Prediction of Carbon Dioxide Solubility in Monoethylene Glycol /Water Mixtures Employing SRK and PR-EOS with Two Different Mixing Rules

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Abstract: A thermodynamic models of binary system carbon dioxide (1) - mixture (monoethylene glycol (MEG)/water) (2) at pressure up to 5 bar and temperatures (288-348 K) are established using SRK and PR equation of state (EOS). Modified van der Waal's and quadratic mixing rules are coupled with the two Equation of state. Prediction of carbon dioxide in pure water and MEG were studied as well using same equations. Average absolute deviation in liquid-phase compositions percentage AADx % used for adjustable parameter optimization. The predicted results are showed very good agreement with the experimental data in all the systems examined. Quadratic mixing rule in all systems gives AADx % lower than Modified van der Waal's and the values differences can be ignored.

Keywords: CO2 solubility, monoethylene glycol, SRK, PR-EOS, mixing rules.

1. Introduction:
Carbon dioxide (CO\textsubscript{2}) represent almost 80\% of greenhouse gases which enters the atmosphere through burning of fossil fuels such as coal, oil, and natural gas, production of energy facilities and power plants as well as solid wastes [1-3]. Increasing of oil and gas production and their exploration are interested issues to all oil companies. According to these circumstances, the offshore projects development is increasing especially in great depths. When the processing is carrying out in some petroleum fields, gas, oil and water as fluids from reservoirs are routed through pipes to the platform directly [4]. This case offering excellent conditions of gas hydrates formation according to remain these pipelines under low temperature and high pressure. pipelines, subsea transfer lines and, in the incident of a gas kick can blocked by hydrates. Usually in this situation the industry injects inhibitors in the head of the wells to avoid hydrates formation during the discard of petroleum to platform. Injection of the inhibitor’s contingent on the well temperature and pressure and categorised into kinetic or thermodynamic [5].

One of the most important thermodynamics inhibitor is monoethylene glycol (MEG) which is used to avoid hydrates formation [6,7]. On the other hand, recycling of MEG is a lot of common due to the huge quantity used for hydrates control [4]. Water separation is undesirable influence, where some of gaseous components dissolve in glycol. In order to design, to operate and to optimize of an effective dehydration system, the effect of pressure and temperature on the dissolution process and the gas dissolved amount it is basic to continuum of the study [6].
In specific, MEG regeneration process is very important and examine the carbon dioxide dissolved amount in the MEG/ water mixture is beneficial way for this process [4, 5].

In this context, increasing of CO₂ emissions and reduced heat of regeneration was taking attention of many researchers on development sorbents improvement. Nevertheless, Phase equilibria, process performance, thermophysical properties (heat capacity, density, etc.) and transport properties (viscosity, diffusion coefficients, etc.) are depending on equilibrium CO₂ capacity as appear in recent results [3,8]. As usually the phase equilibrium experiments are expensive and consuming the time, prediction and/or correlation of the experimental data using equation of state (EOS) models are the most common approach [9]. Therefore, in previous work we focusing on a thermodynamic model of the phase behaviour of physical solvent for capturing carbon dioxide. Phase equilibria at moderate and high-pressures of carbon dioxide with different solvents classes of organic substances, n-methyl-2-pyrrolidone (NMP) and propylene carbonate (PC) [10], alcohols [11], aqueous solution [12,13].

Solubility of carbon dioxide in water, MEG and MEG/ water mixtures in different process performance, thermophysical properties (heat capacity, density, etc.) and transport properties (viscosity, diffusion coefficients, etc.) are depending on equilibrium CO₂ capacity as appear in recent results [9].

Therefore, in previous work we focusing on a thermodynamic model of the phase behaviour of physical solvent for capturing carbon dioxide. Phase equilibria at moderate and high-pressures of carbon dioxide with different solvents classes of organic substances, n-methyl-2-pyrrolidone (NMP) and propylene carbonate (PC) [10], alcohols [11], aqueous solution [12,13]. Solubility of carbon dioxide in water, MEG and MEG/ water mixtures in different concentrations 10, 50 and 90 % were quantify by Fabiane Serpa et.al [14] at temperature range (288.15-348.15) K and up to 5 bars pressures. In this study, experimental data obtained from [14] was correlated using SRK and PR -EOS with two different mixing rule, Modified van der Waal’s mixing rules (R1)[15] and Quadratic mixing rules (R2) [16].

