Transport of CO 2: Presentation of New Thermophysical Property Measurements and Phase Diagrams

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CO₂ transportation is an integral part of the CCS chain. After capture, CO₂ needs to be transported to locations whereby it is stored or alternatively used in various processes. CO₂ can be transported via ship or pipeline. In both cases, the required compression pressure can be 100–300 bar, depending on the distance and intended disposal or use of CO₂. The CO₂ rich stream can contain a number of impurities which can modify the phase diagram and change the thermophysical properties of the stream in comparison with the ones of pure CO₂. Indeed, along with carbon dioxide, a great number of compounds such as water, O₂, N₂, Ar, SOₓ, NOₓ, H₂ and CO can be present at different levels of concentration. During transportation by pipeline, if the pipe suffers a major fracture due to an accidental release or a failure, CO₂ can rapidly expand and cool: vapour cloud followed by solid formation of CO₂ may appear. The impurities could change the characteristics of the leak and change the conditions and compositions of CO₂ clouds and solid. The presence of water can also be a source of gas hydrate formation, ice or corrosion. In this communication we will present new experimental data and their modelling concerning the phase diagrams of systems rich in CO₂ and their thermophysical properties. Comparisons of the results obtained using different equations of state are also reported.
1. Introduction

Carbon dioxide Capture transport and storage (CCS) is one solution to reduce the emission of CO\(_2\) attributed to human activities; particularly in the context of gas processing, the removal of CO\(_2\) from synthesis gas in the production of hydrogen or ammonia or CO\(_2\) removal from combustion gases of power/thermal. Several technologies for CO\(_2\) capture are available depending on the composition of the flue gas (the stream after combustion is mainly composed of N\(_2\) and CO\(_2\)) and the processes used (i.e., post, pre or oxy combustion processes). For example, one can use chemical or physical absorption; another one can use adsorption solution or cryogenic solution (see Lecomte et al. [1]).

At the outlet of such processes, the stream is very rich in CO\(_2\) but some impurities are also present and their compositions may vary between 0.1 and 5%. In the context of gas processing, the CO\(_2\) gas stream can be extremely rich in sulphur components (acid gases). The transport of CO\(_2\) rich stream can be done using pipeline (in supercritical condition) or ship (liquid phase). Before studying the process of CO\(_2\) transportation, it is important to analyze the thermodynamic conditions. Fig. 1 (extract from Li [2]) illustrates the different thermodynamic conditions regarding CO\(_2\) transportation and also storage assuming that the fluid is pure carbon dioxide. Also according to Li et al. [3], the main conditions of transportation are 0.5<P<20 MPa and 218.15<T<303.15 K.

As mentioned earlier, in the context of combustion gases, the CO\(_2\) gas stream is not pure and contains numerous impurities. Some of them are the results of combustion like NO\(_x\), SO\(_2\), Ar, O\(_2\), N\(_2\)O, CO and N\(_2\). We can have also some hydrocarbons, traces of H\(_2\)S, traces of solvent, H\(_2\) in the case of pre-combustion process, water, etc... During the transportation of CO\(_2\), in all the cases it is important to know the thermodynamic behavior in the presence of these impurities and the impact of them on the thermophysical properties of the fluid. The objective is to guaranty a safe design of transportation process. In effect, in case of problem during the transportation, for example a leakage, the presence of the impurities may lead to the apparition of a 2 phases region which can modify the flow and so increase the cost of fluid transportation. The viscosity may also change and so have a non-negligible role in the cost of CO\(_2\) transportation. In 2011, Mines Paris Tech and Heriot University have started a joint industrial project called “Impact of Common Impurities on Carbon Dioxide Capture, Transport and Storage”. This paper highlights some of the results obtained during this project.
Several thermophysical properties of interest need to be known in the context of CO$_2$ transportation by pipeline or vessels. The design of process for CO$_2$ transportation requires thermodynamic model. Consequently, the knowledge of phase diagram of CO$_2$ gas stream with the presence of impurities is essential. Equations of state require parameters, so it is important to determine phase diagram of each binary system between CO$_2$ and impurities and between impurities themselves. Table 1 presents the state of the art concerning the existence of vapour - liquid equilibrium data for each binary systems. As we can see, there is a lack of data with the NO.

