Interfacial Tension of CO2 + Brine Systems: Experiments and Predictive Modelling
Cravo Pereira, Luís Manuel; Chapoy, Antonin; Burgass, Rhoderick William; Tohidi Kalorazi, Bahman

Published in:
Advances in Water Resources

DOI:
10.1016/j.advwatres.2017.02.015

Publication date:
2017

Document Version
Peer reviewed version

Link to publication in Heriot-Watt University Research Portal

Citation for published version (APA):
Highlights:

- CO$_2$ + NaCl(aq) $IFT$s are measured from ambient conditions up to 423 K and 69.51 MPa;
- CO$_2$ + NaCl(aq) $IFT$s exceeded that of CO$_2$ + H$_2$O for all conditions examined;
- A predictive method, based on the DGT, is extended to CO$_2$ + brines;
- $IFT$s are accurately predicted for brines with ionic strength up to 2.7 mol kg$^{-1}$;
- The developed model can predict $IFT$s relevant for CO$_2$ storage in saline aquifers.
Interfacial Tension of CO₂ + Brine Systems: Experiments and Predictive Modelling

Luís M.C. Pereira, Antonin Chapoy, Rod Burgass, Bahman Tohidi*

Institute of Petroleum Engineering, Heriot-Watt University, EH14 4AS Edinburgh, UK

* To whom correspondence should be addressed:
e-mail: B.Tohidi@hw.ac.uk
Phone: +44(0) 1314513672
Abstract

In this study the interfacial tension (IFT) between CO$_2$ and brines, in the context of geological storage of CO$_2$, was investigated. Investigations covered both experimental and theoretical aspects of this property over a broad range of conditions, including those found in subsurface formations. Measurements for CO$_2$ + NaCl(aq) systems, of salt molalities 0.98 and 1.98 mol.kg$^{-1}$, were performed for temperatures and pressures up to 423 K and 69.51 MPa, respectively. Results clearly showed an increase from CO$_2$ + H$_2$O IFT upon the addition of the salt, helping to resolve some discrepancies observed in literature data. Furthermore, a predictive method, based on the Density Gradient Theory, was extended to CO$_2$ + brine systems, with modelled IFT values yielding a good agreement with experiments from this work and literature for brines of single and mixed salts, including NaCl, KCl and CaCl$_2$, and ionic strength up to 2.7 mol.kg$^{-1}$.

Keywords: carbon dioxide, sodium chloride, interfacial tension, cubic plus association, density gradient theory.
1. Introduction

Carbon Capture and Storage (CCS) technologies are seen as one of the most promising, and technically feasible, options for significantly reducing anthropogenic CO\textsubscript{2} emissions [1]. Accordingly, they involve capturing CO\textsubscript{2} directly from large industrial sources such as coal and gas power plants, and subsequently storing it in isolated sites such as deep porous geological structures. Among possible geological sites, deep saline aquifers offer the largest CO\textsubscript{2} capacity, while the frequent utilization of CO\textsubscript{2} in enhanced oil recovery (CO\textsubscript{2}-EOR) operations make oil and gas reservoirs more economically attractive storage options [2,3]. Though various pilot and commercial CO\textsubscript{2} storage projects have been successfully developed with encouraging results [4], long-term underground storage of CO\textsubscript{2} still presents several environmental concerns and technical challenges [5]. For example, one key issue, often of major importance for general public acceptance, concerns the safety and environmental risks of underground storage of large-scale quantities of CO\textsubscript{2}.

One key constraint in the safe geological storage of CO\textsubscript{2} involves the accurate knowledge of the sealing capillary pressure which prevents the migration \textit{(i.e., leakage)} of CO\textsubscript{2} from the storage site through the caprock (structural trapping). This pressure characterises the capillary-sealing efficiency of a caprock and it corresponds to the pressure at which the non-wetting phase (CO\textsubscript{2}) penetrates the largest pore of a caprock previously saturated with a wetting phase (typically H\textsubscript{2}O/brine), leading to the escape of CO\textsubscript{2} from the storage site (reservoir). The sealing capillary pressure (or capillary entry pressure − \(P_{ce}\)) can be approximated with the Young–Laplace equation for a caprock with pores of cylindrical shape and maximum radius \(R\) as follows [3,6–8]:

\[
P_{ce} = P_{CO_2} - P_{H_2O/Brine} \approx \frac{2 \gamma_{CO_2-H_2O/Brine} \cos \theta}{R}
\]  

where \(\theta\) is the contact angle of the H\textsubscript{2}O/brine phase with the solid surface and \(\gamma\) is the interfacial tension between the CO\textsubscript{2} and the H\textsubscript{2}O/brine phases. In this sense, the effective storage of CO\textsubscript{2} requires \(P_{ce}\) to be greater than the buoyancy pressure exerted by fluids in the underlying layer of the caprock; the reader is invited to read Ref. [9] for more details on this topic.

From Eq. 1, it becomes clear that accurate knowledge of CO\textsubscript{2} + H\textsubscript{2}O/brine IFT over geological pressure and temperature conditions is key for the design and maximization of
CO₂ storage projects. In a previous work [10], aiming at filling in experimental gaps and resolving some discrepancies found in literature data, the IFT of the CO₂ + H₂O system over a broad range of pressures (up to 69 MPa) and temperatures (up to 469 K) was measured. However, the investigation of the interfacial tension between CO₂ and brine remains highly relevant as reservoir water presents dissolved ions, mostly cations such as Na⁺, K⁺ Ca²⁺, Mg²⁺ and anions such as Cl⁻, SO₄⁻ and HCO₃⁻, to name just a few, and with total salt concentrations reaching or even exceeding 400 g.L⁻¹ [11].

It is well established that the addition of salts such as NaCl, KCl, CaCl₂ or MgCl₂ affects the physical properties and phase behaviour of aqueous systems, in particular the IFT. Several authors [12–19] have related the increase of gas + water IFT upon the addition of salts to the distribution of ions between the interfacial region and the bulk aqueous phase. Johansson and Eriksson [13] reported surface tension values for different salt solutions that exceeded those of salt-free water under analogous conditions. Using the concept of an electrolyte free layer and Gibbs adsorption equation, the authors [13] showed that the IFT increase must be related to the negative adsorption (i.e., depletion) of ions at the interface and, thereby, to their tendency to remain in the aqueous bulk phase. Hey et al. [20] showed that in 1:1 electrolytes solutions this increase was directly proportional to the enthalpy of hydration of ions (i.e., attraction to water), suggesting that ions were preferably fully hydrated in the bulk aqueous phase than partly hydrated in the interface. In general, the attraction of cations to water molecules is stronger than anions and hence, cations are strongly repelled while anions approach more closely to the interface [13,19]. Such gradient of ions results in an electrostatic potential differential at the interface which enhances the offset of water molecules from the interface towards the aqueous bulk phase and increases the magnitude of the interfacial tension [21]. Cation hydration increases as the ratio of cation charge to cation surface area is increased and thus the impact on the IFT is expected to increase as follows [22]:

$$\text{Cs}^+ < \text{Rb}^+ < \text{NH}_4^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$$

