Modeling of phase equilibria of CO$_2$ mixtures with application to CO$_2$ transport

Georgia Pappa, Epaminondas Voutsas

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Background

✓ CO₂ streams from different processes (post-combustion, pre-combustion, oxy-fuel) contain variable levels of impurities.

✓ Certain impurities can change the physical behaviour of the bulk gas, which need to be taken into account in the design of the compression and transport system.

✓ The water content in CO₂ is critical for transport. The water content should be controlled, because of risks for corrosion and hydrate formation in the pipeline.
There is no consensus among experts to what extent the CO\textsubscript{2} stream should be dried to avoid free water formation.

Some experts argue that full dehydration should be obtained, which is generally achieved through 50 ppm water content (0.005% vol). This 50 ppm water limit is a specification that has been taken for the first applications of CO\textsubscript{2} pipes in the United States. However, full dehydration, e.g. with glycols, is a costly process.

Other specifications are more relaxed and limit the concentration of water to no more than 60% of the dew point in the worst conditions. This limit tolerates about 750 ppm water in CO\textsubscript{2} of 25 °C. For a buried pipeline on the European mainland the water limit will be lower, because the temperature of the CO\textsubscript{2} will adapt to the ambient ground temperature of 5-10 °C (at 5 °C the minimum water solubility is ca. 500 ppm).

Some works report that water levels of 300–500 ppm are accepted by industries for CO\textsubscript{2} transmission in carbon steel pipelines.
Objectives

✓ Thermodynamic modelling of the solubilities in the CO₂/water mixture (water in CO₂-rich phase and CO₂ in water-rich phase) with the CPA EoS. Detailed results were presented in Ankara meeting.

Development of a semi-theoretical correlation for the easy calculation of water solubilities in CO₂ for a wide range of T and P.

✓ Evaluation of equation of state (EoS) models to simulate the risk of hydrate formation in a rich carbon dioxide stream.

✓ CO₂ hydrate phase equilibria was examined for:
  - Pure CO₂
  - CO₂ with other impurities (N₂, CH₄)
  - CO₂ in the presence of hydrate inhibitors (methanol, glycols)
A new semi-theoretical correlation of water solubilities in CO$_2$

From vapor-liquid equilibrium theory

\[ f_{w}^{vapor} = f_{w}^{liquid} \]

where:

- \( y_{w} \) : water solubility (mole fraction) in vapor phase (CO$_2$-rich)
- \( \varphi_{w} \) : water fugacity coefficient in vapor phase
- \( P \) : pressure
- \( x_{w} \) : water mole fraction in liquid phase \((x_{w} \approx 1)\)
- \( \gamma_{w} \) : water activity coefficient in liquid phase \((\gamma_{w} \approx 1, \text{since } x_{w} \approx 1)\)
- \( P_{w}^{s} \) : water vapor pressure
- \( P_{w}^{e} \) : Poynting effect. Effect of pressure in the liquid phase fugacity of water

\[ y_{w} \varphi_{w} P = x_{w} \gamma_{w} P_{w}^{s} P_{w}^{e} \]

\[ y_{w} = \frac{P_{w}^{s} P_{w}^{e}}{\varphi_{w} P} \]

\[ P_{w}^{s} = 7.26 \cdot 10^{-4} - \frac{7.21 \cdot 10^{-2}}{T} - 7.1385 \cdot 10^{-5} \ln(T) + 4.05 \cdot 10^{-11} T^{2} \text{ in bar} \]

\[ V_{l,w} = \frac{0.26214}{4.6137} \left[ 1 + \left(1 - \frac{T}{647.29}\right)^{0.2307} \right] \]

saturated liquid molar volume of water(l/mol)
A new semi-theoretical correlation of water solubilities in CO$_2$