Table 1: State of the art concerning existing VLE data of each binary system. ND: No Data NIST, CD: Confidential Data CTP, CR: Chemical Reaction, Cryo: Cryogenic measurement, DWA: data widely available, NEW: new set of data determined in the context of the Joint Industrial project between Heriot Watt University and CTP Mines Paris Tech

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For multicomponent systems, bubble and dew point pressure for a given temperature can be determined to draw the PT envelop as seen in Fig. 2. As explained above, during transportation, a leakage will decrease the pressure and the new condition can lead to the apparition of vapour and liquid phases and so increases the possibility of damaging compressor, modify the global composition of the CO\textsubscript{2} gas stream, emission of toxics molecules, etc… Fig. 2 shows a PT diagram of two ternary systems composed of CO\textsubscript{2} + O\textsubscript{2} + Ar (mixture 1: 94/3/3 mole%) and CO\textsubscript{2} + O\textsubscript{2} + SO (mixture 2: 94/3/3) (Coquelet et al. [4]).

![PT envelopes of mixture 1 (solid line) and mixture 2 (dashed line). (▲): predicted mixture 1 critical point, (●): predicted mixture 2 critical point.](image)

Densities and speed of sound are also important properties that can be used to test the accuracy of equations of state and to determine compressibility factor. Moreover, density is an essential property for the design of the compressors and pumps, which in turn, also requires the knowledge of transport properties like viscosity (μ). To calculate the regular pressure drop, we need the kinetic viscosity which is estimated using dynamic viscosity and density.

In the case of incompressible fluid, the Darcy-Weisbach relation is used to estimate pressure drop (Eq. 1).

\[
\Delta P = f_D \frac{L}{D_H} \rho \frac{v^2}{2}
\]  

with \(\rho\) the density, \(D_H\) hydraulic diameter, \(L\) the length of the pipeline and \(v\) the velocity of the fluid. The friction factor of Darcy \((f_D)\) is estimated from the Fanning friction factor \(f\) with \(f_D = 4 f\). In laminar regime flow,
(Reynolds number, \( Re = \frac{\rho v D}{\mu} < 2100 \)) we use Fanning relation \( f = \frac{16}{Re} \) and Blasius’s law \( f = \frac{0.0791}{Re^{1/4}} \) for \( 10^4 < Re < 10^5 \). There are others correlations to calculate the friction factor taking into account the roughness of the pipeline (\( \varepsilon \)). We can mention the equation of Colebrook and White (Eq. 2).

\[
\frac{1}{2\sqrt{f}} = 1.74 - 2\log \left( 2 \frac{\varepsilon}{D} + \frac{18.7}{2 \text{Re} \sqrt{f}} \right)
\]  

(2)

In the case of compressible fluids, Hugoniot equation (considering ideal gas law) can be used (Eq. 3). It requires Mach number \( (M) \). During the flow and depending on the value of the speed of sound, we can have an acceleration of the fluid or apparition of pressure drop depending on the design of the canalization.

\[
\frac{dA}{A} = \left( M^2 - 1 \right) \frac{dv}{v}
\]

(3)

with \( A \), the section of the canalization, \( M = \frac{v}{c} \) Mach’s number and \( c \) the speed of sound.

Energetic properties of CO
\(_2\)-rich mixtures are required for the design of heat exchangers and compressors. Consequently, heat capacity \( (C_p) \) is an essential thermodynamic property which has to be determined. Moreover, when the CO
\(_2\) gas stream flows through a valve (restriction of the flow), the fluid pressure drops. This phenomenon appears very quickly and it is known as the Joule-Thompson expansion. The temperature of the fluid may increase or decrease, depending on the fluid. The Joule Thompson coefficient is defined by Eq. 4.

\[
\chi_{JT} = \frac{T \left( \frac{\partial v}{\partial T} \right)_p - v}{C_p}
\]

(4)

The accurate knowledge of density and heat capacity are thus required to estimate the Joule Thompson coefficient.