2. Modelling

The experimental data were modelled using SRK and PR- EOS tied with two mixing rules. The SRK and PR-EOS [17,18] equations of state are listed in Table 1:

Table 1. Soave/Redlich/Kwong and Ping Robinson equations forms.

| SRK- EOS | PR-EOS |
|---------|--------|
| \[ P = \frac{RT}{(v-b)} - \frac{a}{v(v+b)} \] | \[ P = \frac{RT}{(v-b)} - \frac{a}{v(v+b)+b(v-b)} \] |
| \[ a = 0.42747 \frac{R^2 T_r^2}{P_c} \alpha(T_r, \omega) \] | \[ a = 0.45724 \frac{R^2 T_r^2}{P_c} \alpha(T_r, \omega) \] |
| \[ b = 0.08664 \frac{RT_c}{P_c} \] | \[ b = 0.0778 \frac{RT_c}{P_c} \] |
| \[ (\alpha)^{0.5} = 1 + (1-T_r^{0.5})(0.48508 + 1.55171 \omega - 0.15613 \omega^2) \] | \[ (\alpha)^{0.5} = 1 + (1-T_r^{0.5})(0.37464 + 1.5422 \omega - 0.2699 \omega^2) \] |

Table 2 shows the alternative cubic equation of compressibility factor equations [17] and Table 3 shows the coupled mixing rules.

Table 2. Soave/Redlich/Kwong and Ping Robinson compressibility factor equations forms.

| SRK-EOS | PR-EOS |
|---------|--------|
| \[ Z^3 - Z^2 + (A-B - B^2)Z - AB = 0 \] | \[ Z^3 - (1 - B)Z^2 + (A-2B - 3B^2)Z - (AB - B^2 - B^3) = 0 \] |
| \[ A = \frac{aP}{R^2 T_r^2} = 0.42747 \frac{P_r}{T_r^2} \] | \[ A = \frac{aP}{R^2 T_r^2} = 0.45724 \frac{P_r}{T_r^2} \] |
| \[ B = \frac{bP}{RT} = 0.08664 \frac{P_r}{T_r} \] | \[ B = \frac{bP}{RT} = 0.07780 \frac{P_r}{T_r} \] |
Table 3. Mixing Rules Equations [15,16]

| Names | Formula | Adjustable parameters |
|-------|---------|-----------------------|
| 1- Modified van der Waal's mixing rules (R1) | \(a_m = \sum_i \sum_j x_i x_j a_{ij}\) and \(b_m = \sum_i x_i b_i\) | \(k_{12} = \text{value.}\) |
| 2- Quadratic mixing rules (R2) | \(a_m = \sum_i \sum_j x_i x_j a_{ij}\) and \(b_m = \sum_i \sum_j x_i x_j b_{ij}\) | \(k_{12} = \text{value, } L_{12} = \text{value.}\) |

Prediction of CO₂ solubility in MEG/water mixture by using cubic EOS expressions along with physical characteristics of pure components and adjustable parameters of binary system of CO₂ (1)–MEG/water mixture (2). Comparison of calculations with experimental data was made after the computation of CO₂ mole fraction in the liquid phase (x).

3. Result and discussion

Critical parameters of MEG/water mixture at different concentrations, were evaluated using pseudocritical methods:

\[
T_{\text{cmix}} = \sum T_{ci} x_i
\]
\[
P_{\text{cmix}} = \sum P_{ci} x_i
\]
\[
\omega_{\text{mix}} = \sum \omega_i x_i
\]

Where \(T_{ci}, P_{ci} \text{ and } \omega_i\) symbols are the critical parameters of MEG and water. The expression \(x_i\) shows the mole fraction of components (water and MEG). The critical properties of the carbon dioxide, MEG and water are shown in Table 4. The calculations were made using Matlab software for binary mixture (CO₂ 1-MEG/water 2) instead of ternary mixture (CO₂ 1-MEG 2-water 3). Binary mixture MEG-water in different concentrations are converted to single component using pseudocritical equations mentioned above.