$\varphi_w$ is calculated from the Redlich-Kwong EoS

$$P = \frac{RT}{V - b} - \frac{a}{T^{0.5}V(V + b)}$$

$$\ln \varphi = (Z - 1) - \ln(Z - B) - \frac{A}{B} \ln \left(1 + \frac{B}{Z}\right) \text{ where } A = \frac{aP}{R^2T^{2.5}} \text{ and } B = \frac{bP}{RT}.$$ 

$$Z = \frac{PV}{RT} \quad V \text{ is the mixture molar volume } \approx V_{CO_2} @ T, P$$

$a$ and $b$ are constants and were calculated by regressing water solubilities in CO$_2$. 
Results with the new model

- Using the new model, the water solubilities in CO₂, for a wide range of temperatures and pressures, are accurately and easily calculated in an Excel spreadsheet without need of iterative procedures.
- Predicts well the significant reduction of water solubility in CO₂ at pressures where CO₂ changes from liquid to gas.
- Predicts well the effect of temperature. The solubility of water in CO₂ reduces at lower temperatures.
- The water content should be controlled more strictly when CO₂ is transported at low temperatures and at relatively low pressures. Pressure release procedures will bring the CO₂ stream into the low solubility area.
Variation of water solubility in CO$_2$ in case of pipeline depressurization

Impact of operational conditions on pressure and temperature in CO$_2$ pipelines.

Variation of water solubility vs. pressure
What are hydrates?

- Clathrate hydrates or gas hydrates are crystalline complexes where water “host” molecules are linked through hydrogen bonding and create interstitial cavities that can enclose “guest” molecules, typically light gases (CH$_4$, N$_2$, CO$_2$) and hydrocarbons (propane, i-butane, etc).

- They may exist at temperatures below as well as above the freezing point of water.

- They may be of potential benefit as a hydrocarbon resource and as means of storing and transporting natural gas. The amount of methane potentially trapped in natural methane hydrate deposits may be significant ($10^{15}$ to $10^{17}$ m$^3$), which makes them of major interest as a potential energy resource.

- On the other hand, they may form at the conditions found in natural gas and oil pipelines causing blockages during end tail reservoir production or unexpected shutdowns, as well as in CO$_2$ transportation pipelines.
CO₂ hydrate phase diagram

V = vapour, L = liquid, H = hydrate

Q1: Quadruple point (Ice + H + Vₐ CO₂ + L_H₂O)
Q2: Quadruple point (H + L_H₂O + L_CO₂ + V_CO₂)

Can hydrates be formed without a liquid water phase (free water)?
Thermodynamic modeling

- At phase equilibria, the values of the fugacities of all components at the different phases must be equal.

- For water:
  \[ f^H_w = f^L_w = f^{LCO2}_w = f^V_w \]

- \( f^L_w, f^{LCO2}_w, f^V_w \) are calculated with a cubic Equation of State (EoS)

- The fugacity of water in the hydrate phase is calculated by utilizing the empty hydrate (EH) as reference state:

  \[
  f^H_w = f^{EH}_w \exp \left( \frac{\mu^H_w - \mu^{EH}_w}{RT} \right)
  \]

  - \( \mu^H_w \): chemical potential of the water in the hydrate phase
  - \( \mu^{EH}_w \): chemical potential of water in the empty hydrate
  - \( f^{EH}_w \): fugacity of water in the empty hydrate

  solid solution theory of van der Waals & Platteeuw (1959)
Models examined

- The fugacities of the vapor and the liquid phase \( f_w^V, f_w^L \) were calculated using the two most widely used EoS

<table>
<thead>
<tr>
<th>Peng-Robinson (PR)</th>
<th>Soave-Redlich-Kwong (SRK)</th>
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<tbody>
<tr>
<td>[ p = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)} ]</td>
<td>[ p = \frac{RT}{V - b} - \frac{a}{V(V + b)} ]</td>
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where the attractive and repulsive parameters, \( a \) and \( b \), for pure components can be obtained using the critical properties \( T_c, P_c \) and the acentric factor \( \omega \).