In the case of expansion or pressure drop, if the temperature is very low we can enter the phase diagram domain where the CO
\(_2\) is at its solid state. The knowledge of the CO
\(_2\) freezing point is very important particularly in a context of flow assurance. It is important to know how the impurities modify the phase diagram. As an example, Fig. 3 shows the PT diagram of the system CO
\(_2\) – CH
\(_4\). We can see the complete triple point line starting from CO
\(_2\) to methane triple points.
Presence of water in the CO₂ gas stream can lead to corrosion of the material of the pipe but also to the formation of gas hydrates which can create important pressure drop and blockage in the pipeline. Therefore, water content is a very important thermodynamic property which has to be known, as well as the conditions of gas hydrate formation/dissociation in the presence of excess of water or not. Fig. 4 shows the gas hydrate phase diagram of pure CO₂.

2. Experimental work and description of experimental setups

Several apparatuses were used to determine experimentally the above mentioned thermophysical and phase equilibrium properties.

2.1. Equilibrium properties

Vapour - liquid equilibrium properties can be obtained using the “static analytic” method. Herein, the mixture is enclosed in an equilibrium cell equipped with a mixing mechanism to attain fast equilibrium conditions. When the equilibrium is reached, small quantities of the phases are sampled and analyzed through chromatographic analyzers. Complete descriptions of the setups are available in Coquelet et al. [4] and Houssin et al. [7]. The experimental procedures for bubble and dew points measurements are available in Chapoy et al. [8-9]. A variable volume cell is
used for bubble pressure measurements. At fixed temperature, saturating properties (pressure and saturated molar volume) of the mixture are determined through the pressure vs volume curve recorded that display a break point which corresponds to the formation of the first bubble of gas. The variable volume cell technique can be cited as a static-synthetic method [10-11]. The isochoric method is used for dew point measurements. Dew point pressures are determined through the pressure vs temperature curve recorded that displays a break point which corresponds to the apparition of the liquid phase.

2.2. Volumetric properties

Densities are determined using a vibrating tube densitometer. A mixture with known composition circulates through a vibrating U-tube. Density is deduced from careful calibration. The calibration consists on the determination of a correlation linking the density to the acquired data (vibration period of U-tube, temperature and pressure). This apparatus can be used to obtain \((P\rho T)\) data of compressed phases. A complete description of this technique is available in the papers of Nazeri et al. [12] and Gonzalez-Perez et al. [13].

To determine the speed of sound (Eq. 5), an equilibrium cell equipped with temperature and pressure sensors is used. There are two ultrasonic transducers in each side of the acoustic cell to convert electrical signal to ultrasonic wave and vice versa. An oscilloscope is used to observe the signal and to determine the speed of sound from the period of vibration (Eq. 6).

\[
c = \sqrt{\frac{\dot{c} \rho}{\dot{c} \rho}} \quad (5)
\]

\[
c = \frac{\lambda}{\tau} \quad (6)
\]

with \(\lambda\) the wavelength and \(\tau\) the period of vibration. A complete description of this technique is available in the papers of Siyabi et al. [14].

2.3. Viscosity

Mainly, two methods can be used for measuring viscosity: methods using falling ball and capillary tube. Herein we have used the capillary tube viscosity measurement method. In each test, the setup was loaded with the sample mixtures after vacuuming the entire system. Then after disconnecting the sample cylinder from the system, the sample fluid was pushed through the capillary tube into the other cylinder using the push-pull mercury pump. The temperature of the system was set to the desired condition and the desired pressure was set using the hand pump. To ensure the consistency of the measurements, at each pressure, viscosities were determined at two or three different flow rates. Measurements are done in laminar flow conditions. Poiseuille equation (Eq. 7) can relate the pressure drop across the capillary tube to the viscosity, tube characteristics and also flow rate for laminar flow.

\[
\Delta P = \frac{128LQ\mu}{C\pi D^4} \quad (7)
\]

where, \(\Delta P\) is the differential pressure across the capillary tube viscometer in psi, \(Q\) represents the flow rate in \(\text{cm}^3/\text{sec}\), \(L\) is the length of the capillary tube in cm, \(D\) refers to the internal diameter of the capillary tube in cm equals 0.029478 cm, \(\mu\) is the viscosity of the flown fluid in cP and \(C\) is the unit conversion factor equal to 6894757 if the above units are used. A complete description of this technique is available in the paper of Kashefi et al. [15].
2.4. Energetic properties

