\square$, 373 K; Yan et al. [8] at $\circ$, 298 K and $*$, 373 K. Surface tensions for pure water, $\times$, as implemented in REFPROP 9.1 [35; 36].

Figure 8. Difference in interfacial tension measurements of the ($\text{N}_2 + \text{H}_2\text{O}$) system from the fitting equation (6) at four isotherms: $\diamond$, 298 K; $\square$, 323 K; $\triangle$, 373 K; and $\circ$, 448 K. Deviations of the fitting equation from literature data are also shown: Wiegand and Franck [7] at $+$, 298 K; $*$, 373 K; and $\blacktriangle$, 473 K; Tian et al. [9] at $\triangle$, 298 K; $\square$, 373 K; and $\diamond$, 473 K; Yan et al. [8] at $\circ$, 298 K and $*$, 373 K. Error bars show the expanded uncertainty of the measured data. Dashed lines show the absolute average deviation of the model.

Figure 9. Interfacial tensions at various pressures for the gas phase mixture composition of $[x \text{ CO}_2 + (1 - x) \text{ N}_2]$: $\diamond$, measured values with $x = 0.5120$; $+$, values from Yan et al. [8] with $x = 0.5072$; — —, $(\text{CO}_2 + \text{H}_2\text{O})$ from Eq. (4) and (5); - - -, $(\text{N}_2 + \text{H}_2\text{O})$ from Eq. (6); — · —, $(\text{CO}_2 + \text{N}_2 + \text{H}_2\text{O})$ prediction from Eq. (7). From top left to right at $T = 298 \text{ K}$ and $T = 323 \text{ K}$; bottom left to right at $T = 373 \text{ K}$ and $T = 448 \text{ K}$.

Figure 10. Difference in interfacial tension measurements of the (CO₂ + N₂ + H₂O) system from the molar average prediction, Eq. (7), determined using binary system (N₂ + H₂O) and (CO₂ + H₂O) empirical equation interfacial tension values, at ◇, 298 K; □, 323 K; △, 373 K; and ○, 448 K. Error bars show the expanded uncertainty of measured data. Dashed lines show the absolute average deviation of the model.

Table 1. Description of chemical samples, where x denotes mole fraction of a single substance or a mixture of defined composition and ρ_e denotes electrical resistivity.

Chemical name	Source	Purity	Additional purification
Nitrogen	BOC	$x \geq 0.99998$	None
(0.5120 CO ₂ + 0.4880 N ₂) ^a	BOC	$x \geq 0.99995$	None
Water	Millipore Direct-Q UV3 apparatus	$\rho_e \geq 18 \text{ M}\Omega \cdot \text{cm}$ at $T = 298 \text{ K}$	Vacuum degassed

^a The expanded uncertainty at 95 % confidence of the mole fraction of N₂ is 0.005.

Table 2. Thermodynamic properties of the pure components for the PR EoS

Component	T_c/K	p_c/MPa	ω
N ₂	126.20	3.3900	0.03900
CO ₂	304.13	7.3773	0.22394
H ₂ O	647.10	22.064	0.34430

Table 3. Thermodynamic properties of the binary systems for the PR-NRTL model

System	Parameter Correlations	Ref.
CO ₂ -H ₂ O	$k_{ij} = 0.33810 - 0.46426 \left(\frac{T_0}{T} \right)$	[40]
	$\ln(H_{ij} / \text{MPa}) = -6.1384 + 42.842 \left(\frac{T_0}{T} \right) - 44.358 \left(\frac{T_0}{T} \right)^2 + 12.786 \left(\frac{T_0}{T} \right)^3$	
	$T_0 = 298.15 \text{ K}$	
N ₂ -H ₂ O	$k_{ij} = -2.1008 + 5.82466 \times 10^3 T + 3.7711 \times 10^6 T^2$	[46]
	$\ln(H_{ij} / \text{MPa}) = -\frac{9.67578}{T_r} + \frac{4.72162}{T_r} (1 - T_r)^{0.355} + \frac{11.70585}{T_r^{0.41}} \exp(1 - T_r) + \ln(p_{\text{H}_2\text{O}}^{\text{sat}} / \text{MPa})$	[45]
	$T_r = T / (647.096 \text{ K})$	
CO ₂ -N ₂	$k_{ij} = -0.097$	[55]

