Report on

the metrological infrastructure comprising the instruments adopted to determine the thermophysical properties of mixtures of interest for CCUS processes. The report will include at least 2 simplified formulations for the prediction of the density of typical CO2 mixtures (in liquid and gas phase), suitable for use by flow computers to support the CCUS process design.

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1 Summary

With the aim to validate models needed to support the design of CCUS processes and to provide the necessary support to flow metering operations involving CO_2 mixtures in the liquid phase, vapour phase or in supercritical conditions, significant progress was made on the study of amines, their mixtures with CO_2 and H_2O, and for transportation of CO_2 mixtures in pipelines.

This report describes the characteristics of the metrological infrastructure implemented during the development of the MetCCUS project with the aim to obtain the thermophysical properties of CO_2 mixtures of interest for industrial applications. To provide a simple access to the measured properties, two simplified equations of state were implemented: one for designing CO_2 transport infrastructure and one for modeling carbon capture processes using aqueous amines.

2 The meteorological infrastructure for properties of CO_2 thermophysical systems

With the aim to provide procedures, measurements and the specific instrumentation needed to build up confidence in the safe and efficient operation of pipelines transporting CO_2 mixtures, innovative methods for the online monitoring of eventual phase transitions in the CO_2 through the measurements in-site were developed. In particular, two spectroscopy-based systems were developed for online monitoring of phase transitions in CO_2 such as gas to super-critical fluid flows. The first system is based on far-UV method and the second one on NIR method. Both systems were successfully tested at laboratory conditions with use of a commercial CO_2 gas cylinder with deep tube and validated at ExtrateX company (Nancy, France). The measurements at ExtrateX have been done on a proprietary dedicated setup, where it was possible to utilize gas-, super-critical or liquid- phase CO_2 flows. The far-UV and NIR systems have been coupled to the ExtrateX's setup. The far-UV and NIR measurements of CO_2 gas-super-critical phase transitions at ExtrateX agree with the laboratory measurements. DTU is investigating the possibilities for a patent application for the NIR method.

Moreover, considering that even a small amount of water can chemically react with the CO_2 to form corrosive compounds, part of the contribution was dedicated to the development of a **calibration method for the online humidity sensors** that are used in CCUS processes. NPL have developed a new facility for **corrosion testing of pipeline** steel in impurity-containing dense phase CO_2 environment. Methods for controlling and measuring the concentration of impurities (H_2O and O_2) in dense phase CO_2 during corrosion testing were successfully optimised and validated.

A robust test method was successfully developed to assess the corrosion rate of X65 pipeline steel in dense phase CO_2 containing H_2O and O_2 at 80 bar and 25 °C. Key steps of the method include:

1. **Deaeration**: Adequate deaeration (i.e., O_2 below 1 ppm_v) at ambient pressure requires purging the autoclave with CO_2 with a volume at least 15 times greater than the autoclave volume. This protocol prevents exposure of test specimens to residual atmospheric O_2 during testing, thereby avoiding artefacts in corrosion rate measurements.
2. **Test Environment Establishment**: Gradual pressurisation (~ 40 minutes) combined with continuous stirring at 700 rpm enables rapid and uniform distribution of impurities within the autoclave, achieving target concentrations near test specimens within 1 hour. This procedure minimises uncertainty in exposure time and test environment composition, which is critical for short-duration corrosion tests.
3. **Depressurisation**: Diluting the test environment with pure CO_2 to reduce H_2O concentration below 500 ppm_v, followed by controlled depressurisation (1 L/min or 3 L/min), effectively prevents artefacts in corrosion rate measurements arising from unintended H_2O condensation on test specimens.

Corrosion tests on X65 steel in H_2O-saturated dense phase CO_2 conducted using the developed robust test method demonstrated good repeatability. The corrosion products were uniform and semi-protective, with no significant difference between horizontally and vertically orientated specimens. This result contributed to the development of an international best practice guide:

AMPP Guide 21577 - Laboratory Corrosion Testing for CO_2 Transport and Injection, supporting standardisation efforts in corrosion testing of CO_2 infrastructure.