The determination of heat capacity is done using a calorimeter with a measurement and a reference cells. A sample is introduced into the measurement cell and a temperature ramp is applied. The heat flux transferred (absorbed or released) is considered to calculate the heat capacity (Eq. 8).

\[
C_p = \frac{\frac{\partial H}{\partial t}}{\frac{\partial T}{\partial t}}
\]

(8)

where \( H \) is the enthalpy, \( T \) the temperature and \( t \) the time. A complete description of this technique is available in the paper of Ahmadi et al. [16].

2.5. Gas hydrate and CO\(_2\) freezing point

Isochoric method is considered here to determine hydrate dissociation points (see Hajiw et al. [17]). Water is loaded into the cell and the mixture is loaded in a single liquid phase to reach the desired pressure. The system temperature is set to a point well above the expected hydrate dissociation temperature for the system under study. The temperature is then decreased to form hydrates. The hydrate formation and growth is detected by an associated abrupt pressure drop and/or temperature increase. Then, the temperature of the cell is increased step by step. For each step, the temperature is maintained long enough to allow equilibrium to be reached. At temperatures below the point of complete dissociation of hydrates, gas is released from hydrates dissociation, giving a marked rise in the cell pressure with each temperature step. However, as soon as all clathrates have disappeared, a further rise in the temperature will result only in a relatively small pressure rise due to thermal expansion of the fluids. This process results in two traces with very different slopes on a pressure versus temperature (P/T) plot, one before and one after the dissociation point (i.e., an abrupt change in the slope of the P/T plot). The point where these two traces intersect is taken as the dissociation point. A similar technique (Zhang et al. [18]) is used for the determination of the frost points of solid CO\(_2\).

3. Models and correlation useful for the determination of the thermophysical properties

3.1. Equations of state

The representation of thermodynamic properties requires an equation of state (EoS). We can consider three types of equations of state. The most known EoSs are cubic type. The Peng Robinson EoS [19] is the most used EoS. They are easy to solve and can be used to predict phase diagrams of pure components and mixtures. For mixtures, the mixing rules must be able to take into account the ideal and non-ideal characteristics of the components in the mixture. With the two-parameter cubic equations of state, the objective is to calculate \( a \) and \( b \) parameters considering the mutual influence of the various compounds and the composition of the mixture. These equations are not accurate to predict the density of liquids but they can be corrected by considering volume translation (Peneloux et al. [20]). In 2001, Jaubert and Mutelet [21] have proposed a method to predict the binary interaction parameter based on a group contribution approach (PPR 78).

The second type of EoS which can be used are molecular type. The Helmholtz energy is calculated by considering all the molecular interactions like dispersion, polarity, H bonding (association), etc… Eq. 9 details the method of calculation of the Helmholtz energy \( A \).
The most known molecular EoSs of this type are SAFT type. Based on the Wertheim's statistical theory of associative fluids (1984), Chapman et al. [22-23] developed the first EoS SAFT (Statistical Associating Fluid Theory) called SAFT-0. Many versions exist today, such as LJ-SAFT (1994), SAFT-VR (1997), Soft-SAFT (1997) PC-SAFT (2001, Gross and Sadowski [24]) etc. The various versions differ mainly in the choice of the reference fluid, the radial distribution function and explicit expressions of the terms of perturbation.

Considering the same approach, Kontogeorgis et al. [25] have combined classical equation of state and the Wertheim’s term for the associative interaction. The model called Cubic Plus Association (CPA) allows a better representation of phase diagrams of systems involving water. Recently Hajiw et al. [26] have combined CPA and PPR 78 approach to propose the predictive GC PR CPA EoS.