Table 4. Density-Corrected Interfacial Tension γ for (CO₂ + H₂O) Data of Georgiadis et al.; phases in equilibrium are designated with G = gas, L = liquid, or SC = supercritical; x_i and y_i are the calculated liquid- and vapour-phase compositions respectively, where 1 = CO₂ and 2 = H₂O.^a

T/K	p/MPa	$\gamma/\text{mN}\cdot\text{m}^{-1}$	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	Phases	x_1	x_2	y_1	y_2
297.8	1.01	65.9	981.5	L-G	0.0057	0.9943	0.9964	0.0036
297.9	2.00	59.2	963.6	L-G	0.0106	0.9894	0.9978	0.0022
297.9	3.00	52.9	941.9	L-G	0.0150	0.9850	0.9982	0.0018
297.9	4.00	47.5	914.9	L-G	0.0187	0.9813	0.9983	0.0017
297.9	5.01	41.8	878.3	L-G	0.0218	0.9782	0.9982	0.0018
297.9	6.01	36.7	819.3	L-G	0.0242	0.9758	0.9978	0.0022
297.9	7.02	31.9	264.7	L-L	0.0245	0.9755	0.9682	0.0318
297.9	8.02	31.9	233.1	L-L	0.0247	0.9753	0.9642	0.0358
297.9	10.01	31.8	194.3	L-L	0.0251	0.9749	0.9577	0.0423
297.9	14.99	30.6	138.9	L-L	0.0258	0.9742	0.9454	0.0546
297.9	19.99	30.0	103.8	L-L	0.0264	0.9736	0.9358	0.0642
312.9	1.00	63.7	977.0	L-G	0.0040	0.9960	0.9916	0.0084
312.9	2.00	59.0	959.8	L-G	0.0076	0.9924	0.9951	0.0049
312.8	3.01	51.4	939.8	L-G	0.0110	0.9890	0.9962	0.0038
312.8	4.01	47.3	916.7	L-G	0.0139	0.9861	0.9966	0.0034
312.8	5.02	44.3	888.6	L-G	0.0164	0.9836	0.9966	0.0034
312.8	6.00	40.6	854.2	L-G	0.0185	0.9815	0.9964	0.0036
312.9	7.02	37.3	805.1	L-G	0.0202	0.9798	0.9958	0.0042
312.9	8.02	33.9	723.3	L-SC	0.0215	0.9785	0.9941	0.0059
312.9	10.00	32.1	373.7	L-SC	0.0224	0.9776	0.9759	0.0241
312.9	15.00	30.8	228.1	L-SC	0.0235	0.9765	0.9594	0.0406
313.2	20.02	30.4	172.8	L-SC	0.0243	0.9757	0.9492	0.0508
312.9	24.92	29.5	134.9	L-SC	0.0250	0.9750	0.9411	0.0589
333.5	1.00	62.6	968.2	L-G	0.0027	0.9973	0.9773	0.0227
333.5	1.99	60.1	952.3	L-G	0.0053	0.9947	0.9872	0.0128
333.5	2.99	56.2	934.5	L-G	0.0076	0.9924	0.9903	0.0097
333.5	3.99	52.7	914.8	L-G	0.0098	0.9902	0.9916	0.0084
333.5	5.00	49.8	892.4	L-G	0.0118	0.9882	0.9922	0.0078
333.5	6.00	46.6	867.1	L-G	0.0135	0.9865	0.9924	0.0076
333.5	7.01	43.7	837.4	L-G	0.0150	0.9850	0.9922	0.0078
333.5	8.01	40.8	802.6	L-SC	0.0163	0.9837	0.9917	0.0083
333.5	8.99	38.2	761.0	L-SC	0.0174	0.9826	0.9908	0.0092
333.6	10.00	32.4	708.1	L-SC	0.0183	0.9817	0.9891	0.0109
333.6	10.57	31.7	672.3	L-SC	0.0188	0.9812	0.9878	0.0122
333.5	15.01	31.2	397.8	L-SC	0.0207	0.9793	0.9714	0.0286
333.5	20.00	30.1	279.9	L-SC	0.0219	0.9781	0.9583	0.0417