For mixtures:

- vdW one-fluid mixing rules:
  \[ a = \sum_i^n \sum_j^n x_i x_j a_{ij} \quad b = \sum_i^n \sum_j^n x_i x_j b_{ij} \]

- Combining rules:
  \[ a_{ij} = (a_{ii} a_{jj})^{1/2} \quad b_{ij} = (b_{ii} + b_{jj})/2 \]

  \[ a_{ij} = (a_{ii} a_{jj})^{1/2} (1 - k_{ij}) \] adjustable parameter between molecules i & j
Prediction of hydrate formation in $\text{CO}_2$

**Comparison of SRK and PR**

- PR and SRK predict very accurately the phase equilibrium curves and the hydrate formation conditions for $\text{CO}_2$ that contains water.
- Their performance is quite similar.
- PR has a marginal advantage at the very high pressure region.
SRK and PR predict very accurately the hydrate dissociation curves for CO₂ and CH₄.

PR is better than SRK in the prediction of N₂ hydrate dissociation curve.
Hydrate formation predictions: \( \text{CO}_2 + \text{N}_2 \) mixture

- PR and SRK perform quite satisfactory in the prediction of the hydrate formation conditions for \( \text{CO}_2+\text{N}_2 \) mixtures.

- The small advantage of PR over SRK is due to the better description of the pure \( \text{N}_2 \) behavior.
Hydrate formation predictions: CO₂ + CH₄ mixture

- PR and SRK can capture the effect of the mixture composition on the hydrate formation temperature and pressure.
- PR shows again a small advantage over SRK.
Hydrate inhibitors

- Hydrate formation is controlled in practice by injection of a thermodynamic hydrate inhibitor such as *small alcohols or glycols*. Inhibitors move the hydrate dissociation curve to lower temperatures.

- **Alcohols (up to butanol)** have two effects on water: the hydroxyl group hydrogen bonds the water molecules (dominating effect), and the hydrocarbon end of the alcohol tends to organize the water into solvent clusters (weaker effect).

- The **glycols (MEG, DEG and TEG)** provide more hydrogen bonding opportunity with water than alcohols (two hydroxyl groups plus oxygen atoms in the case of the larger glycols). They generally have lower volatility, so they may be easily recovered from gas processing/transmission equipment. Thus, MEG is frequently preferred to methanol.
SRK is not able to predict, i.e. $k_{ij}=0$, the inhibitor effect on hydrate formation.

The performance of SRK can, however, be greatly improved with the introduction of a single interaction parameter ($k_{ij}=-0.129$) between water and methanol, independent of the inhibitor concentration.

Here, using a $k_{ij}$ fitted to the 10% methanol curve, very good predictions of the methanol effect on the hydrate formation curve are obtained for the rest of the methanol concentrations.
The methanol effect on the hydrate conditions for CO₂ mixtures is accurately predicted with SRK using the same interaction parameter ($k_{ij}=-0.129$) between water and methanol as for pure CO₂.
SRK can successfully predict the inhibition effect caused by MEG addition for CO₂ and CH₄ using a common interaction parameter (k_ij) between water and MEG fitted to a single P-T data set for CO₂.
Conclusions

- A new semi-theoretical correlation for the prediction of water solubilities in CO₂-rich vapor phase was developed. It is very easily implemented in an excel spreadsheet and it yields very accurate predictions over a wide range of temperatures and pressures.

- Two commonly used EoSs (SRK and PR) were used to simulate the risk of hydrate formation in a carbon dioxide rich stream. CO₂ hydrate phase equilibria was examined for:
  - Pure CO₂
  - CO₂ with other impurities (N₂, CH₄)
  - CO₂ in the presence of hydrate inhibitors (methanol, glycols)

  - Both EoSs predict very accurately the hydrate dissociation curves for pure CO₂ and CH₄, while PR is better than SRK for pure N₂.
  - Both EoSs perform quite satisfactory in the prediction of the hydrate formation conditions for CO₂ with the presence of impurities (N₂, CH₄).
  - EoSs are not able to predict, i.e. with k_ij=0, the inhibitor effect (methanol, glycol) on hydrate formation.
  - SRK gives quite satisfactory predictions using a single interaction parameter between water and inhibitor, independent of the inhibitor’s concentration.