A further activity was dedicated to the implementation of the standard test procedures necessary to ensure the safe and **cost-effective selection of materials for CO_2 pipelines**. A robust and reproducible test method was developed that is more representative of conditions in service than conventional test methods that have been employed to date in the literature.

NPL has adapted the use of an existing commercially made **humidity generator** to operate with CO_2. A Thunder 3900 Low Humidity generator was adapted so that it can dynamically generate humidity values in CO_2 in the frost-point temperature range -60°C to 0 °C (equivalent to water vapour amount fraction range 10 µmol mol^{-1} to 0.5 %). This involved considering materials compatibility, operating range relevant to CCUS, gas-specific flow measurement and control, the CO_2 phase diagram, safe exhaust of the gas, and establishing that operation in the ice regime minimises any issue of dissolved CO_2. For CO_2, there is little published literature for **water vapour enhancement factor**, but NPL has identified available data and used this to enable conversion from frost point to amount fraction. The primary traceability to dew-point temperature units (°C) is via a reference platinum resistance thermometer (PRT) calibrated against NPL Temperature Standards. The adapted standard was used to calibrate a chilled-mirror hygrometer in terms of frost point in both CO_2 and air.

Finally, an experimental apparatus comprising an acoustic/microwave resonant cavity and a simplified saturator was designed and realized in order to be able to measure **speed of sound and refractive index** of gaseous pure CO_2 and CO_2 + H_2O mixtures. Test measurements were carried out in Ar in order to evaluate the performances of it. Using the novel experimental system, comprising an acoustic/microwave resonant cavity and a simplified saturator, measurements of speed of sound and refractive index of gaseous pure CO_2 and humid CO_2 at two isotherms (323 and 330) K, spanning the overall pressure range between 0.5 and 1.2 MPa with water mole fractions 0.5% and 1%, respectively, were carried out; besides along an isochoric line at 0.7 MPa at 11 temperatures between 323 K and 357 K, with a water mole fraction x = 1.0 % (by mass).

With the aim to estimate the interaction carbon dioxide – water virial coefficient, measurements will be continued spanning beyond the lifetime of the project.

4. A dedicated equation for designing CO_2 transport infrastructures

Multiparameters equations of state have proven to be able to provide predictions of the thermodynamic properties of mixtures with an accuracy that is comparable to the one of the experimental data when their parameters are adjusted using available experimental measurement results. However, the update of such equations requests time, especially when they are needed to describe multicomponents mixtures. For this reason, while updated formulations will be available, a **simplified model** is proposed to support the design of CO_2 compression, liquefaction and pumping systems. More than the accuracy of the formulation, its simplicity was privileged so that it can be easily implemented in open- and closed-source designing software platforms.

Considering that CO_2 applications can range from low to high temperature cycles involving necessary or sometimes undesired phase transitions, it has been chosen to adopt cubic equations of state optimized in the range of CCUS processes. Historically, cubic equations are utilized for designing hydrocarbon distillation and their coefficients are calculated specifically to reproduce the saturation curve and the saturated liquid density. However this is not the main scope of the CO_2 transport applications where the estimation of thermophysical properties of CO_2 mixtures are necessary to define dimensions and range of operativity of compressors and pumping systems. So that, the coefficients of a Patel-Teja equation of state were recalculated for pure CO_2, O_2, SO_2, Ar, CO and N_2 to optimize the predictions in the range of temperature between 263 K and 423 K, and for pressure up to 12 MPa. Available experimental measurements of mixtures of the selected components were used to determine the binary interaction coefficients and then they have been used to predict the density of a quaternary mixture composed by CO_2 + N_2 + O_2 + Ar. Comparisons of the implemented model with Soave-Redlich-Kwong (SRK), Peng-Robinson (PR) cubic equation and with EOS-CG-2021 fundamental equation is provided.