Table 4. CO₂, MEG and water Critical properties [8,16]

| Component | \(T_c/\text{K}\) | \(P_c/\text{bar}\) | \(\omega\) |
|-----------|-----------------|-----------------|------|
| CO₂       | 304.7           | 73.8            | 0.225 |
| MEG       | 790             | 66.53           | 0.147 |
| water     | 647             | 221             | 0.344 |

Adjustable parameters \(k_{12}\) and \(L_{12}\) which are used in R1 and R2 respectively were approximated using two deferent approach \(k_{12}\) by fitting an experimental data, \(L_{12}\) was found by trial and error. Mole fraction solubility was performed by using all pressure isotherm. Binary interaction parameters optimization for R1 and R1are presented in Table 5 with the average absolute deviation in liquid-phase compositions (AADx %) which is calculate by the equation:
\[ AADx(\%) = \frac{1}{N_{exp}} \sum_{i=1}^{N_{exp}} |x_i^{exp} - x_i^{calc}| \times 100 \]

Table 5 Summarize the comparative of calculated and experimental data sets for (CO2-water, CO2-MEG and CO2-MEG/water at different compositions) systems which is took place at temperature range 288 to 348 K and pressure up to 5 bar. Columns 5 and 9 listed \( L_{12} \) in R2 are coupled with same \( k_{12} \) value used in R1.

In Table 5 can observe adjustable parameter \( k_{12} \) increasing with temperature increasing. This data is applicable for pristine MEG and MEG/water mixture (50 and 90%). A decrease in \( k_{12} \) value was reported in water and 10 % MEG mixture. This is agreed with the fact that CO2 is more soluble in MEG than water, therefore increase MEG concentrations causes an increase in gas amount solubility in the solvent mixture as Fabiane Serpa[14] observed. \( L_{12} \) values which are found by trial and error are oscillation values.

Table 5. Optimized binary interaction parameters (\( k_{12}, L_{12} \)) and AADx %.

| Component | T (K) | R1 K12 | AADx R1 | R2 L12 | AADx R2 | R1 K12 | AADx R1 | R2 L12 | AADx R2 |
|-----------|-------|--------|---------|--------|---------|--------|---------|--------|---------|
| water     | 298.15| -0.15404 | 0.001968 | 0.157 | 0.00218 | -0.12618 | 0.00415 | -0.209 | 0.00165 |
|           | 323.35| -0.11779 | 0.0026 | -0.034 | 0.00215 | -0.09567 | 0.002 | 0.121 | 0.00137 |
|           | 288.15| 0.2319 | 0.02091 | -0.324 | 0.0194 | 0.235 | 0.02098 | -0.339 | 0.0181 |
|           | 303.15| -0.1261 | 0.002014 | -0.094 | 0.00376 | -0.1262 | 0.00407 | -0.126 | 0.00371 |
| MEG       | 318.15| 0.26211 | 0.00274 | 0.182 | 0.00296 | 0.2638 | 0.0018 | 0.19 | 0.00225 |
|           | 333.15| 0.28774 | 0.00427 | -0.138 | 0.00355 | 0.288 | 0.00427 | -0.128 | 0.00362 |
|           | 348.15| 0.29617 | 0.0111 | -1.41 | 0.01005 | 0.2956 | 0.0112 | -0.339 | 0.00657 |