The findings described above are in agreement with Molecular Dynamics simulations performed by Li et al. [23] for CO₂ + brine systems and salts with the chloride (Cl⁻) anion over a broad range of pressure and temperature conditions. In their work, computed IFT values and density profiles of species across the interface also indicated a negative adsorption (negative surface excess) of ions at the interface.
Another important factor influencing the magnitude of experimentally determined IFT values, and often less discussed, may be associated to the density increase of the aqueous phase and gas solubility decrease ("salting-out" effect). The addition of salts increases the average molecular weight of the aqueous phase, which under the assumption that the excess volume of mixing is zero [24] results in a departure of the brine density from that of pure water. Such increase in density of the aqueous phase amplifies the density difference between phases ($\Delta \rho$). This effect greatly influences the experimental determination of IFT values through indirect measurement techniques which require the use of $\Delta \rho$, such as the pendant drop method. For example, at $T = 373$ K and $P = 50$ MPa, the density differences between phases of CO$_2$ + H$_2$O [10] and CO$_2$ + CaCl$_2$(aq) [25] systems reach a relative difference of approximately 94 and 179 % for CaCl$_2$ molalities $m = 2.5$ and 5.0 mol kg$^{-1}$, respectively. Furthermore, in the case of gas + brine systems, the well-known salting-out effect on the gas solubility enhances the differences between the equilibrated phases promoting the increase of IFT.

In spite of their relevance, and somewhat surprisingly, examination of literature shows that few studies have investigated the IFT between CO$_2$ and single/binary salt solutions at reservoir conditions. These studies are limited not only in the type of salt and brine composition, as summarized in Table 1, but also in some cases the results are inconsistent. For example, most of these studies show that IFT increases with salt concentration for any temperature and pressure state. However, as can be seen in Figure 1, IFT values reported by Chalbaud et al. [18] and Li et al. [21] for different brines containing NaCl against CO$_2$ are lower for all salinities than those between CO$_2$ and pure water at $T = 298$ K [10,26]. It is worth noting that Chalbaud et al. [18] and Li et al. [21] have already accounted for the increase in density of the brine-rich phase due to the dissolution of CO$_2$, and in turn its impact on the magnitude of the IFT. Therefore, it is necessary to perform further measurements to clarify such discrepancies ("low" IFT), especially for systems with NaCl as this is the most abundant salt in the reservoir brine [11].
The development of robust thermodynamic modelling tools capable of predicting the IFT between CO₂ and brines over geological conditions would help overcome the difficulties associated with the experimental determination of this property as well as the costs, as such measurements require high-pressure and corrosion-resistant equipment. Additionally,
modelling tools are essential for a proper design and overall optimisation of CO₂ sequestration projects. Therefore, in this work we further explore and validate the modelling treatment proposed in a previous work [33] for predicting the IFT of CO₂ + brine systems. In this modelling approach, the impact of water salinity on the interfacial tension of gas + brine is accounted for by considering the impact of salts on the phase equilibria of the system, namely the salting-out effect on the solubility of gases, and the IFT predicted using the profile density distribution through the interface calculated within the framework of the Density Gradient Theory [34] for the corresponding hypothetical salt-free system. Such approximated treatment of effect of salts does not account for their impact on the interfacial structure. Nonetheless, as it will be shown, not only modelled CO₂ + brine IFTs show a linear relationship between brine molality and IFT increase, consistent with experimental observations, but the method can also effectively predict the additive effect of salts.

In summary, the aim of this work is to contribute with experimental IFT data of CO₂ + NaCl(aq) systems at conditions representative of those found in underground formations and to examine the capability of our proposed modelling approach for predicting the interfacial tension of CO₂ + brine systems by comparison with experimental data from this work and gathered from literature.
2. Experimental

2.1. Chemicals

The specification and sources of the chemicals used in this work are summarized in Table 2. The water used has better specifications than double-distilled water (electrical conductivity $<0.02 \ \mu$S.cm$^{-1}$ at $T = 298$ K). Toluene and $n$-heptane were used in this work for cleaning purposes only.

Two NaCl aqueous solutions of molalities 0.98 and 1.98 mol.kg$^{-1}$ were prepared gravimetrically by adding the salt (dried in an oven at $T = 373$ K for 24h) to water. The mass of salt was determined using a Mettler Toledo balance (model PB3002) with a resolution of 0.001 g and thus, the relative uncertainty in the molality of the NaCl aqueous solutions is taken equal to the purity of the salt (0.5 %).

Table 2. Suppliers and specification as stated by the supplier of the materials used in this work.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Supplier</th>
<th>Mass fraction purity</th>
<th>Chemical analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>BOC</td>
<td>0.99995</td>
<td>$\leq$0.01 ppm silicate</td>
</tr>
<tr>
<td>Toluene</td>
<td>Fischer Scientific</td>
<td>$&gt;0.995$</td>
<td>$\leq$0.4 ppm Cl$^{-}$</td>
</tr>
<tr>
<td>$n$-Heptane</td>
<td>RathBurn Chemicals</td>
<td>$&gt;0.99$</td>
<td>$\leq$0.4 ppm NO$_3$$^-$</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>Fischer Scientific</td>
<td>$&gt;0.995$</td>
<td>$\leq$1.0 ppm PO$_4$$^{3-}$</td>
</tr>
<tr>
<td>Water</td>
<td>Sigma-Aldrich</td>
<td></td>
<td>$\leq$1.0 ppm SO$_4^{2-}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\leq$0.01 ppm heavy metals (as Pb)</td>
</tr>
</tbody>
</table>

2.2. Apparatus

The high pressure/high temperature apparatus used in this work is the same used by us in a previous work [10] to measure IFT of the CO$_2$ + H$_2$O system; the reader is referred to this work for a detailed description of the apparatus. In summary, the IFT setup consists of a see-through windowed equilibrium cell of cylindrical shape (internal volume of 23 cm$^3$), made of Hastelloy C-276 and with 4 fluid ports, an imaging capturing and analysing system, sample piston vessels and a hand pump.