333.5	25.00	28.9	219.0	L-SC	0.0229	0.9771	0.9490	0.0510
333.5	30.00	28.7	178.0	L-SC	0.0236	0.9764	0.9418	0.0582
333.5	40.00	27.2	121.9	L-SC	0.0249	0.9751	0.9310	0.0690
333.5	50.00	26.8	82.7	L-SC	0.0259	0.9741	0.9233	0.0767
333.5	60.00	25.3	52.6	L-SC	0.0267	0.9733	0.9176	0.0824
343.3	1.00	61.4	963.2	L-G	0.0023	0.9977	0.9653	0.0347
343.3	2.00	57.1	947.6	L-G	0.0046	0.9954	0.9806	0.0194
343.3	3.00	55.7	930.6	L-G	0.0067	0.9933	0.9855	0.0145
343.3	4.00	51.8	912.0	L-G	0.0086	0.9914	0.9877	0.0123
343.3	5.00	48.7	891.5	L-G	0.0104	0.9896	0.9888	0.0112
343.3	6.00	45.6	868.7	L-G	0.0120	0.9880	0.9893	0.0107
343.3	7.05	42.7	841.8	L-G	0.0135	0.9865	0.9893	0.0107
343.3	8.03	40.1	813.1	L-SC	0.0147	0.9853	0.9890	0.0110
343.3	9.02	37.7	779.9	L-SC	0.0158	0.9842	0.9884	0.0116
343.3	10.03	35.7	740.7	L-SC	0.0168	0.9832	0.9873	0.0127
343.3	11.04	34.4	695.0	L-SC	0.0176	0.9824	0.9856	0.0144
343.3	12.05	33.1	643.1	L-SC	0.0183	0.9817	0.9834	0.0166
343.3	15.09	30.8	484.0	L-SC	0.0197	0.9803	0.9740	0.0260
343.3	20.20	29.2	333.3	L-SC	0.0212	0.9788	0.9600	0.0400
343.3	25.25	28.5	258.8	L-SC	0.0223	0.9777	0.9501	0.0499
343.3	35.28	27.1	175.4	L-SC	0.0239	0.9761	0.9365	0.0635
343.3	41.32	26.3	142.2	L-SC	0.0247	0.9753	0.9305	0.0695
374.3	1.00	56.2	944.0	L-G	0.0016	0.9984	0.8871	0.1129
374.3	2.00	53.5	929.9	L-G	0.0033	0.9967	0.9386	0.0614
374.3	3.00	51.3	914.9	L-G	0.0049	0.9951	0.9554	0.0446
374.3	4.00	48.9	899.1	L-G	0.0064	0.9936	0.9635	0.0365
374.3	5.00	46.6	882.3	L-G	0.0078	0.9922	0.9680	0.0320
374.3	6.00	44.8	864.3	L-G	0.0092	0.9908	0.9707	0.0293
374.3	9.00	39.9	803.0	L-SC	0.0127	0.9873	0.9735	0.0265
374.3	10.00	38.3	779.8	L-SC	0.0137	0.9863	0.9734	0.0266
374.3	11.00	36.9	755.0	L-SC	0.0146	0.9854	0.9729	0.0271
374.3	12.00	35.3	728.6	L-SC	0.0154	0.9846	0.9722	0.0278
374.3	13.00	34.1	700.8	L-SC	0.0162	0.9838	0.9711	0.0289
374.3	14.00	33.1	671.8	L-SC	0.0169	0.9831	0.9697	0.0303
374.3	15.00	32.5	642.0	L-SC	0.0175	0.9825	0.9681	0.0319
374.3	16.00	31.6	611.8	L-SC	0.0181	0.9819	0.9663	0.0337
374.3	17.00	30.8	581.9	L-SC	0.0187	0.9813	0.9643	0.0357
374.3	18.00	30.3	552.8	L-SC	0.0192	0.9808	0.9622	0.0378
374.3	19.00	29.7	524.9	L-SC	0.0196	0.9804	0.9600	0.0400
374.3	20.00	29.6	498.7	L-SC	0.0200	0.9800	0.9578	0.0422
374.3	30.00	25.9	322.1	L-SC	0.0232	0.9768	0.9389	0.0611

374.3	40.00	24.5	231.5	L-SC	0.0253	0.9747	0.9262	0.0738
374.3	49.99	23.6	173.8	L-SC	0.0270	0.9730	0.9175	0.0825
374.3	60.05	23.1	131.7	L-SC	0.0285	0.9715	0.9114	0.0886

^aStandard uncertainties u are $u(T) = 0.1$ K, $u(p) = 0.001p$ MPa, and $u(\gamma) = 0.011\gamma$ mN·m⁻¹.