Details of the adopted Patel-Teja (PT) equation can be found in [Patel *et al.*] while only necessary information to implement this model are hereafter reported. PT equation is a cubic equation explicit in pressure *p* as a function of the temperature *T* and molar volume *v*:

$$p(T,v) = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)-c(v-b)} \tag{1}$$

where *R*=8.31446 J/(mol K) is the molar gas constant, *b* and *c* are the co-volumes and *a(T)* is the thermal function. The parameters of the equation are the critical temperature T_c, and the critical pressure p_c while the coefficients to be fitted are ζ_c and one, or more, coefficients used to define the function *a(T)* not reported in the equation (1). From those quantities *a*, *b* and *c* can be obtained. However, for a sake of simplicity, final expressions for *a*, *b* and *c* are explicitly given in table 1. Equation (1) has the property to become an SRK equation when *c*=0 and a PR equation when *c*=*b*. Thanks to this flexibility, PT equations perform, usually, a bit better than both SRK and PR but its quality remains in the range of expected capability of cubic equations thus non comparable with performances of multiparameters equations of state like BWR and equations in Helmholtz free energy.

To calculate the density expressed in kilogram per cubic meter, the pressure must be expressed in pascal and the temperature in kelvin. Solving equation (1), the molar volume *v*, expressed in cubic meters per mole, is obtained while the corresponding density can be calculated as $\rho=m/v$, when the molar mass *m* is expressed in kilograms per mole.

To predict the properties of a multicomponent mixture, at least the binary interaction parameters are needed when the mixing rules described in Patel *et al.* are adopted. Thanks to the stability of cubic equations, the determination of interaction coefficients can be usually performed using very few experimental points since they are approximated by constants and thus are not dependent on the temperature, as reported in table 1. In the proposed approximation, the coefficients not reported in the table have been removed from the model since this simplified approximation considers only mixtures with a molar fractions of CO_2 higher than 90 %. No theoretical formulations for evaluating the binary interaction coefficients were adopted. Values reported in table 1 seem unreasonable since expected values should be positive and in a boundary of 0.1. This is probably

a side of having removed some interactions that cannot be considered negligible. This problem will be corrected in future contributions.

Table 1. Binary interaction coefficients k_{12} to be used in the term $(1-k_{12})$ of Patel-Teja mixing rules.

Mixture	k_{12}	Mixture	k_{12}	Mixture	k_{12}
CO_2-CO	−0.2231	CO_2-O_2	0.1860	CO_2-SO_2	-0.0894
CO_2-N_2	0.8833	CO_2-Ar	-4.9065		

5. CO2 gas mixtures: a comparison among EOS-CG-2021, Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state

Correctly estimating the thermodynamic properties of a real gas is a challenge that scientists have been trying to solve for more than a century. A milestone in that direction was achieved by van der Waals and his proposed equation of state (EOS) for real gases and liquids (van der Waals, 1873). This equation was the first EOS relating the pressure, volume, number of molecules and temperature in a fluid. The Van der Waals EOS formulation is cubic in volume and was the first EOS that could represent a two-phase system (i.e., liquid and gas). Since then, many modifications to this equation have been proposed to, e.g., enhance the phase behaviour predictions of the model. Currently, the equation proposed by Soave-Redlich-Kwong (SRK) (Soave, 1971) and the one presented by Peng-Robinson (PR) (Peng & Robinson, 1976) are the two cubic EOS that are used the most both in the industry and in the scientific community. These EOS find ample application thanks to their ease of use and low computational requirements although do not always reach the required level of accuracy.

An alternative to cubic EOS is to use Helmholtz-energy based EOS. One of the most notable examples of this class of EOS is given by the GERG-2008 EOS for natural gas mixtures (Kunz & Wagner, 2012). EOSs based on the Helmholtz energy include a multicomponent mixture model based on the combination of binary mixture models of the constituents. Each binary-specific model is built on highly accurate Helmholtz energy equations of state for pure fluids, which are then combined with interaction parameters fitted to experimental data. The level of tuning for each binary system thus depends on the availability of experimental data. However, as more and more data become available, EOS formulations based on the Helmholtz energy become more and more accurate as it was the case for the GERG-2008 EOS.