The equilibrium cell has a capillary tube (o.d. 1.610 ± 0.001 mm) inserted through the top fluids port and positioned so a pendant drop of the brine solution can be formed at the tip of
the capillary and maintained in equilibrium with a CO$_2$ atmosphere. According to the applied measurement technique, the IFT from pendant drops was evaluated using the Axisymmetric Drop Shape Analysis (ADSA) method, commercially available through SCA 20 (Data Physics, Germany). A detailed description of the theoretical background of this method can be found elsewhere [35–38]. In short, the principle of the ADSA method is based on matching the experimental drop profile from a digitalized image to a series of Laplacian curves with known interfacial tension values. The objective function to minimise is equal to the sum of squares between the coordinates extracted through edge detection of an image of the pendant drop (experimental curve) and theoretical curves. The best calculated curve identifies the interfacial tension value ($\gamma$) which, in turn, is related to the parameters of the pendant drop by:

$$\gamma = \frac{\Delta \rho g}{(Bk_{\text{apex}})^2}$$  \hspace{1cm} (3)

where $\Delta \rho$ is the density difference between the equilibrated phases, $g$ is the gravitational acceleration and $B$ and $k_{\text{apex}}$ are parameters adjusted to the profile of the drop. As part of the inputs in Eq. 3, the density of the equilibrated phases, in the form of $\Delta \rho$, is required for an accurate estimation of the IFT values.

Considering the effect of CO$_2$ solubility on the phase density difference of the CO$_2$ + H$_2$O system and, in turn, the impact on the experimental determination of IFT values [6,10], it becomes also important to properly account for the effect of CO$_2$ dissolution on the density of NaCl solutions. Experimental CO$_2$-saturated liquid density data of NaCl brines were reported by Yan et al. [39]. In their work, the densities of CO$_2$-saturated solutions with NaCl molalities of 1 and 5 mol.kg$^{-1}$ were measured using a vibrating U-tube densitometer at temperatures in the range 323 to 413 K and pressures up to 40 MPa. In order to estimate the density of the CO$_2$-saturated brine phase at pertinent pressure and temperature conditions, and salt molalities, the model developed by Duan et al. [40] was used (through computer programs mentioned therein). Accordingly, this model is a multi-parameter correlation based on the Duan et al. [41] EoS, and improved versions of the model [42,43], and on the theory of Pitzer [44]. The Duan model is expected to be capable of predicting the CO$_2$-saturated brine density of CO$_2$ + NaCl(aq) systems for temperatures and pressures up to 573 K and 100 MPa, respectively, and NaCl molalities up to 4.5 mol. kg$^{-1}$. To check the validity of this approach, deviations of the Duan et al. [40] model to CO$_2$-saturated water and CO$_2$-saturated brine
density data measured by Pereira et al. [10] and Yan et al. [39], respectively, were calculated and the results plotted in Figure 2. As can be seen, the model allows a reproduction of the density of the aqueous phase of the CO$_2$ + H$_2$O and CO$_2$ + NaCl(aq) systems above 99.50 % and 99.75 %, respectively, with an average absolute deviation to experimental data of 1.3 (0.13 %) and 0.7 kg.m$^{-3}$ (0.06 %), respectively, confirming to some extent the validity of this approach. In contrasts, several studies (see Refs. [6,10,45,46] and additional references mentioned therein) have shown that the departure of the density for the water-saturated CO$_2$ phase in the CO$_2$ + H$_2$O system from that of pure CO$_2$ is nearly negligible, and thus the density of this phase can be fairly approximate to that of pure CO$_2$ without any significant loss of accuracy in the IFT measurements for the range of conditions of interest. Therefore, in this work the density of water-saturated CO$_2$ phase was taken to be equal to that of pure CO$_2$, calculated using Span and Wagner EoS, as implemented in REFPROP [47], under analogous pressure and temperature conditions.

Figure 2. Relative deviation–pressure and absolute deviation–pressure diagrams of (a and b) CO$_2$ + H$_2$O and (c and d) CO$_2$ + NaCl(aq) ($m_{NaCl}$ = 1 mol.kg$^{-1}$) systems. Symbols represent deviations of CO$_2$-saturated liquid
densities calculated using the Duan et al. [40] model to measured data from: Pereira et al. [10] (circles) and Yan et al. [39] (triangles).

2.3. Experimental Procedure

After thorough cleaning with n-heptane and toluene, and vacuuming of the cell, CO$_2$ was introduced under pressure into the cell, from a piston vessel and by means of high pressure tubing, and the pressure inside the cell maintained by isolating the cell from the CO$_2$ source. The tested brine was degassed by means of an ultra-sonic bath during 30 min before it was transferred to the hand pump and connected to the top of the cell. Following this, sufficient brine solution was introduced into the cell until this phase was visible on the bottom of the cell and the system left to reach equilibrium. This procedure helped ensuring saturation of the CO$_2$ atmosphere in water molecules. In order to measure CO$_2$ + NaCl(aq) IFT values, a drop of the brine solution was formed inside the cell at the tip of the capillary tube by means of turning the hand pump and the drop was recorded for at least 900 s and frames taken each 10 s. A minimum of 3 consecutive drops were considered for each pressure and temperature state and the IFT taken as the average of IFT values computed from frames captured within the $300^{th}$ and $600^{th}$ second.

3. Modelling

3.1. Theoretical Background

The Density Gradient Theory (DGT) is a rigorous theoretical approach which converts the statistical mechanics of inhomogeneous fluids (interface) into a set of non-linear equations to compute the density profiles ($d\rho_i/dz$) of species $i$ and interfacial tension values. Based on the original work of van der Waals for inhomogeneous fluids [48], and later reformulated by Cahn and Hilliard [34], the DGT is built around the minimization of the Helmholtz free energy of inhomogeneous fluid ($F$). For a planar interface of area $A$ and in the absence of external forces it is given by [49]:

$$F = A \int_{-\infty}^{\infty} \left[ f_0(\rho(z)) + \sum_i \sum_j c_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} \right] dz \quad (4)$$

It is clear from previous equation that the minimization of $F$ involves a contribution of the Helmholtz free energy density of the homogeneous fluid ($f_0$) at local density $\rho(z)$ and a corrective term a corrective term consisting on the influence parameter ($c_{ij}$) and the density
gradients in the inhomogeneous fluid \((d\rho_i/dz \text{ and } d\rho_j/dz)\). The density gradients in the interfacial region are calculated by solving the Euler-Lagrange equations obtained by applying the free energy minimum criterion to \textbf{Eq. 4}, which under the assumption that the influence parameters are weakly dependant on the density gradients \([50,51]\), yields:

\[
\sum_j c_{ij} \frac{d^2 \rho_i}{dz^2} = \mu_i(\rho_1(z),...,\rho_N(z)) - \mu_i^{eq} \quad \text{for } i,j = 1...N_{comp}
\]

where \(\mu_i\) are the pure component chemical potentials evaluated at each spatial point \((i.e., \, z^k)\) and at the phase equilibrium conditions of the bulk phases \((\mu_i^{eq})\). \textbf{Eq.5} represents the set of equations governing the density distribution of components across the interfacial region. The applied method for solving these equations is based on \(i)\) a discretization of the density derivatives in space \(z\) by a finite difference method and \(ii)\) solving the resultant set of non-linear equations by a Newton-Raphson iteration scheme for increasing values of interface thickness \([49,52,53]\). The boundary conditions of the differential problem are defined by the homogeneous phases in contact \(I\) and \(II\): \(\rho_i(z \rightarrow z^k) = \rho_i^k\) with \(k = I\) and \(II\). Once the density distribution across the interface is known, the IFT is computed by \([54,55]\):

\[
\gamma = \int_{-\infty}^{\infty} \left[ \sum_j \sum_i c_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} \right] dz
\]