**Future work:**
CPA will be extended to simulate the risk of hydrate formation in CO₂ rich streams
Thank you for your attention !!!
Mutual solubility prediction in the CO₂/water mixture with the CPA EoS

The CPA (Cubic-Plus-Association) is an Equation of State that combines a cubic EoS (SRK or PR), which is used to account for the physical interactions (attractive and repulsive), with the statistical associating fluid theory, which is used to account for specific hydrogen bonding interactions.


- CPA predicts the significant reduction of water solubility in CO₂ at pressures where CO₂ changes from liquid to gas.
- CPA predicts well the effect of temperature. The solubility of water in CO₂ reduces at lower temperatures.
- The water content should be controlled more strictly when CO₂ is transported at low temperatures and at relatively low pressures. Pressure release procedures will bring the CO₂ stream into the low solubility area.
History (Milestones)

1810  Chlorine hydrate discovery by Sir Humphrey Davy

1882-3  The first evidence for the existence of CO2 hydrates. Wroblewski reported clathrate formation while studying carbonic acid. He noted that gas hydrate was a white material resembling snow, and could be formed by raising the pressure above a certain limit. He was the first to estimate the CO2 hydrate composition, finding it to be approximately CO2·8H2O.

1888  Villard first determines the existence of methane, ethane, ethylene, acetylene and nitrous oxide hydrates

1934  Hammerschmidt discovers hydrates as pipeline plugs. He also discovers thermodynamic inhibitors
The first evidence for the existence of CO₂ hydrates was back in 1882, when Wroblewski reported clathrate formation while studying carbonic acid. He noted that gas hydrate was a white material resembling snow, and could be formed by raising the pressure above a certain limit.

CO₂ and water can form hydrates at temperatures around and below 10°C, depending on pressure.

Precautions should be taken regarding design of systems containing water and carbon dioxide, since CO₂ hydrates can cause plugging in pipes and equipment, leading to blockage or even rupture.

**The formation of hydrates requires the following three conditions:**

- The right combination of temperature and pressure. Hydrate formation is favoured by low temperatures and high pressure;
- Hydrate forming molecules (CO₂ or/and other impurities), must be present;
- A sufficient amount of water to form the cage-like structure, but note that free water is not always required
Hydrates structure

There are three known hydrate structures: sI, sII and sH

- **structure I**
  - 2 pentagonal dodecahedron ($5^{12}$)
  - 6 tetrakaidecahedron ($5^{12}6^2$)
  - 20 water molecules/cavity in $5^{12}$, 24 in $5^{12}6^2$

- **structure II**
  - 6 pentagonal dodecahedron ($5^{12}$)
  - 8 hexakaidecahedron ($5^{12}6^4$)
  - 20 water molecules in $5^{12}$, 28 in $5^{12}6^4$

- **structure H**
  - $3 \times 5^{12}$
  - $2 \times 4^35^66^3$
  - $1 \times 5^{12}6^8$
  - 20 in $5^{12}$, 20 in $4^35^66^3$, 36 in $5^{12}6^8$
prediction of inhibitor effect

- SRK is not able to predict, i.e. $k_{ij}=0$, the inhibitor effect on hydrate formation.
- For CH$_4$ hydrates, the methanol effect on the hydrate conditions is accurately predicted with SRK using the same interaction parameter ($k_{ij}=-0.129$) between water and methanol as for CO$_2$.
- The same stands for CO$_2$/CH$_4$ mixtures in a gas mixture consisting of 31% CO$_2$ and 69% CH$_4$. 

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Methanol effect on the hydrate formation conditions for CH$_4$

Methanol effect on the hydrate formation conditions for a CO$_2$ (31%)/CH$_4$ mixture