The CCUS (carbon capture, utilisation and storage) industry has been widely using cubic EOS however CCUS mixtures often require the modelling of chemical association and polar components, which is not properly captured by cubic EOS. It is possible to include such modelling in cubic EOS, at the expense of increasing the complexity of the EOS and limiting the ability of the EOS to extrapolate beyond experimental data, thus losing some of the attraction of cubic EOS. In recent years, the scientific community has developed a Helmholtz energy EOS specific for CCUS-mixtures, EOS-CG (Gernert & Span, 2016), which is being updated and constantly improved as more and more experimental data on CO_2 mixtures with relevant impurities are being

collected. It is important to mention that although GERG-2008 includes many CCUS-relevant compounds, these are treated as minor components in the formulation of the GERG-2008. Therefore, when using GERG-2008 for the calculation of thermodynamic properties of a CCUS-relevant mixture the uncertainties associated with the EOS result can exceed those of the experimental measurements.

In MetCCUS, it has been performed a numerical comparison of the predictions provided by SRK, PR and EOS-CG-2021 against experimental measurement results available in the literature on CO_2 mixtures (with CO_2 as the most abundant component). For the comparison, we use SRK, PR and EOS-CG as implemented in TREND 6.0 (Span, et al., 2025).

5.1.   Numerical comparison on CO_2 mixtures relevant for the CCUS industry

As a first comparison, we analyse the predictions of EOS-CG, SRK, PR and PT (as newly implemented in this project) on binary mixtures of carbon dioxide and sulfur dioxide, oxygen or carbon monoxide. The presence of any of these three impurities may have fatal consequences for the CO_2 transportation system causing, e.g., corrosion and running ductile fraction (Simonsen, Hansen, & Pedersen, 2025). It is therefore of vital importance to monitor the presence of these impurities in CCUS processes. The experimental data used for the comparison are given in (Gimeno, Artal, Velasco, Fernández, & Blanco, 2018) for the mixture with sulfur dioxide, (Mantovani, Chiesa, Valenti, Gatti, & Consonni, 2012) for the mixture with oxygen, and (Souza, Herrig, Span, & Trusler, 2019) for the mixture with carbon monoxide.

The comparison is performed in terms of the average of absolute deviations (AAD), which is calculated as

$$AAD = \frac{100}{N} \sum_{i=1}^{N} \frac{|\rho_{exp,\,i} - \rho_{EOS,i}|}{\rho_{exp,i}} \qquad (2)$$

where ρ_{exp} denotes the experimental value of the density of the CO_2 mixture, and ρ_{EOS} the density value predicted using an equation of state. We calculated the AAD per phase, where we estimated the critical point based on the characteristics of the pure components and on the proportion of the components. The results are summarized in Table 2.

In most cases of the mixtures with sulfur dioxide and oxygen, the EOS-CG-2021 (Neumann, Herrig, Bell, Beckmüller, Lemmon, Thol & Span, R., 2023). provides predictions with a lower AAD than the cubic EOS. However, in the case of the mixtures with carbon monoxide EOS-CG-2021 returns considerably larger AAD values, while the fitted PT equation returns AAD values similar as for the other mixtures.These results emphasize that some of the binary models (e.g., for carbon monoxide) in EOS-CG-2021 need more data to better represent the interactions between the different components (or at least in the temperature and pressure ranges here considered).

Table 2: AAD calculated per phase and per EOS on binary mixtures of CO_2 with CCUS relevant impurities. For all mixtures, the amount fraction of CO_2 is calculated as $x_{CO_2} = 100 - x_{XX}$ cmol/mol where XX is either SO_2, O_2 or CO.