The cross influence parameters \(c_{ij}\) are related to pure component influence parameters \(c_i\) and \(c_j\) by the following mixing rule \([51]\):

\[
c_{ij} = (1 - \beta_{ij}) \sqrt{c_i c_j}
\]

where \(\beta_{ij}\) is the adjustable binary interaction coefficient of influence parameters. The influence parameters relate the response of the density gradients to the local deviations of the chemical potentials from their bulk values and, in turn, the energy of the interface \([49,55,56]\).

From what was presented above, the only inputs of the DGT are the Helmholtz free energy density of the homogeneous fluid and the influence parameters of pure components. The Helmholtz free energy density of the homogeneous fluid is accessible through an equation of state (EoS), whereas influence parameters are in general calculated from surface tension data of pure fluids or estimated from correlations available in literature (see Ref. \([57]\) and references mentioned therein).
3.2. Modelling the CO$_2$ + H$_2$O system

Several authors [58–63] have described the IFT of the CO$_2$ + H$_2$O system by coupling the DGT with SAFT (Statistical Association Fluid Theory)-type EoSs. Of these, Chow et al. [64] applied the SAFT-VR Mie and described the IFT of this system over a broad range of temperatures (up to 448 K) and pressures (up to 60 MPa), with an overall deviation between calculated and experimental values of only 4.8 %. In their work, the authors used the geometric-mean of influence parameters (i.e., $\beta_{ij} = 0$ in Eq. 7) and adopted the influence parameters to be linear functions of temperature estimated for H$_2$O from pure component surface tension data and for CO$_2$ from experimental interfacial tension data of the binary. This procedure corresponds to an attempt by the authors of overcoming the challenges that arise from the use of an influence parameter for CO$_2$ estimated from properties in subcritical conditions ($T_c \sim 304.1$ K) which, in turn, may not be enough for providing an accurate representation of the influence parameters at/or above supercritical conditions. Their method seemed to also capture effectively the IFT between water and sparingly soluble gases such as nitrogen ($T_c \sim 126.2$ K) and argon ($T_c \sim 150.7$ K), as well as the IFT of CO$_2$ + N$_2$ + H$_2$O and CO$_2$ + Ar + H$_2$O mixtures, with overall deviations between calculated and experimentally determined IFT values ranging from 1.5 to 7.9 % [64]. Other authors, such as Li et al. [60], Niño-Amezquita et al. [59] and Lafitte et al. [58], applied the PC-SAFT, PCP-SAFT and SAFT-VR Mie EoSs, respectively, together with constant influence parameters estimated from pure component surface tension data, and successfully modelled CO$_2$ + H$_2$O IFT for moderate pressures (up to 20 MPa) and temperatures (up to 344 K). Both Niño-Amezquita et al. [59] and Lafitte et al. [58] used a single, temperature independent, binary coefficient different from zero in the mixing rule of influence parameters for describing correctly the IFT of the CO$_2$ + H$_2$O system, whereas Li et al. [60] opted for using the geometric-mean mixing rule and on adjusting the binary coefficients of the selected EoS (i.e., $k_{ij}$s) simultaneously to bulk phase densities and interfacial tensions of the investigated binary system.

In our previous work [10], the DGT was combined with the Cubic-Plus-Association (CPA) EoS [65,66], and by using the geometric-mean of influence parameters along with the method proposed by Khosharay et al. [62,63] for estimating the influence parameters of CO$_2$ and H$_2$O, the IFT of the CO$_2$ + H$_2$O system was predicted over a broad range of temperatures (up to 469 K) and pressures (up to 69 MPa) with remarkably low overall deviations (4.5 %) to experimentally determined IFT values. The method proposed by Khosharay and co-workers
[62,63] involved correlating the influence parameters adjusted from surface tension data to saturated vapour and liquid density of pure fluids. Subsequently, the influence parameters in the mixture were estimated taking into account the molar density of each component in the bulk phases. Khosharay et al. applied the CK-SAFT [62] and the sPC-SAFT [63] EoSs to model the IFT of several aqueous binary systems including carbon dioxide, hydrogen sulphide, methane, ethane and propane, with binary interaction coefficients of the selected EoS \( (k_{ij}) \) regressed simultaneously against density and IFT binary data. The method of Kosharay et al. [62,63] for the influence parameters seemed to improve the description of \( \text{CO}_2 + \text{H}_2\text{O} \) IFT when compared to using constant influence parameters calculated from surface tension data. However, their approach for the influence parameters showed negligible improvement in the modelling of the IFT of water against methane and ethane [62], and in the case of \( \text{H}_2\text{S} + \text{H}_2\text{O} \) IFT, overall deviations from experimental values from two experimental data sets were even seen to increase from 5.8 % (constant influence parameters) to 11.5 % (density dependent influence parameters) [63]. Furthermore, Khosharay and Varaminian [62] reported not being able to determine the density profiles and accompanied IFT of the \( \text{C}_3\text{H}_8 + \text{H}_2\text{O} \) system when using the new proposed approach for the influence parameters. Indeed, we experienced similar problems when using their influence parameter method for modelling \( \text{CH}_4 + \text{H}_2\text{O} \) IFT [33]. It is believed that such problems are intrinsically associated to the magnitude of the influence parameters together with the use of the geometric-mean mixing rule for the influence parameters in aqueous systems which, in turn, can lead to the appearance of infinitely steep density profiles for the adsorbed components creating numerical difficulties in the calculation of the density gradients; these results have been described in detail elsewhere [52,53].