Table 5. Density-Corrected Zero-Molality Extrapolated Interfacial Tension γ for (CO₂ + H₂O + Brine) Data of Li et al. [20; 24] for the brine composition of (0.864 NaCl + 0.136 KCl) at brine molalities from (1 to 5) mol·kg⁻¹. Phases in equilibrium are designated with G = gas, L = liquid, or SC = supercritical; x_i and y_i are the calculated liquid- and vapour-phase compositions respectively, where 1 = CO₂ and 2 = H₂O.^a

$p/$ MPa	$\gamma/$ mN·m ⁻¹	$\Delta\rho/$ kg·m ⁻³	Phases	x_1	x_2	y_1	y_2	$\gamma/$ mN·m ⁻¹	$\Delta\rho/$ kg·m ⁻³	Phases	x_1	x_2	y_1	y_2
$T = 323.15 \text{ K}$								$T = 343.15 \text{ K}$						
2	58.0	956.3	L-G	0.0063	0.9937	0.9920	0.0080	56.0	947.7	L-G	0.0046	0.9954	0.9807	0.0193
4	50.4	916.4	L-G	0.0115	0.9885	0.9946	0.0054	50.1	912.0	L-G	0.0086	0.9914	0.9878	0.0122
6	43.6	862.8	L-G	0.0156	0.9844	0.9948	0.0052	45.2	868.7	L-G	0.0120	0.9880	0.9893	0.0107
8	37.6	781.0	L-SC	0.0186	0.9814	0.9936	0.0064	39.6	813.9	L-SC	0.0147	0.9853	0.9891	0.0109
10	34.9	617.6	L-SC	0.0204	0.9796	0.9880	0.0120	37.0	741.5	L-SC	0.0167	0.9833	0.9873	0.0127
12	33.0	418.5	L-SC	0.0212	0.9788	0.9767	0.0233	34.4	644.9	L-SC	0.0182	0.9818	0.9835	0.0165
14	32.0	332.1	L-SC	0.0218	0.9782	0.9692	0.0308	33.1	535.5	L-SC	0.0193	0.9807	0.9775	0.0225
16	31.5	283.2	L-SC	0.0223	0.9777	0.9634	0.0366	31.8	445.5	L-SC	0.0200	0.9800	0.9711	0.0289
18	31.0	249.2	L-SC	0.0227	0.9773	0.9586	0.0414	30.9	382.1	L-SC	0.0207	0.9793	0.9654	0.0346
20	30.6	223.0	L-SC	0.0230	0.9770	0.9545	0.0455	30.5	336.4	L-SC	0.0212	0.9788	0.9605	0.0395
25	29.8	175.6	L-SC	0.0238	0.9762	0.9459	0.0541	29.4	261.1	L-SC	0.0222	0.9778	0.9506	0.0494
30	28.6	141.6	L-SC	0.0245	0.9755	0.9391	0.0609	28.5	212.4	L-SC	0.0231	0.9769	0.9429	0.0571
35	28.3	115.1	L-SC	0.0251	0.9749	0.9334	0.0666	27.9	176.7	L-SC	0.0238	0.9762	0.9368	0.0632
40	26.9	93.2	L-SC	0.0256	0.9744	0.9286	0.0714	27.3	148.4	L-SC	0.0245	0.9755	0.9317	0.0683
45	26.8	74.7	L-SC	0.0260	0.9740	0.9245	0.0755	26.6	124.9	L-SC	0.0251	0.9749	0.9275	0.0725
50	26.8	58.4	L-SC	0.0265	0.9735	0.9210	0.0790	26.2	105.0	L-SC	0.0256	0.9744	0.9238	0.0762
$p/$ MPa	$\gamma/$ mN·m ⁻¹	$\Delta\rho/$ kg·m ⁻³	Phases	x_1	x_2	y_1	y_2	$\gamma/$ mN·m ⁻¹	$\Delta\rho/$ kg·m ⁻³	Phases	x_1	x_2	y_1	y_2
$T = 373.15 \text{ K}$								$T = 393.15 \text{ K}$						
2	52.9	930.6	L-G	0.0033	0.9967	0.9410	0.0590	50.7	916.8	L-G	0.0028	0.9972	0.8880	0.1120
4	48.3	899.7	L-G	0.0064	0.9936	0.9648	0.0352	47.2	888.2	L-G	0.0057	0.9943	0.9351	0.0649
6	44.1	864.7	L-G	0.0092	0.9908	0.9717	0.0283	43.7	856.9	L-G	0.0083	0.9917	0.9496	0.0504
8	40.0	824.8	L-SC	0.0116	0.9884	0.9740	0.0260	40.6	822.4	L-SC	0.0107	0.9893	0.9555	0.0445
10	37.1	779.2	L-SC	0.0137	0.9863	0.9742	0.0258	37.6	784.4	L-SC	0.0128	0.9872	0.9579	0.0421
12	35.3	727.3	L-SC	0.0155	0.9845	0.9728	0.0272	35.2	743.0	L-SC	0.0147	0.9853	0.9581	0.0419
14	33.3	669.4	L-SC	0.0169	0.9831	0.9703	0.0297	33.2	698.3	L-SC	0.0164	0.9836	0.9570	0.0430
16	31.8	608.4	L-SC	0.0182	0.9818	0.9668	0.0332	31.6	651.5	L-SC	0.0178	0.9822	0.9548	0.0452
18	30.5	548.5	L-SC	0.0192	0.9808	0.9626	0.0374	30.0	604.0	L-SC	0.0191	0.9809	0.9518	0.0482
20	29.6	494.0	L-SC	0.0200	0.9800	0.9582	0.0418	28.7	557.7	L-SC	0.0202	0.9798	0.9484	0.0516
25	28.3	389.0	L-SC	0.0218	0.9782	0.9478	0.0522	26.3	456.4	L-SC	0.0226	0.9774	0.9392	0.0608
30	26.6	318.2	L-SC	0.0231	0.9769	0.9392	0.0608	25.3	379.6	L-SC	0.0245	0.9755	0.9307	0.0693
35	25.9	267.4	L-SC	0.0243	0.9757	0.9322	0.0678	24.4	322.1	L-SC	0.0260	0.9740	0.9235	0.0765
40	25.1	228.6	L-SC	0.0252	0.9748	0.9265	0.0735	23.5	277.5	L-SC	0.0274	0.9726	0.9176	0.0824
45	24.7	197.3	L-SC	0.0261	0.9739	0.9218	0.0782	22.9	241.6	L-SC	0.0286	0.9714	0.9126	0.0874