Mixture	Phase	EOS-CG-2021	SRK	PR	PT
$x_{SO_2} = .69$ cmol/mol	Gas	**0.98**	1.59	1.63	1.35
	Liquid	**0.36**	11.29	2.59	2.28
$x_{SO_2} = 4.68$ cmol/mol	Gas	3.19	3.72	2.36	**2.22**
	Liquid	2.84	12.69	3.16	**2.04**
$x_{O_2} = 6.07$ cmol/mol	Gas	**1.44**	1.79	2.17	2.30
	Supercritical	**1.70**	8.81	2.16	2.31
$x_{O_2} = 12.91$ cmol/mol	Gas	**1.72**	1.90	2.75	2.25
	Supercritical	2.54	7.78	**1.46**	2.25
$x_{CO} = 5.031$ cmol/mol	Gas	7.31	8.00	6.22	**1.25**
	Liquid	3.49	12.53	4.40	**2.35**
	Supercritical	13.52	20.22	14.34	**2.46**
$x_{CO} = 10.107$ cmol/mol	Gas	4.13	5.06	3.12	**1.78**
	Liquid	6.27	14.14	5.75	**2.13**
	Supercritical	8.10	15.02	8.94	**1.95**

Alongside the EOS predictions for binary mixtures, we analysed also the predicted density for a more complex mixture of carbon dioxide ($x_{CO_2} = 89.83$ cmol/mol), nitrogen ($x_{N_2} = 5.05$ cmol/mol), oxygen ($x_{O_2} = 3.07$ cmol/mol) and argon ($x_{Ar} = 2.05$ cmol/mol) for which experimental results are given in (Nazeri, Chapoy, Burgass, & Tohidi, 2017). These impurities can seriously compromise the integrity of the pipelines and thus increase the risk of failure of CO_2 transportation systems. Results are reported in Table 3.

In this case, the fitted PT EOS has the lowest AAD for all the three phases considered, with EOS-CG-2021 returning similar AAD values in two out of three phases. However, the AAD values are in general quite high, as seen also for the binary mixture CO_2 + CO and might not meet the accuracy requirements needed in the CCUS industry. Thus more work should be done to improve the binary-specific models in EOS-CG-2021 or the binary interaction parameters in PR or in the proposed PT EOS.

Table 3: AAD calculated per phase and per EOS on a CO_2 mixture with $x_{N_2} = 5.05$ cmol/mol, $x_{O_2} = 3.07$ cmol/mol and $x_{Ar} = 0.02$ cmol/mol.

Phase	EOS-CG-2021	SRK	PR	PT
Gas	3.25	3.55	2.76	**2.13**
Liquid	4.45	9.86	5.28	**4.32**
Supercritical	5.10	9.50	6.05	**4.40**

In all numerical comparisons performed here, SRK always has noticeably higher AAD when predicting the density in the liquid or in the supercritical phase, while in the gas phase it has similar performance as EOS-CG-2021 and PR. The adapted PT equation returns lower AAD values in most cases with EOS-CG-2021 returning similar or lower values in case of mixtures that do not include carbon monoxide. PR performs, in general, quite well considering that it is not an CO_2 dedicated EOS, however occasionally (e.g., in the gas phase of the binary mixture with oxygen) it is the EOS with highest AAD, i.e., higher than SRK too. Based on these results, it is evident that some of the binary-specific models in EOS-CG-2021 need more data to better represent the interactions between different components. This in turn implies that the outcome of this comparison can not be readily extended to mixtures with different components and the only practical conclusion is to not use SRK to predict the density of CCUS mixtures in the liquid or in the supercritical phase.

6. A dedicated formulation for designing carbon capture systems

In order to improve the empirical models, currently lacking experimental measurements of the thermophysical properties of amine+CO_2 mixtures, were carried out by UVa and INRiM. Among the most important thermophysical properties, the density, speed of sound, viscosity and specific heat capacity were chosen to be measured in pure MEA (monoethanolamine) and DEA (diethanolamine), in CO_2 + MEA and in CO_2 + DEA at three different concentrations.

The first part of the activities was developed around the EOS-CG-2021 formulation that is able to predict the thermodynamic properties of mixtures, including amines. Moreover, while the fundamental equation of state is improving, an open source simplified novel formulation was developed, specifically to be included in chemical processing design software.