To circumvent the constraint described above, and as a way of keeping the model accessible to a wider class of systems and the number of adjustable parameters to a minimum, it was decided to use in this work only constant influence parameters. The \( \text{H}_2\text{O} \) influence parameter was calculated using the correlation developed by Queimada et al. [67], whereas the \( \text{CO}_2 \) influence parameter was estimated from surface tension data [47]. \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) influence parameters, calculated at fixed reduced temperatures of 0.45 and 0.72, respectively, are listed in Table 3. Aiming at mitigating the numerical difficulties associated to the appearance of very sharp peaks in the density profiles and at providing a correct description of \( \text{CO}_2 + \text{H}_2\text{O} \) IFT, a single, temperature independent, value for \( \beta_{ij} \neq 0 \) was used. In order to keep the modelling approach as predictive as possible, the value of \( \beta_{ij} \) was estimated with the aid of
one experimental binary IFT data point [10], at intermediate conditions ($T = 374.0 \text{ K}$ and $P = 12.09 \text{ MPa}$), and then used to compute, in a predictive manner, tensions at other pressure and temperature conditions. The estimated value was found to amount $\beta_{ij} = 0.27$.

The required phase equilibrium properties and Helmholtz free energy density of the system were evaluated using the CPA EoS. A brief description of this EoS, along with the association scheme considered for CO$_2$ and H$_2$O and the expression used for estimating the EoS binary interaction coefficients ($k_{ii}$s), both established in previous works, are provided in the Supporting Information; H$_2$O and CO$_2$ CPA parameters used are listed in Table 3. At this point it is important to mention that the selected modelling approach ensures that both phase equilibrium properties and IFT values of the CO$_2$ + H$_2$O system are effectively described.

**Table 3.** CPA parameters and DGT influence parameters used in this work. CPA parameters for H$_2$O and CO$_2$ were taken from the works of Kontogeorgis *et al.* [68] and Tsivintzelis *et al.* [69], respectively.

<table>
<thead>
<tr>
<th></th>
<th>$a_0$ (J.m$^3$.mol$^{-2}$)</th>
<th>$c_1$</th>
<th>$b$ (10$^{-5}$ m$^3$.mol$^{-1}$)</th>
<th>$e$ (J.mol$^{-1}$)</th>
<th>$\beta_{IPA}$</th>
<th>$c_i$ (10$^{-20}$ J m$^2$ mol$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>0.12277</td>
<td>0.6736</td>
<td>1.45</td>
<td>16655</td>
<td>0.0692</td>
<td>1.80137</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.35079</td>
<td>0.7602</td>
<td>2.72</td>
<td>2.84620</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3** shows a comparison between computed and experimental [10] IFT values of the CO$_2$ + H$_2$O system. While very good agreement was obtained at moderate and high temperatures, greater deviations were observed at low temperatures ($T = 298$ and $313 \text{ K}$), resulting in an overall percentage average absolute deviation between computed and experimental IFTs of 6.5 %. Nonetheless, considering the wide range of conditions examined, the results are very satisfactory. The adopted approach presents a slightly higher overall deviation than that obtained when using bulk density dependent functions for the influence parameters (4.5 %) [10], but with the advantage of being numerically stable.
As an example of the distribution of components across the interfacial region, density profiles of CO$_2$ and H$_2$O calculated for two distinct pressures at $T = 298$ and 373 K are shown in Figure 4. Observation of this figure reveals the strong adsorption of CO$_2$ on the CO$_2$-rich side of the interface, as noticed by the appearance of a peak in the CO$_2$ density profile, whereas H$_2$O density increases monotonically from the bulk CO$_2$-rich phase, through the interfacial region and into the H$_2$O-rich phase. Increasing pressure resulted in a decrease of the relative height of the CO$_2$ adsorption peaks, as the density of the CO$_2$-rich bulk phase also increased, corresponding to the isothermal phase change of CO$_2$ from vapour/gaseous to liquid/supercritical. These results are consistent with those of others [58–61].
3.3. Predictive Modelling of the Impact of Salts

As already explained in the introduction, the increase in IFT upon the addition of salts appears to be related to their effect on the bulk properties as well as to the negative surface excess of ions at the interface. Based on this, we explored the idea of predicting the IFT between CO$_2$ and brines solutions by considering only the IFT increase associated with changes on the phase equilibria. In our approximated approach, the impact of salts on the bulk properties are modelled via the CPA EoS combined with an electrolyte model and the accompanying IFT predicted via the density profiles of CO$_2$ and H$_2$O through the interface in a hypothetical salt-free system computed using the DGT. In other words, the change in IFT is modelled by considering the salting-out effect and its influence on the energy of both bulk phases and interface in a salt-free system. Such approach does not account for the depletion of ions at the interface; however, initial results showed [33] that this method lead to successful predictions of the IFT of CH$_4$ + NaCl(aq) systems with salt molalities up to 1.91 mol.kg$^{-1}$. In this work, the model is extended to CO$_2$ + brine systems and the validity of such idea (approximation) is tested for higher salt molalities.

The electrolyte model used to describe the salting-out effect is based on the method proposed by Aasberg-Petersen et al. [70] and applicable to any EoS, where the gas solubility is modelled by adding a modified Debye-Hückel electrostatic contribution term to the fugacity coefficient term of components in the aqueous phase. For the sake of brevity, the description of the applied method for modelling the phase equilibria of CO$_2$ + brine mixtures along with parametrisation and evaluation procedure are provided in the Supporting Information. In short, the developed CPA EoS + Electrolyte model can be used to readily obtain an accurate description of the phase equilibria of CO$_2$ and brines composed of single and mixed salts, including NaCl, KCl and CaCl$_2$, for salt molalities up to 5 mol.kg$^{-1}$ and temperatures up to 473 K.

4. Results and Discussion

4.1. Experimental Measurements

The interfacial tension of CO$_2$ + NaCl(aq) systems were measured at temperatures ranging from 298 to 423 K and pressures up to 69.51 MPa, and salt molalities 0.98 and 1.98 mol.kg$^{-1}$. The results are listed in Tables 4 and 5, and plotted in Figure 5. It can be observed that the addition of NaCl resulted in an increase of the IFT from that of the CO$_2$ + H$_2$O system for all
investigated pressure and temperature conditions. This effect appeared to be less marked at $T = 298 \text{ K}$ and below the saturation pressure of CO$_2$, where $IFT$ varies rapidly with pressure. On the other hand, measurements at higher pressures and temperatures, where $IFT$ reaches a pseudo-plateau, suggest that the increment in $IFT$ due to the presence of NaCl was approximately constant and nearly doubled with salt molality. Indeed, the average relative increase observed on the $IFT$ values from that of the CO$_2 +$ H$_2$O system [10], over the investigated pressure range, was found to amount 7.2 % (2.01 mN.m$^{-1}$) and 13.2 % (3.73 mN.m$^{-1}$) at $T = 333$, 373 and 423 K, and around 4.4 % (1.42 mN.m$^{-1}$) and 7.8 % (2.67 mN.m$^{-1}$) at $T = 298$ K, for NaCl molalities 0.98 and 1.98 mol.kg$^{-1}$, respectively, as depicted in Figure 6.