50	24.1	171.3	L-SC	0.0269	0.9731	0.9179	0.0821	22.1	211.9	L-SC	0.0298	0.9702	0.9085	0.0915
$p/$ MPa	$\gamma/$ $\text{mN}\cdot\text{m}^{-1}$	$\Delta\rho/$ $\text{kg}\cdot\text{m}^{-3}$	Phases	x_1	x_2	y_1	y_2	$\gamma/$ $\text{mN}\cdot\text{m}^{-1}$	$\Delta\rho/$ $\text{kg}\cdot\text{m}^{-3}$	Phases	x_1	x_2	y_1	y_2
$T = 423.15 \text{ K}$								$T = 448.15 \text{ K}$						
2	45.0	892.5	L-G	0.0022	0.9978	0.7424	0.2576	40.5	868.9	L-G	0.0016	0.9984	0.5338	0.4662
4	41.8	866.8	L-G	0.0049	0.9951	0.8554	0.1446	38.6	845.1	L-G	0.0042	0.9958	0.7428	0.2572
6	39.5	839.4	L-G	0.0075	0.9925	0.8914	0.1086	36.4	820.2	L-G	0.0067	0.9933	0.8107	0.1893
8	37.8	810.1	L-SC	0.0099	0.9901	0.9080	0.0920	34.2	794.0	L-SC	0.0090	0.9910	0.8430	0.1570
10	35.6	779.2	L-SC	0.0122	0.9878	0.9166	0.0834	32.3	766.7	L-SC	0.0111	0.9889	0.8609	0.1391
12	33.3	746.4	L-SC	0.0143	0.9857	0.9210	0.0790	29.6	738.4	L-SC	0.0130	0.9870	0.8715	0.1285
14	31.2	712.1	L-SC	0.0162	0.9838	0.9229	0.0771	27.5	709.2	L-SC	0.0148	0.9852	0.8778	0.1222
16	29.6	676.8	L-SC	0.0180	0.9820	0.9232	0.0768	25.7	679.3	L-SC	0.0164	0.9836	0.8814	0.1186
18	27.6	640.9	L-SC	0.0197	0.9803	0.9223	0.0777	24.8	649.1	L-SC	0.0179	0.9821	0.8831	0.1169
20	26.2	605.1	L-SC	0.0212	0.9788	0.9206	0.0794	24.0	619.0	L-SC	0.0193	0.9807	0.8835	0.1165
25	23.9	520.1	L-SC	0.0245	0.9755	0.9144	0.0856	21.8	545.8	L-SC	0.0223	0.9777	0.8810	0.1190
30	22.5	447.0	L-SC	0.0274	0.9726	0.9073	0.0927	19.8	479.5	L-SC	0.0247	0.9753	0.8762	0.1238
35	21.2	386.9	L-SC	0.0298	0.9702	0.9007	0.0993	18.0	421.9	L-SC	0.0268	0.9732	0.8709	0.1291
40	20.2	338.2	L-SC	0.0320	0.9680	0.8948	0.1052	17.2	373.0	L-SC	0.0286	0.9714	0.8659	0.1341
45	19.5	298.0	L-SC	0.0340	0.9660	0.8899	0.1101	16.2	331.5	L-SC	0.0302	0.9698	0.8615	0.1385
50	18.9	264.4	L-SC	0.0359	0.9641	0.8858	0.1142	15.6	296.1	L-SC	0.0316	0.9684	0.8578	0.1422