Considering pure MEA, the existing set of measurements used by EOS-CG-2021 was extended using the new results for density in the temperature range from 293 K to 394 K at a maximum pressure of 70 MPa. The experimental results confirmed the present data although the new measurements were systematically lower by approximately 0.06 % of Scholz and Span (Scholz & Span, 2021). Both datasets indicate that the equation EOS-CG-2021 fits well the data up to approximately 20 MPa. Deviations increase with increasing pressure. This effect should be corrected in a future revision of the fundamental equation of state. Furthermore, literature data for the speed of sound have, so far, included only measurements at atmospheric pressure. The novel

speed of sound results obtained in this project represent a significant extension of the measurement range. In the overlapping temperature range, at 0.1 MPa, MetCCUS new data and those of Álvarez et al. (Álvarez, Cerdeira, Gómez-Diaz & Navaza, 2010) agree very well with each other and within 0.1 % according to the equation of state. With increasing pressure, the equation of state increasingly deviates from the new results up to 0.8 %. This shows that despite limited experimental data when it was developed, the equation extrapolates quite well, although there is still room for improvement.

For pure DEA, the new MetCCUS data represent a significant extension of the measurement range. As with MEA, the measurements set for speeds of sound of DEA from the literature is limited to atmospheric pressures. The new speed of sound experimental results extend the covered state region considerably. Deviations from the equation of state are increasing with rising temperature, but not showing pressure dependency. Deviations are up to 4 %, which demonstrates that there is still room for improvement of the equation of state.

The binary system MEA + CO_2 was so far only investigated experimentally by Neumann et al. (Neumann, Bernhardsen, Knuutila, Poplsteinova &. Span, 2021). The new MetCCUS density results extend the database by 396 points in the homogeneous liquid state region, covering a temperature range from 293 K to 394 K with a maximum pressure of 70 MPa. The measurements were carried out at three loadings, α equal to (0.15, 0.2 and 0.3) mol_{CO2}/mol_{MEA}, corresponding to the molar compositions of (0.13, 0.17 and 0.23) mol_{CO2}/mol_{Mix}. The new density data show deviations with EOS-CG-2021 within 1.6 %, that increase with rising temperature and mole fractions of CO_2. The new speed of sound data is represented within 3.8 % and no clear trend with respect to temperature, pressure, or composition can be observed. Since there were no experimental measurements available in the literature, a validated equation of state was not available for the binary system CO_2 + DEA within the EOS-CG-2021 (Neumann, Herrig, Bell, Beckmüller, Lemmon, Thol & Span, R., 2023). In this case, a new equation for those mixtures should be developed in future.

Besides the dedicated fundamental Equation of state (EOS-CG-2021), a novel thermodynamic model of MEA and MEA + CO_2 systems was developed out and improved by combining an Aspen Model (ENRTL-RK) with more accurate liquid density models: one based on the NIST REFPROP database for pure MEA, and another using a modified Peng–Robinson approach with activity coefficients for mixtures. These choices gave the best agreement with ENRTL-RK and are useful for process simulations. Still, noticeable large density deviations appeared at high CO_2 loadings (~ 20-30 %) and at higher temperatures and pressures, pointing to the presence of a component not represented in the model. To address these deviations, a regression approach was developed to estimate both the amount and density of this missing component as functions of CO_2 loading, temperature, and pressure. This correction matched the experimental data very closely and provides a practical way to extend thermodynamic models for reactive absorption systems.

Furthermore, with the aim to support industries' activities in CO_2, a provisional formulation for mixtures of CO_2, MEA and H_2O has been developed to provide more accurate predictions of the thermodynamic properties than those provided by today's available "cubic plus association" models (Tellez & Medeiros, 2013). Already available models were developed when none or very few experimental measurements were obtained and their capabilities of predictions were based on the theoretical description of very complex molecules association processes. Thanks to the results

obtained in the MetCCUS project, the new available experimental measurements allow to implement new models and validate their predictions or, alternatively, improve the "cubic plus association" models. Again, the simplicity of the model here described was privileged with respect to its accuracy. This means that the obtained formulation can be considered a stable formulation only when operating in the region of its validation.

The system CO_2 and amines is not only a mixture because different kinds of reactions can occur at different conditions. While the most part of the published work tried to model possible reactions and equilibrium constants, in this simplified formulation all the complexities have been hidden in a "corrections factors". This approach is only practical and has the limitation to not add any knowledge to the modelization of CCUS reactions but, when validated using experimental measurements, it allows end users to integrate this provisional model into their CCUS designing software.