The measurement of any thermophysical property is always susceptible to uncertainties which affect the overall accuracy of experimental data. The combined expanded uncertainties in the interfacial tension measurements, $U_c(IFT)$, were estimated as in our previous work [10]. Accordingly, $U_c(IFT)$ was estimated considering the uncertainties that arise from the ADSA method, $U_1(IFT)$, and the uncertainties associated to the estimation of the density difference for the equilibrated phases, $U_2(IFT)$. The combined expanded uncertainties, estimated with a confidence greater that 95 %, for each experimental condition are given in Tables 4 and 5. Overall, the combined expanded uncertainty for the applied measurement method had an average value of 0.27 mN.m$^{-1}$ (0.84 %) and reached a maximum value of 0.68 mN.m$^{-1}$ (2.33 %) at the state point with the lowest calculated density difference ($\Delta \rho = 100.1$ kg.m$^{-3}$ in Table 4).

Although the impact of NaCl on the $IFT$ of the CO$_2 +$ H$_2$O system was already studied in literature (Table 1), only measurements from Refs. [28,30] permit a fairly direct comparison with the values presented in this work at $T = 298$ K. To allow some discussion at other temperatures, data from Chalbaud et al. [18] at $T = 373$ K and different NaCl molalities are also plotted in Figure 5 along with data from Li et al. [21] at $T = 373$ and 423 K for a brine composed of 0.864 (mole fraction) NaCl and 0.136 (mole fraction) KCl, and total salt molalities 0.98 and 1.98 mol.kg$^{-1}$. From this figure it can be observed that the data measured in this work appear to be in good agreement with those of Liu et al. [28], but in reasonable agreement with those of Liu et al. [30] and Chalbaud et al. [18]. CO$_2 +$ NaCl(aq) $IFT$ data from Liu et al. [30] at $T = 298$ K display a less marked change in behaviour near the saturation pressure of CO$_2$, with measurements showing an apparent continuous decrease of $IFT$ at higher pressures. In the case of $IFT$ data from Chalbaud et al. [18] at $T = 373$ K and

19
NaCl molalities $m = 0.09$ and $0.87 \, \text{mol.kg}^{-1}$, they are generally lower than $\text{CO}_2 + \text{H}_2\text{O} \, \text{IFT}$ at identical pressure, similar to what was already described for other experimental data sets in the introduction. Regarding the data from Li et al.[21], despite the discrepancies observed at $T = 298 \, \text{K}$ (Figure 1), comparison with the isotherms at $T = 373$ and $423 \, \text{K}$ indicates that $\text{Na}^+$ and $\text{K}^+$ ions have similar impact on the $\text{IFT}$ values as their data are very close to $\text{CO}_2 + \text{NaCl(aq)} \, \text{IFT}$ measured in this work at identical pressure, temperature and brine molality. It is also important to note that, even though higher water salinities than those investigated in the present work can be found in deep reservoirs [11], $\text{IFT}$ is expected to increase linearly with salt molality [19,21,25,31,32] and thus, the $\text{IFT}$ reported here can be extrapolated to systems with higher NaCl content with fairly good confidence.

Overall, these measurements helped to resolve the inconsistencies (“low” $\text{IFT}$) observed in $\text{CO}_2 + \text{NaCl(aq)} \, \text{IFT}$ data available in literature, while extending both pressure and temperature conditions from previous maximum (45 MPa and 398 K).
Table 4. Measured interfacial tension data of the CO$_2$ + H$_2$O + NaCl system for a salt molality 0.98 mol.kg$^{-1}$. The density difference used corresponds to the difference between the values estimated with the model of Duan et al. [40] for the CO$_2$-saturated brine phase and pure CO$_2$ obtained from REFPROP [47].

<table>
<thead>
<tr>
<th>$P$ (MPa)</th>
<th>$\Delta \rho$ (kg.m$^{-3}$)</th>
<th>$IFT$ (mN.m$^{-1}$)</th>
<th>Experimental Error (mN.m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T = 298.6$ K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.00</td>
<td>980.1</td>
<td>53.39</td>
<td>0.04 0.12 0.16</td>
</tr>
<tr>
<td>4.96</td>
<td>918.2</td>
<td>42.37</td>
<td>0.05 0.12 0.17</td>
</tr>
<tr>
<td>5.66</td>
<td>882.7</td>
<td>38.43</td>
<td>0.03 0.14 0.17</td>
</tr>
<tr>
<td>10.31</td>
<td>236.1</td>
<td>32.98</td>
<td>0.07 0.32 0.59</td>
</tr>
<tr>
<td>15.58</td>
<td>177.4</td>
<td>32.35</td>
<td>0.04 0.38 0.42</td>
</tr>
<tr>
<td>20.21</td>
<td>145.0</td>
<td>32.33</td>
<td>0.08 0.46 0.54</td>
</tr>
<tr>
<td>3.91</td>
<td>952.0</td>
<td>52.1</td>
<td>0.04 0.12 0.16</td>
</tr>
<tr>
<td>7.40</td>
<td>858.8</td>
<td>41.7</td>
<td>0.04 0.12 0.16</td>
</tr>
<tr>
<td>18.84</td>
<td>331.5</td>
<td>31.7</td>
<td>0.06 0.21 0.27</td>
</tr>
<tr>
<td>40.94</td>
<td>150.5</td>
<td>29.4</td>
<td>0.14 0.40 0.54</td>
</tr>
<tr>
<td>55.07</td>
<td>100.1</td>
<td>29.2</td>
<td>0.09 0.59 0.68</td>
</tr>
<tr>
<td>$T = 333.2$ K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.19</td>
<td>876.9</td>
<td>44.04</td>
<td>0.06 0.11 0.17</td>
</tr>
<tr>
<td>12.32</td>
<td>753.1</td>
<td>35.94</td>
<td>0.11 0.11 0.22</td>
</tr>
<tr>
<td>20.14</td>
<td>525.2</td>
<td>30.60</td>
<td>0.05 0.13 0.18</td>
</tr>
<tr>
<td>40.89</td>
<td>255.9</td>
<td>26.81</td>
<td>0.05 0.21 0.26</td>
</tr>
<tr>
<td>69.50</td>
<td>131.6</td>
<td>25.10</td>
<td>0.06 0.38 0.44</td>
</tr>
<tr>
<td>$T = 373.4$ K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.69</td>
<td>882.2</td>
<td>42.3</td>
<td>0.04 0.10 0.14</td>
</tr>
<tr>
<td>11.12</td>
<td>798.9</td>
<td>35.6</td>
<td>0.05 0.09 0.14</td>
</tr>
<tr>
<td>22.37</td>
<td>600.1</td>
<td>27.3</td>
<td>0.06 0.10 0.16</td>
</tr>
<tr>
<td>43.07</td>
<td>346.6</td>
<td>22.2</td>
<td>0.06 0.13 0.19</td>
</tr>
<tr>
<td>69.07</td>
<td>204.2</td>
<td>19.9</td>
<td>0.05 0.20 0.25</td>
</tr>
</tbody>
</table>
Table 5. Measured interfacial tension data of the CO$_2$ + H$_2$O + NaCl system for a salt molality 1.98 mol.kg$^{-1}$. The density difference used corresponds to the difference between the values estimated with the model of Duan et al. [40] for the CO$_2$-saturated brine phase and pure CO$_2$ obtained from REFPROP [47].

