# $CO_2$-water equilibrium from ambient conditions to 300ºC and 500bar. A fugacity-activity coefficient approach.

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## 1. Introduction

The broad spectrum of industrial applications in which the $CO_2$-$H_2O$ equilibrium is present has resulted in several approaches to model the solubility of this gas in water. The complexity of the thermodynamic models is diverse depending on the operating conditions selected. Simple models (based on the regression of experimental data as Henry constants) can be used at near ideal conditions (low pressures, temperatures near ambient temperature). On the other hand, more complex models have been proposed at higher pressures and temperatures. This work presents a fugacity-activity coefficient thermodynamic model that reproduces the $CO_2$-$H_2O$ equilibrium from ambient conditions to 300ºC and 500bar with an absolute average deviation (AAD%) between experimental data and model predictions of only a 4.2%. The applicability of the model ranges from supercritical fluid, biotechnological and geochemistry applications, to the power and oil and gas industries within others.

## 2. Materials and Methods

The thermodynamic model presented in this work is based on a fugacity–activity coefficient approach to account for the pressure and temperature effect on the vapor and liquid phase fugacities. While the vapor phase fugacity coefficient is calculated by the Peng Robinson-Boston Mathias equation of state (EOS), the liquid phase activity coefficient is computed combining the Non-Random-Two-Liquid (NRTL) activity coefficient model with the Poynting correction factor. The calculation of the Poynting correction factor has been performed approaching the $CO_2$ partial molar volume to that at infinite dilution, computed with a regressed Krichevskii parameter.

Once that the model is fully defined, the NRTL activity parameters are obtained by non-linear regression, minimizing the differences between the experimental points and the model predictions.

## 3. Results and discussion

Figure 1 compares the experimental data provided by Lide[1] on $CO_2$ solubility in water in the low to moderate temperature (from 10ºC to 100ºC) low to moderate pressure region (partial pressure of $CO_2$ up to 10bar) with the model predictions.

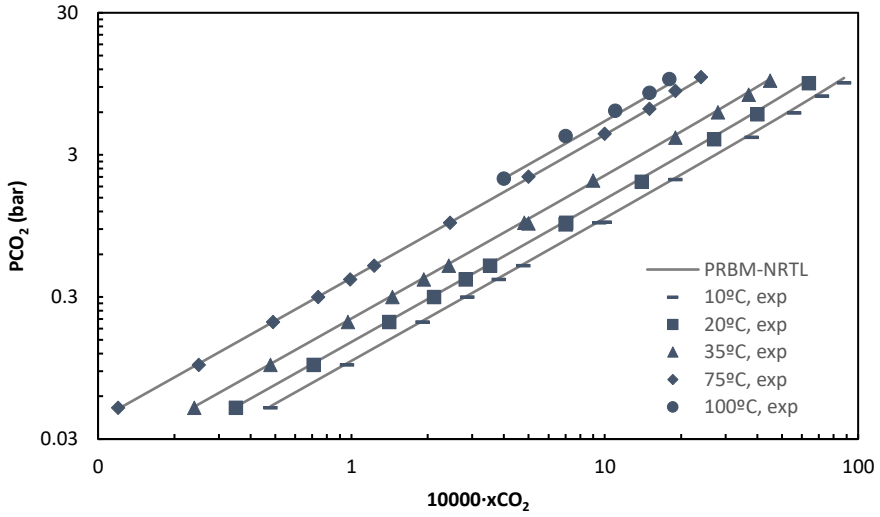


**Figure 1.** Solubility of $CO_2$ in water from low to moderate temperatures and pressures. $CO_2$ partial pressure vs $CO_2$ mole fraction in liquid phase.

As it can be seen from Figure 1, the model correlates very well with the experimental data in this region. The absolute average deviation for this set of data is lower than 3.5%.

Figure 2 compares the experimental data provided by Takenouchi[2] on $CO_2$ solubility in water in the high temperature (from 100ºC to 300ºC) high pressure region (partial pressure of $CO_2$ up to 430bar) with the model predictions.

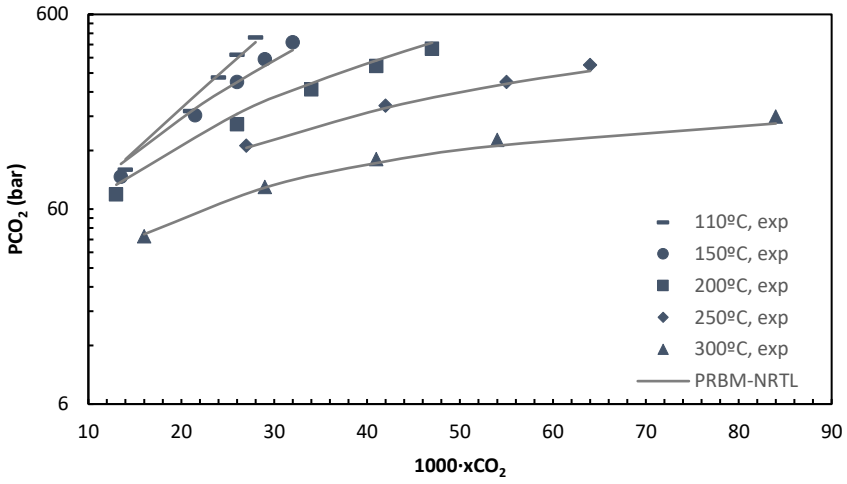


**Figure 2.** Solubility of $CO_2$ in water at high temperatures and pressures. $CO_2$ partial pressure vs $CO_2$ mole fraction in liquid phase.

As it is shown in Figure 2, the model is also able to accurately reproduce the solubility of $CO_2$ in water at high temperatures and high pressures. In this case, the absolute average deviation for this second set of experimental data is lower than a 6%.

As explained in Section 2, the NRTL parameters have been adjusted to minimize the differences between the experimental data and the model predictions by means of nonlinear regression. While the first NRTL parameter is temperature independent, the second one is temperature dependent. Table 1 shows the adjusted NRTL parameters used in the model, where subscript 1 represents $CO_2$ and subscript 2 water:

| $NRTLA_{12}$ | $NRTLA_{21}$ | $NRTLB_{12}$ | $NRTLB_{21}$ |
|---|---|---|---|
| 280.36 | 14.55 | 5456.2 | -6841.9 |

**Table 1:** NRTL regressed parameters.

As it can be seen from the results (AAD% of a 4.2%), the model is accurate enough to be used for the engineering design of applications involving a $CO_2$-$H_2O$ equilibrium.

## 4. Conclusions

This work presents a thermodynamic model that accurately reproduces the $CO_2$-water vapor-liquid equilibrium from ambient conditions to 300ºC and 500bar. The model, based on a fugacity-activity coefficient approach, accounts for the pressure and temperature effect on the vapor and liquid phase fugacities. The simplicity and accuracy of the model, with an absolute average deviation between experimental data and model predictions of only a 4.2%, together with the range of pressures and temperatures covered, provides the Supercritical Fluid Community with a powerful tool for the engineering design of a wide range of technological applications.

## References

1. D.R. Lide, G. Baysinger, L.I. Berger, R.N. Goldberg, H. v Kehiaian, K. Kuchitsu, D.L. Roth, D. Zwillinger, CRC Handbook of Chemistry and Physics.
2. S. Takenouchi, G.C. Kennedy, *American Journal of Science* **1964,** *262*, 1055–1074.