The model implemented has the same form reported in equation (1) where the coefficients were determined by fitting the measurements carried out by INRiM and UVa. The coefficients of pure MEA have been calculated and the binary interaction coefficient k_{12} for CO_2- MEA mixtures were obtained.

For determining the coefficients of pure MEA, nominal critical temperature, critical pressure and normal boiling point together with experimental density measurements in compressed liquid were used. Some experimental measurements of vapor pressures will be included in further works when the model will be improved.

Mixing rules for the binary mixture of CO_2 and MEA should account for their chemical reaction. In this simplified version, the usual Peng-Robinson (Peng & Robinson, 1976) mixing rules were adopted although they are indicated to describe mixtures and not associating or reacting components as in this case. For this reason it was decided to add a new parameter to the mixing rule, to correct the molar mass of the products of the reaction, as

$$ m = x\, m_{CO2} + (1 - x)m_{MEA} + \mu \sqrt{x\,(1 - x)} \tag{3} $$

where m_{CO2} and m_{MEA} are the molar masses of CO_2 and MEA, x is the molar fraction of CO_2, before the reaction with MEA, and μ is a sort of "excess molar mass" to be fitted from experimental measurements. It formally adjusts the molar mass of the reaction product with respect to the nominal composition. The form of the expression (3) has been chosen to be quite linear in terms of x and with a correction term that disappears when pure fluids are considered. This approximation is not physically correct, since it does not account for the real products and the equilibrium constants of the reaction however it is simple and leads to acceptable agreement with experimental results.

Considering the model has its intrinsic limitations and that the atomization of MEA mixtures in the scrubber is obtained for pressures up to 20 bar, this formulation is validated up to 3 MPa (30 bars) and temperatures from 293 K to 393 K. The model does not reproduce amine freezing and degradations so that temperature extrapolation is possible but in some conditions can provide unreliable results. The parameters needed for modeling CO_2 and MEA mixtures are k_{12}=-1.51357 for the binary interaction coefficient and μ=0.0111 g/mol for the "excess molar mass". Figure 1 shows the relative deviation of this simplified model with respect to experimental measurements for

three different compositions. Deviations show a clear linear dependency from the temperature but they are almost independent from the pressure. A linear temperature dependence of the interaction coefficient will be able to reduce the gaps but cannot completely eliminate them since slopes change with the compositions.
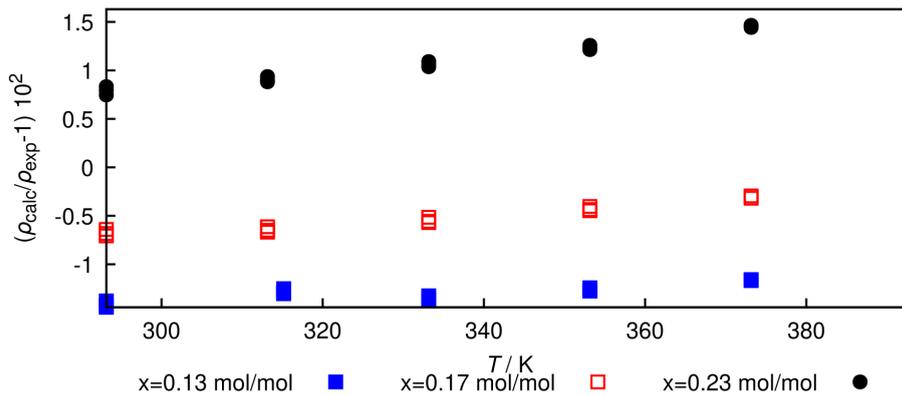

Figure 1. Relative deviations of predicted densities (calc) with respect to the reference experimental values (exp) for three different compositions and for pressure up to 3 MPa.