<table>
<thead>
<tr>
<th>$P$ (MPa)</th>
<th>$\Delta \rho$ (kg.m$^{-3}$)</th>
<th>$IFT$ (mN.m$^{-1}$)</th>
<th>Experimental Error (mN.m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$U_1$</td>
</tr>
<tr>
<td>$T = 298.6$ K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.96</td>
<td>1015.9</td>
<td>54.98</td>
<td>0.04</td>
</tr>
<tr>
<td>4.12</td>
<td>983.3</td>
<td>48.43</td>
<td>0.03</td>
</tr>
<tr>
<td>5.69</td>
<td>914.7</td>
<td>39.59</td>
<td>0.03</td>
</tr>
<tr>
<td>10.25</td>
<td>270.4</td>
<td>34.09</td>
<td>0.06</td>
</tr>
<tr>
<td>14.82</td>
<td>217.1</td>
<td>33.74</td>
<td>0.07</td>
</tr>
<tr>
<td>19.90</td>
<td>179.8</td>
<td>33.61</td>
<td>0.07</td>
</tr>
<tr>
<td>$T = 333.2$ K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.09</td>
<td>981.9</td>
<td>53.20</td>
<td>0.07</td>
</tr>
<tr>
<td>7.86</td>
<td>875.2</td>
<td>42.14</td>
<td>0.03</td>
</tr>
<tr>
<td>18.85</td>
<td>363.0</td>
<td>33.34</td>
<td>0.06</td>
</tr>
<tr>
<td>41.72</td>
<td>178.6</td>
<td>31.22</td>
<td>0.04</td>
</tr>
<tr>
<td>54.76</td>
<td>132.1</td>
<td>30.99</td>
<td>0.06</td>
</tr>
<tr>
<td>$T = 373.3$ K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.61</td>
<td>959.3</td>
<td>50.69</td>
<td>0.08</td>
</tr>
<tr>
<td>11.49</td>
<td>809.5</td>
<td>39.01</td>
<td>0.13</td>
</tr>
<tr>
<td>21.94</td>
<td>515.3</td>
<td>31.76</td>
<td>0.08</td>
</tr>
<tr>
<td>43.18</td>
<td>273.1</td>
<td>28.34</td>
<td>0.11</td>
</tr>
<tr>
<td>69.51</td>
<td>162.6</td>
<td>27.16</td>
<td>0.04</td>
</tr>
<tr>
<td>$T = 423.2$ K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.65</td>
<td>918.1</td>
<td>44.36</td>
<td>0.07</td>
</tr>
<tr>
<td>12.17</td>
<td>815.9</td>
<td>36.00</td>
<td>0.09</td>
</tr>
<tr>
<td>21.88</td>
<td>642.5</td>
<td>29.07</td>
<td>0.05</td>
</tr>
<tr>
<td>44.35</td>
<td>369.5</td>
<td>23.25</td>
<td>0.09</td>
</tr>
<tr>
<td>69.00</td>
<td>236.5</td>
<td>21.64</td>
<td>0.05</td>
</tr>
</tbody>
</table>
CO₂ + H₂O: ○ Pereira et al.[10]
CO₂ + NaCl(aq): ▽ 0.98 and ▼ 1.98 mNaCl This work
△ 1.03 mNaCl Liu et al.[28]
☆ 0.90 and ◊ 1.90 mNaCl Liu et al.[30]
△ 0.09, △ 0.87, △ 1.79 and △ 2.75 mNaCl Chalbaud et al.[18]
CO₂ + [0.864NaCl + 0.136 KCl] (aq): ▽ 0.98 and ◊ 1.98 mNaCl Li et al.[21]

Figure 5. IFT−pressure diagrams of CO₂ + H₂O and CO₂ + brine systems.
Figure 6. Average IFT increase−temperature diagram of CO$_2$ + NaCl(aq) systems. IFT increase was calculated relative to CO$_2$ + H$_2$O IFT values correlated from previous measurements [10] and averaged over the pressure range investigated. Error bars correspond to averaged experimental uncertainties listed in Tables 4 and 5 for each isotherm.

4.2. Comparison of Model and Experiments

IFT of CO$_2$ + brines systems were predicted and the results compared to experimental data measured in the present work and gathered from literature for selected single and binary salt systems, as depicted in Figures 7 and 8. IFTs between CO$_2$ and brines have been predicted by keeping the binary interaction coefficient $\beta_{ij} = 0.27$ between CO$_2$ and H$_2$O within the DGT framework and the phase equilibria modelled trough the CPA EoS + Electrolyte model, without any further adjustments to IFT data.

As shown in Figures 7 and 8, the present modelling approach can adequately predict the increase in IFT due to the presence of salts such as NaCl, KCl and CaCl$_2$ as well as their mixtures; very good agreement with experimental data measured here for CO$_2$ + NaCl(aq) at $T = 333$ and 373 K and salt molalities up to 1.98 mol.kg$^{-1}$ is observed. In addition, as substantiated experimentally [19,21,25,31,32], predicted IFT values increase linearly with salt molalities; as an example, results for CO$_2$ + [0.864 NaCl + 0.136 KCl](aq) at $T = 373$ K and selected isobars are plotted in Figure 9. However, for very concentrated brines, and depending on the computed CO$_2$ + H$_2$O IFT for the examined isotherm, the model appears to overpredict severely the IFT of CO$_2$ + brine systems, in particular for brines containing CaCl$_2$. It is important to mention that IFT data measured by Aggelopoulos et al.[31,32] for diluted brines containing CaCl$_2$ persisted in being lower than CO$_2$ + H$_2$O IFT data [10], as shown in Figures 7b and 8b, similar to what was already described for other data sets (Figure 1); yet, the differences between predicted and experimentally determined IFT values
at higher salt concentrations cannot be attributed to the inconsistencies in the experiments alone. In turn, such overprediction of IFT values may be most probably due to the strong salting-out effect of CaCl$_2$ compared to NaCl or KCl, which is intrinsically related to the ionic strength of the brine. Based on these observations and on the modelling results for the examined brines, it can be argued that such approximated treatment of the rise in IFT due the presence of salts (via solubility change) appears to be adequate only for brines with low and medium ionic strength (up to $I = 2.7$ mol$\cdot$kg$^{-1}$ or 0.9 $m_{\text{CaCl}_2}$) under the temperature and pressure conditions examined.