^aStandard uncertainties u are $u(T) = 0.025 \text{ K}$, $u(p) = 35 \text{ kPa}$, and $u(\gamma) = \max(0.008\gamma, 0.3) \text{ mN}\cdot\text{m}^{-1}$.

Table 6. Fitting Parameters of the Density Corrected Interfacial Tensions for the (CO₂ + H₂O) system.

Dual Linear Correlation (Eq 4)									
T/K	$p \leq p_i$				p_i/MPa	$p \geq p_i$			
	a_1	b_1	σ	$10^2 \Delta_{\text{AAD}}$		a_1	b_1	σ	$10^2 \Delta_{\text{AAD}}$
297.90	71.049	5.815	0.6210	0.87	6.694	33.226	0.165	0.2156	0.45
312.90	66.075	4.188	1.6852	2.48	7.877	34.864	0.226	0.6888	1.45
323.15	64.410	3.352	0.6819	0.82	9.516	34.078	0.164	0.9214	1.67
333.50	66.053	3.230	0.6892	1.16	10.741	32.718	0.127	0.4499	1.18
Multiple Multiplication Factor Model (Eq 5)									
T/K	a_2	b_2	c_2	d_2	σ	$10^2 \Delta_{\text{AAD}}$			
343.15	26.009	0.034	59.583	-1.776	0.4465	0.88			
343.30	26.325	0.015	60.784	-2.235	0.6178	0.95			
373.15	22.034	0.037	56.158	-1.522	0.2288	0.43			
374.30	21.412	0.028	56.242	-1.605	0.3474	0.50			
393.15	19.820	0.021	52.692	-1.610	0.2339	0.48			
423.15	15.641	0.010	45.669	-1.715	0.4119	0.68			
448.15	11.642	0.011	41.487	-1.631	0.3673	0.91			

Table 7. Interfacial tension γ for (N₂ + H₂O) at Temperatures T and Pressures p ; phases in equilibrium are designated with G = gas, L = liquid, or SC = supercritical. ^a

p/MPa	T/K	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$\gamma/\text{mN}\cdot\text{m}^{-1}$	Phases	T/K	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$\gamma/\text{mN}\cdot\text{m}^{-1}$	Phases
2	298.24	974.1	71.1	L-G	373.25	941.6	58.2	L-G
5	298.19	943.0	69.3	L-SC	373.23	916.5	57.2	L-SC
10	298.15	888.6	66.9	L-SC	373.15	875.1	55.6	L-SC
20	298.25	792.2	63.2	L-SC	373.15	799.8	53.3	L-SC
30	298.17	712.8	60.8	L-SC	373.13	738.2	51.2	L-SC
40	298.20	651.8	59.2	L-SC	373.13	685.6	50.4	L-SC
2	323.22	967.9	67.1	L-G	448.02	877.7	43.3	L-G
5	323.22	938.6	65.7	L-SC	447.98	858.3	42.8	L-SC
10	323.21	888.1	63.5	L-SC	448.05	826.2	41.9	L-SC
20	323.21	800.8	60.4	L-SC	448.02	766.7	40.5	L-SC
30	323.13	728.9	58.2	L-SC	448.03	715.8	39.5	L-SC
40	323.13	670.4	56.5	L-SC	448.00	671.2	38.9	L-SC

^a Standard uncertainties u are $u(T) = 0.025$ K, $u(p) = 35$ kPa, and $u(\gamma) = 0.009\gamma$ mN·m⁻¹.