In industrial applications, binary mixtures of CO_2 and amines are not very used, but the measurements obtained in MetCCUS were specifically identified to support the improvement of EOS-CG-2021 thermodynamic models based primarily on binary interaction coefficients to describe multicomponents mixtures. For designing absorber and desorber systems, the properties of the ternary mixtures composed by CO_2 + MEA + H_2O are necessary. Usually, these can be obtained by considering the contributions of each of the three possible interactions of binary components, however, with reacting components this approach cannot guarantee accurate results. For these reasons, UVa measured the densities not only of binary mixtures, but for some ternary mixtures in interval of temperature and pressure ranges of interest for CCUS industrial applications. Thanks to those measurements, it was possible to extend the simplified model to aqueous MEA + CO_2 in a way that it can be easily integrated in designing software. For industrial applications MEA(aq) is prepared with a load $\alpha = 0.3 \text{ mol}_{MEA} / \text{mol}_{H2O}$ and UVa added CO_2 to this mixture. Recalculating the molar fractions of the components, the content of water was always higher than 87 % and, in this approximation, only the binary interaction coefficients of CO_2-MEA (already determined), CO_2-H_2O and MEA-H_2O were considered. No further CO_2 + H_2O association terms were considered. Fitting the coefficients using experimental density measured with different compositions, the value of $k(CO_2, H_2O) = 4.15167$ was obtained while the interaction coefficient $k(MEA, H_2O) = 2.95142 + 0.001446\, T$ was found to depend by the temperature. Obtained values for interaction coefficients seem physically unreasonable because they are used to approximate experimental measurements using a simplified model unable to describe each reaction and equilibrium constants.
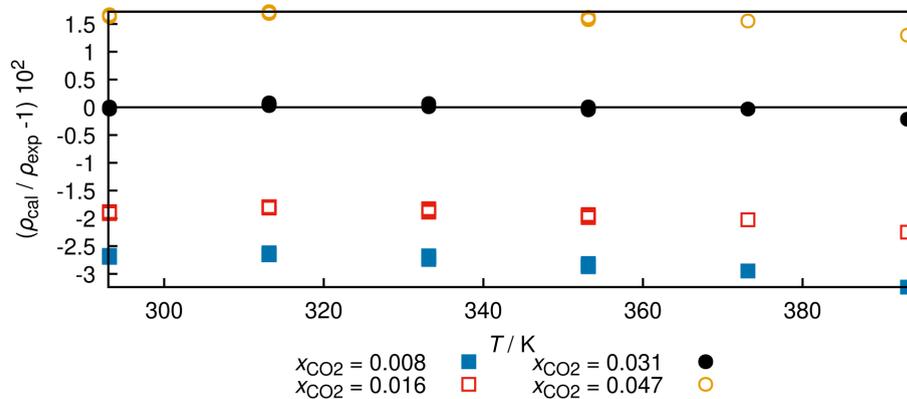
Figure 2. Relative deviations of predicted densities (cal) with respect to the reference experimental values (exp) for three different compositions and for pressure up to 3 MPa.

Figure 2 shows the deviations of the model predictions with respect to the reference experimental measurements as a function of the temperature and pressure. Although pressures range from 0.1 MPa to 3 MPa and temperatures span from 293 K to 393 K, in most of the cases, the deviations are almost independent from pressures and temperatures while the main dependence is from the composition. This effect is probably due to the poor capability of the model to represent the products of the chemical reactions.

7.   Conclusion

This report describes the characteristics of the metrological infrastructure implemented during the development of the MetCCUS project with the aim to obtain the thermophysical properties of CO_2 mixtures of interest for industrial applications. To provide a simple access to the measured properties, two simplified equations of state were implemented: one for designing CO_2 transport infrastructure and one for modeling carbon capture processes using aqueous amines. Proposed formulations are useful for industrial applications till new and more accurate models will be available.

8.   Formulations available on Zedono

As already stated, the advantage of the two simplified formulations is not in their accuracy, but in their possibility to be included in designing software when this model represents an improvement in the prediction of the thermal properties of CCUS mixtures. Described models are available on Zenodo using the following references:
- MetCCUS-Dataset (DOI): 10.5281/zenodo.17208811
- MetCCUS-EoS (DOI): 10.5281/zenodo.17209074

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