The modelling results explained above are better interpreted by means of the Gibbs adsorption equation. Accordingly, the change in CO$_2$ + brine IFT ($d\gamma$) can be related to the chemical potentials ($\mu$) of CO$_2$ and ions as follows [71]:

$$-d\gamma = \Gamma_{\text{CO}_2}\mu_{\text{CO}_2} + \Gamma_{\text{cation}}\mu_{\text{cation}} + \Gamma_{\text{anion}}\mu_{\text{anion}} \quad \text{at constant } T$$  \hspace{1cm} (8)

where $\Gamma_i$ is the surface/interfacial excess (or adsorption/desorption) of species $i$. By convention, a dividing surface is chosen such that $\Gamma_{\text{H}_2\text{O}} = 0$. From this equation it can be shown that changes on CO$_2$ + brine IFT are related to the individual contribution of each species in the system: increasing the chemical potential of a species with positive surface excess (such as CO$_2$) would result in a decrease in IFT, whereas increasing the chemical potential of a species with negative surface excess (such as the salt ions examined) would result in an increase in IFT. Therefore, it can be concluded that the differences between predictions and experimental IFT data for CO$_2$ + brines may be due to the fact that in the model only the salting-out effects were accounted for (i.e., decrease in the chemical potential of CO$_2$) while the contribution of ions to the IFT has been neglected. Nevertheless, the modelling results obtained here are encouraging, given the fully predictive treatment of the current approach when compared to that often used based on purely empirical methods [18,21,25,72–74].
Figure 7. IFT−pressure diagrams of (a) CO$_2$ + NaCl(aq) and (b) CO$_2$ + CaCl$_2$(aq) systems. Solid lines represent DGT predictions at pertinent salt molalities and temperatures. Predictions were obtained using a binary interaction coefficient $\beta_{ij} = 0.27$, as estimated for the CO$_2$ + H$_2$O system.
Figure 8. IFT−pressure diagrams of (a) CO$_2$ + [NaCl + KCl](aq) and (b) CO$_2$ + [NaCl + CaCl$_2$](aq) systems. Solid lines represent DGT predictions at pertinent salt molalities and temperatures. Predictions were obtained using a binary interaction coefficient $\beta_{ij} = 0.27$, as estimated for the CO$_2$ + H$_2$O system.
Figure 9. IFT−total salt molality diagram of CO$_2$ + [0.864 NaCl + 0.136 KCl](aq) systems at $T = 373$ K. Symbols represent experimental data from Li et al. [21] for fixed pressure. IFT data points for zero salt molality were interpolated from CO$_2$ + H$_2$O IFT data [10]. Solid lines represent DGT predictions.

5. Conclusions

In this communication we have investigated experimentally and theoretically the interfacial tension between CO$_2$ and brines over a broad range of conditions, including those relevant to geological storage of CO$_2$ in deep aquifers. IFTs were measured for CO$_2$ + NaCl(aq) systems from ambient conditions up to 423 K and 69.51 MPa, and for two salt molalities, 0.98 and 1.98 mol.kg$^{-1}$. Additionally, a modelling approach for predicting the impact of salts on the magnitude of the interfacial tension of gas + brine systems, established in a previous work [33], was further extended to CO$_2$ + brine systems and tested for higher salt molalities. The applied modelling approach consisted on accounting for the salting-out effect on the solubility of the gas, via the CPA EoS in combination with an electrolyte model, and subsequent computation of density profiles and accompanied IFT in a hypothetical salt-free system with the DGT.

Experimental results clearly showed that CO$_2$ + NaCl(aq) IFT exceeded that of the corresponding salt-free system for all pressure and temperature states examined. This served to amplify previous studies and to resolve some of the inconsistencies observed for data reported in literature, in particular at low temperatures where various studies reported IFT values lower than that of CO$_2$ + H$_2$O. The increase in interfacial tension from the salt-free system averaged an amount between 1.42 and 2.01 mN.m$^{-1}$ for $m_{NaCl} = 0.98$ mol.kg$^{-1}$ and between 2.67 and 3.73 mN.m$^{-1}$ for $m_{NaCl} = 1.98$ mol.kg$^{-1}$. This corresponds to an average relative increase from CO$_2$ + H$_2$O IFT between 4.4 and 13.2%, over the examined range of pressures, temperatures and salt molalities.
IFT data of CO₂ + brine systems, including single and binary salt mixtures of NaCl, CaCl₂ and KCl, measured in this work and gathered from literate were used to assess the predictive capabilities of the modelling scheme. The only adjusted parameter, the binary coefficient for the cross influence parameter between CO₂ and H₂O within the framework of the DGT, was estimated from one interfacial tension data point of CO₂ + H₂O at intermediate conditions. Comparison with experiments showed that the model is able to predict, with a high degree of accuracy, CO₂ + brine interfacial tensions for brine solutions of low and medium ionic strength (up to I = 2.7 mol.kg⁻¹). The dependence of IFT on salt molality and the additive effects of different salts are also effectively predicted, although the IFT is overpredicted for concentrated brines solutions with the current model. All things considered, we have demonstrated that the model developed in this work is a useful tool for predicting interfacial tensions relevant to CO₂ storage in deep saline aquifers as function of pressure, temperature and brine composition.

6. Acknowledgements

This research work is part of an ongoing Joint Industrial Project (JIP) conducted jointly at the Institute of Petroleum Engineering, Heriot-Watt University and the CTP laboratory of MINES ParisTech. The JIPs is supported by Chevron, GALP Energia, Linde AG Engineering Division, OMV, Petroleum Expert, Statoil, TOTAL and National Grid Carbon Ltd, which is gratefully acknowledged. The participation of National Grid Carbon in the JIP was funded by the European Commission’s European Energy Programme for Recovery. The authors would also like to thank the members of the steering committee for their fruitful comments and discussions. Luis M. C. Pereira acknowledges the financial support from Galp Energia through his PhD grant.
7. References


S. Khosharay, M. Abolala, F. Varaminian, *Modeling the surface tension and surface properties of (CO\textsubscript{2} + H\textsubscript{2}O) and (H\textsubscript{2}S + H\textsubscript{2}O) with gradient theory in combination with sPC–SAFT EOS and a new proposed influence parameter*, J. Mol. Liq. **198**, 292–298 (2014).