Table 8. Fitting parameters of empirical model (6) for the (N₂ + H₂O) interfacial tension measurements.

a_{31}	a_{32}	b_{31}	b_{32}	c_3	d_3	σ	$10^2 \Delta_{\text{AAD}}$
-1.718×10^{-3}	3.290×10^{-3}	9.829×10^{-3}	-1.020×10^{-5}	1.092×10^{-4}	0.896	0.0861	0.40

Table 9. Interfacial tension γ for (CO₂ + N₂ + H₂O) at Temperatures T and Pressures p ; phases in equilibrium are designated with G = gas, L = liquid, or SC = supercritical; x_i and y_i are the calculated liquid- and vapour-phase compositions respectively, where 1 = CO₂, 2 = H₂O and 3 = N₂.^a

p/MPa	T/K	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$\gamma/\text{mN}\cdot\text{m}^{-1}$	Phases	x_1	x_2	x_3	y_1	y_2	y_3
2	298.18	969.0	64.0	L-G	0.0055	0.9943	0.0001	0.5103	0.0021	0.4876
5	298.17	921.8	55.9	L-G	0.0112	0.9885	0.0003	0.5099	0.0015	0.4886
10	298.17	824.1	46.6	L-G	0.0160	0.9835	0.0005	0.5092	0.0019	0.4889
20	298.16	634.4	39.6	L-SC	0.0175	0.9815	0.0010	0.5072	0.0056	0.4872
30	298.17	479.2	38.3	L-SC	0.0174	0.9812	0.0014	0.5044	0.0113	0.4843
40	298.15	399.0	37.7	L-SC	0.0174	0.9810	0.0017	0.5014	0.0174	0.4812
2	323.12	963.9	63.0	L-G	0.0030	0.9969	0.0001	0.5075	0.0082	0.4844
5	323.11	919.7	56.2	L-G	0.0070	0.9928	0.0002	0.5088	0.0046	0.4866
10	323.12	839.0	46.4	L-G	0.0109	0.9887	0.0004	0.5084	0.0045	0.4870
20	323.10	678.1	40.4	L-SC	0.0137	0.9855	0.0008	0.5064	0.0079	0.4856
30	323.10	537.2	39.1	L-SC	0.0145	0.9844	0.0011	0.5037	0.0132	0.4830
40	323.10	452.0	38.1	L-SC	0.0149	0.9837	0.0014	0.5010	0.0186	0.4804
2	373.25	937.0	55.2	L-G	0.0016	0.9983	0.0001	0.4813	0.0596	0.4590
5	373.25	901.4	50.1	L-G	0.0040	0.9959	0.0002	0.4965	0.0295	0.4740
10	373.25	840.1	45.9	L-G	0.0068	0.9928	0.0004	0.5002	0.0217	0.4781
20	373.23	716.1	40.6	L-SC	0.0103	0.9890	0.0007	0.4996	0.0221	0.4782
30	373.25	605.6	37.7	L-SC	0.0121	0.9869	0.0010	0.4973	0.0265	0.4763
40	373.22	523.5	35.8	L-SC	0.0132	0.9855	0.0013	0.4937	0.0311	0.4752
2	448.03	879.7	43.1	L-G	0.0008	0.9991	0.0001	0.2743	0.4642	0.2615
5	448.02	849.0	40.6	L-G	0.0028	0.9969	0.0003	0.4041	0.2094	0.3864
10	448.02	802.2	37.7	L-G	0.0055	0.9939	0.0006	0.4438	0.1299	0.4262
20	447.98	711.4	33.0	L-SC	0.0096	0.9892	0.0011	0.4603	0.0949	0.4447
30	448.02	631.5	30.2	L-SC	0.0124	0.9859	0.0017	0.4630	0.0880	0.4490
40	448.03	560.0	28.1	L-SC	0.0144	0.9835	0.0022	0.4631	0.0868	0.4501

^a Standard uncertainties u are $u(T) = 0.025$ K, $u(p) = 35$ kPa, and $u(\gamma) = 0.016\gamma$ mN·m⁻¹.

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