The last type of equation of state are based on multi-fluid approximation. It is well known that from the knowledge of Helmholtz energy, all thermodynamic properties can be calculated. Fundamental equations of state are explained in terms of reduced molar Helmholtz free energy (Eq. 10).

$$\frac{A}{Nk_b T} = \frac{A^{\text{IDEAL}}}{Nk_b T} + \frac{A^{\text{CHAIN}}}{Nk_b T} + \frac{A^{\text{ASSOCIATION}}}{Nk_b T}$$ (9)

where the exponent $id$ stands for the ideal gas contribution and exponent $res$ is the residual contribution. $\rho_r$ and $T_r$ are the reduced density and temperature, respectively. An expression is chosen for the residual term (Eq. 11 is used to calculate ideal term).

$$a^{id}(T, \rho) = \frac{\hbar_0^{id}}{RT} + \frac{\mathcal{S}_0^{id}}{R} - 1 + \ln \frac{\rho T}{\rho_0 T_0} + \frac{1}{RT} \int_{T_0}^{T} c_p^{id} dT - \frac{1}{R} \int_{T_0}^{T} \frac{c_p}{T} dT$$ (11)

For mixtures, the first possibility is to consider mixing rules for each parameter like in the BWR EoS [27]. The second approach is the multi-fluid approximation like in the GERG EoS [28]. This approach was introduced by Tillner – Roth [29]. The mixing rules are applied to the Helmholtz free energy of the mixture components (Eq. 12).

$$a(T, \rho, \bar{x}) = \sum_j x_j \left( a_j^{id}(T, \rho, \bar{x}) + a_j^{res}(T, \rho, \bar{x}) \right) + x_j \ln x_j + \sum_{p=1}^{\infty} \sum_{q=p+1}^{\infty} x_p x_q F_{pq} a_{pq}^E$$ (12)

$$\Delta a_{pq}^{res} = \sum_{p=1}^{\infty} \sum_{q=p+1}^{\infty} x_p x_q F_{pq} a_{pq}^E$$ is called the departure function from the ideal solution. It is an empirical function fitted to experimental binary mixture data. With the multi-fluid approximation, it is important to calculate the pseudo-critical properties corresponding to the mixture studied as reduced parameters are used. Eqs. 13 and 14 present one type of mixing rules.

$$T_{c}^{\text{mel}} = \sum_{p=1}^{\infty} \sum_{q=p+1}^{\infty} k_{T,pq} x_p x_q (T_p c_p c_q)^{0.5}$$ (13)

$$V_{c}^{\text{mel}} = \sum_{p=1}^{\infty} \sum_{q=p+1}^{\infty} k_{V,pq} x_p x_q \left( \left( V_p c_p \right)^{1/3} + \left( V_q c_q \right)^{1/3} \right)^3$$ (14)

$k_{T,pq}$ and $k_{V,pq}$ are adjustable parameters.
3.2. Transport properties models

Different approaches are available to model transport properties. One consists in using the corresponding state method. The most famous approach is the TRAPP method developed by the NIST. Huber et al. [29] and Klein et al. [30] have developed a series of equations adapted to the prediction of viscosities and thermal conductivities of pure components and mixtures. The approach consists in modifying the transport properties in the ideal dilute gas state taking into account the molecular interactions (and so the density of the fluid with temperature and pressure).

3.3. Approach for CO\textsubscript{2} freezing point and gas hydrate dissociation point calculations

The determination of the CO\textsubscript{2} freezing point requires the determination of the fugacity of pure solid (here CO\textsubscript{2}). Eq. 15 presents the equation used to estimate the fugacity of solid CO\textsubscript{2}. Fugacity of the fluid is obtained by using an equation of state previously described.

\[
\frac{f_{CO_2}^S}{f_{CO_2}^L} = \exp \left[ \frac{\Delta h_{CO_2}^{S\rightarrow L}}{RT} \left( \frac{T}{T_{m,CO_2}} - 1 \right) \right]
\]

with, \(f^L\) the fugacity of the liquid, \(T_m\) the melting temperature of CO\textsubscript{2} and \(\Delta h_{S\rightarrow L}\) the heat of melting at the temperature \(T_m\). The determination of the gas hydrate dissociation point is obtained by considering the solid solution of van der Waals and Platteeuw [31], as implemented by Parrish and Prausnitz [32]. As for phase equilibrium calculation, the hydrate phase model is based on the thermodynamic equilibrium, which means equality of temperatures, pressures and fugacities. A complete description of the model and parameters used are given in Chapoy et al. [9].