Composition of (MEG/Water)

| Composition | T (K) | R1 K12 | AADx R1 | R2 L12 | AADx R2 | R1 K12 | AADx R1 | R2 L12 | AADx R2 |
|------------|-------|--------|---------|--------|---------|--------|---------|--------|---------|
| 0.1 MEG + 0.9 H2O | 288.15| -0.1292 | 0.00454 | 0.328 | 0.00357 | 0.01736 | 0.00451 | 0.324 | 0.00355 |
|           | 303.15| -0.1159 | 0.00889 | 0.888 | 0.00683 | -0.0945 | 0.00886 | 0.891 | 0.00681 |
|           | 318.15| -0.10257 | 0.001882 | 0.471 | 0.00151 | -0.0809 | 0.00186 | 0.431 | 0.00153 |
|           | 333.15| -0.08427 | 0.00251 | 0.989 | 0.00154 | -0.06291 | 0.00251 | 0.998 | 0.00147 |
|           | 348.15| -0.06167 | 0.00394 | -1.92 | 0.00338 | -0.03347 | 0.00394 | -0.911 | 0.00159 |
| 0.5 MEG + 0.5 H2O | 288.15| 0.001312 | 0.00884 | -0.271 | 0.00706 | -0.108 | 0.00892 | -0.26 | 0.00634 |
|           | 303.15| 0.01286 | 0.00234 | 0.248 | 0.00292 | 0.0304 | 0.0023 | -0.073 | 0.00212 |
| 0.9 MEG + 0.1 H2O | 318.15| 0.01997 | 0.00842 | -0.447 | 0.00804 | 0.0365 | 0.00845 | -0.444 | 0.00674 |
|           | 333.15| 0.03061 | 0.00823 | 0.659 | 0.00556 | 0.04714 | 0.00799 | 0.675 | 0.00545 |
|           | 348.15| 0.07001 | 0.007507 | -1.38 | 3.02E-03 | 0.0851 | 0.00686 | -1.38 | 0.00237 |
|           | 288.15| 0.1768 | 0.0251 | -0.573 | 0.0092 | 0.1836 | 0.025 | -1.87 | 0.0077 |
|           | 303.15| 0.1864 | 0.003505 | -0.038 | 0.00589 | 0.21196 | 0.00413 | 0.027 | 0.0056 |
|           | 318.15| 0.196 | 0.00523 | 0.437 | 0.00907 | 0.21896 | 0.00522 | -0.0108 | 0.00594 |
|           | 333.15| 0.2098 | 0.00946 | 0.437 | 0.00907 | 0.2154 | 0.00876 | 0.469 | 0.00663 |
|           | 348.15| 0.2296 | 0.00774 | 2.53 | 2.00E-03 | 0.24244 | 0.00721 | -0.911 | 0.00159 |

Generally, the thermodynamic models using SRK and PR equation of state coupled with R1 and R2 were found a suitable to run these systems. However, using R2 in the two equations gives AADx % lower than R1 and the values differences can be ignored. In the context, there is very small deviation between the results of the two equations where the AADx of the SRK that is more than the AADx for the PR-EOS for the two mixing rules. The comparative analysis of models and experimental data are shown in Figures 1-3. CO2-MEG and CO2-water systems analysis is shown in Figure 1 and 2 respectively. Figure 3 is displayed CO2-MEG/water mixture systems.
Figure 1. literature [16] and prediction data comparison models for carbon dioxide (1) + MEG (2) system. a (288.15 K), b (303.15K), c (318.15K), d (333.15K) and e (348.15K).

Figure 2. literature [16] and prediction data comparison models for carbon dioxide (1) + water (2) system at 298.5 and 323.35 K
Figure 3. Literature [16] and prediction data comparison models for carbon dioxide (1) + MEG/water (2) system. a (288.15 K), b (303.15K), c (318.15K), d (333.15K) and e (348.15K).
4. Conclusion
SRK and PR-EOS along with R1 and R2 were used to predict the experimental data of CO₂ solubility in water, MEG and its mixtures in varies concentrations and temperatures up to 5 bars pressure. K₁₂ and L₁₂ are used as adjustable parameters in R2 which gives AADₓ % lower than R1 that concocted with one adjustable parameter K₁₂. Besides this, AADₓ alteration between R1 and R2 was insignificant. According to this results and observation using R1 with k₁₂ is preferred in study gas-liquid equilibrium. In all the systems examined, L₁₂ was variation values cannot be followed by any criteria.

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