4. Presentation of some experimental and modeling results of systems of interest

During our joint project, we have determined new experimental data and used several models, presented previously to correlate them. Concerning phase diagram determination, Fig. 4 presents new VLE experimental data for the system composed of the two impurities N\textsubscript{2} and NO. The measurements were carried out between -167.5 °C and -146 °C. Comparisons were done with existing literature data.

Bubble and dew point pressure measurements are very useful to determine phase diagram of multicomponent system. By this way, it is possible to plot PT envelop of a mixture. Fig. 5 presents results obtained with a mixture rich in CO\textsubscript{2} (MIX 1: 95 mol % of CO\textsubscript{2} and 5% of impurities like methane, O\textsubscript{2}, H\textsubscript{2}, N\textsubscript{2}, Ar and CO). Peng Robinson EoS is used to correlate these data. EoS parameters were determined from VLE data of the corresponding binary systems. As we can see, the model predictions are in good agreement with experimental data.
Fig. 4. (P, x, y) phase diagrams for the N$_2$ + NO binary system at -146, -153.6 (data from Scheunemann and Wagner (1985) [33]), -159.3(data from Scheunemann and Wagner (1985)) and 167.5°C.

Fig. 5. Experimental and predicted bubble/dew points for MIX 1 (Model predictions are independent from experimental data, Blue and Red Lines: PR-EoS with tuned kij; Dotted lines: PR-EoS with kij=0).

Fig. 6 presents new density data published in 2016. It concerns the binary system CO$_2$-H$_2$S (95/5 mole %) at 5 temperatures. GERG EoS is used to correlate the data. As we can see, there is a very good agreement between experimental work and modelling. Fig. 7 presents new results of gas hydrate dissociation points measurements and prediction of the binary system CO$_2$+H$_2$S (97/3 mole % and 92/8 mole %). CPA equation of state is used to estimate the fugacity of the guest molecules. As we can see, the model predicts very well the new experimental data. Fig. 8 presents frost points measurements of MIX 3 mainly composed of CO$_2$ (70% mol fraction) and others impurities like methane, ethane, propane, n-butane and i-butane. Fig. 8 presents the PT envelop of the MIX 3. It includes bubble and dew point measurements. The Peng Robinson EoS with parameters previously adjusted on VLE experimental data of each binary system predicts very well the phase diagram.
Fig. 6. Experimental and modelling results of CO$_2$ - H$_2$S at different isotherms, experimental results: (Δ) 273.15 K, (*) 283.15 K, (○) 298.15 K, (●) 323.15 K and (□) 353.15 K. Lines: Predictions using the GERG-2008 EoS.

Fig. 7. Experimental and predicted hydrate dissociation conditions for the 96.72 mole % CO$_2$ + 3.28 mole% H$_2$S and 91.60 mole% CO$_2$ + 8.40 mole% H$_2$S binary systems in the presence of distilled water (broken lines are predictions with an aqueous fraction of 0.95; lines are predictions with an aqueous fraction of 0.4).

Fig. 9 presents some dynamic viscosity measurements of MIX 1. Comparison are done with previous measurements of Al-Sylabi et al. [14]. The CO$_2$-Pedersen model is used to correlate the data [8]. We can observe a very good agreement between the experimental results and the model.
Fig. 8. PT envelop and CO$_2$ frost point line of MIX 3. Lines correspond to prediction using the Peng Robinson EoS.

Fig. 9. Viscosity measurement of MIX1 at two different temperatures.

5. Conclusion

The two research teams from Mines ParisTech and Heriot Watt University have developed, through a joint industrial project, important expertise for the determination of thermophysical properties of systems of interest in the context of CO$_2$ transportation. New results are presented and other studies are under progress. First results show that impurities have non negligible effect on the phase diagram but also on thermophysical properties. It is important to continue these investigations. We can also highlight that there is still an experimental gap for nitrous components like NO$_2$ / NO and sulphur components.

To conclude, this research project has focused on:
- Collecting data available in literature;
- Contributing with reliable experimental data;
- Developing thermodynamic models and testing their predictive capabilities;
- Initiating the discussion between academics and industrial partners.
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