# The Thermodynamics of Aqueous Potassium Carbonate/Piperazine for $CO_2$ Capture

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## Introduction

Concern over global warming has sparked the development of technologies for the capture and sequestration of greenhouse gases. Amine-based solvents in absorber/stripper processes have been developed as one option for separating $CO_2$ from waste gas streams. A new aqueous solvent containing potassium carbonate ($K_2CO_3$) and piperazine (PZ) shows promise as a commercially viable solvent, possessing favorable equilibrium behavior and a low heat of absorption.

The equilibrium in these solvents can be represented with the reactions shown below. PZ is a cyclic diamine, forming a variety of species. Carbonate and bicarbonate are also present in significant quantities. The pH in useful solutions varies from 8 to 13.

$$PZH^+ + H_2O \leftrightarrow PZ + H_3O^+$$
$$PZ + CO_2(aq) + H_2O \leftrightarrow PZCOO^- + H_3O^+$$
$$H^+PZCOO^- + H_2O \leftrightarrow PZCOO^- + H_3O^+$$
$$PZCOO^- + CO_2 + H_2O \leftrightarrow PZ(COO^-)_2 + H_3O^+$$
$$CO_2(aq) + 2\cdot H_2O \leftrightarrow HCO_3^- + H_3O^+$$
$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$$
$$2\cdot H_2O \leftrightarrow H_3O^+ + OH^-$$
$$CO_2(g) \leftrightarrow CO_2(aq)$$

The evaluation of this solvent for use in a commercial system depends on the ability to effectively model rates of $CO_2$ absorption, energy requirements, and absorption capacity, requiring a thorough understanding of equilibrium behavior. This work identifies important equilibrium characteristics of the solvent at various concentrations (0.0 to 6.2 m $K^+$ and 0.0 to 3.6 m PZ) and temperatures (25 to 80°C) and develops a rigorous thermodynamic model applicable over these ranges.

## Experimental

**Electrolyte NRTL Model.** The equilibrium modeling of the solutions was accomplished using the electrolyte NRTL model, originally developed by Chen et al. (1). Previous work has used this model extensively for aqueous electrolyte solutions and acid gas systems (2, 3).

**Liquid Speciation.** The equilibrium distribution of piperazine and its carbamates was quantified with the use of $^1H$ spectra from a Varian INOVA 500 NMR. Samples were prepared with 80% $H_2O$, 20% $D_2O$, $K_2CO_3$ or $KHCO_3$, and PZ.

**Vapor-Liquid Equilibrium.** The equilibrium vapor pressure of $CO_2$, $P_{CO2}$*, was determined with a wetted-wall column. A description of the equipment can be found in previous work (4, 5). Nitrogen and $CO_2$ are fed into the column where it contacts the flowing solvent. The outlet concentration of $CO_2$ is measured using IR spectroscopy. By adjusting the $CO_2$ partial pressure in the gas stream, absorption and desorption conditions can be obtained and a flux of $CO_2$ can be calculated. Interpolating to a flux of zero allows the calculation of $P_{CO2}$*.

## Results and Discussion

An equilibrium model was developed for $K^+$/PZ mixtures using existing literature data and new experimental investigations. Boiling point elevation, activity of water, and $P_{CO2}$* data were used to regress parameters relevant to $K_2CO_3/KHCO_3$ solutions (6, 7, 8). $P_{CO2}$* data for aqueous PZ is available from Bishnoi (4). Speciation in aqueous PZ was previously found by Ermatchkov (9). Additional data for $K^+$/PZ solutions were investigated in this work.

Parameters for the model are shown in Table 1. In this work, default parameters for water-ion pair and ion pair-water interations are 8.0 and -4.0 respectively. Molecule-molecule interactions are 0.0. The model reference temperature is 353K; therefore, A represents a binary interaction parameter, $\tau$, at 353K and B represents a temperature dependence in the form $B\cdot(1/T - 1/353)$. The regressed parameters show minor variations from default values. Confidence intervals are generally less than 10% for A and 50% for B.

**Table 1. Regressed Binary Interaction Parameters in the Electrolyte NRTL Model for $K^+$/PZ Mixtures**

| Interaction | A, $\tau_{353K}$ | $\sigma_A$ | B | $\sigma_B$ |
|---|---|---|---|---|
| $H_2O$, ($K^+$ $CO_3^{2-}$) | 9.36 | 0.21 | 867 | 560 |
| ($K^+$ $CO_3^{2-}$), $H_2O$ | -4.49 | 0.04 | -331 | 90 |
| $H_2O$, ($K^+$ $HCO_3^-$) | 7.68 | 0.04 | 2410 | Indet. |
| ($K^+$ $HCO_3^-$), $H_2O$ | -3.40 | Indet. | -404 | 80 |
| $H_2O$, PZ | 12.90 | 0.25 | -3321 | Indet. |
| PZ, $H_2O$ | 0.92 | 0.13 | -837 | Indet. |
| ($PZH^+$ $PZCOO^-$), $H_2O$ | -4.47 | 0.42 | * | N/A |
| $H_2O$, ($PZH^+$ $PZ(COO^-)_2$) | 5.46 | 0.81 | * | N/A |
| ($PZH^+$ $PZ(COO^-)_2$), $H_2O$ | * | N/A | -625 | 380 |
| $H_2O$, ($K^+$ $PZCOO^-$) | 11.21 | 0.27 | -6921 | 1110 |
| $H_2O$, ($K^+$ $PZ(COO^-)_2$) | 7.72 | 0.29 | -2098 | 920 |
| $H_2O$, ($PZH^+$ $HCO_3^-$) | 8.93 | 0.10 | * | N/A |
| $H_2O$, ($PZH^+$ $CO_3^-$) | * | N/A | 7987 | 1270 |
| ($PZH^+$ $CO_3^{2-}$), $H_2O$ | -6.40 | 0.59 | * | N/A |

* Default parameter used.
Indet. = Indeterminate

Proton NMR was used to speciate various $K^+$/PZ mixtures. As shown in Figure 1, the addition of 5.0 m $K^+$ to 2.5 m PZ dramatically changes the distribution of PZ species. Over equivalent partial pressures, the presence of more $CO_2$ converts free PZ to $PZCOO^-$ and $PZ(COO^-)_2$. Conversely, the carbonate/bicarbonate buffer reduces the protonation of PZ and $PZCOO^-$ resulting in an overall increase in reactive amine species.

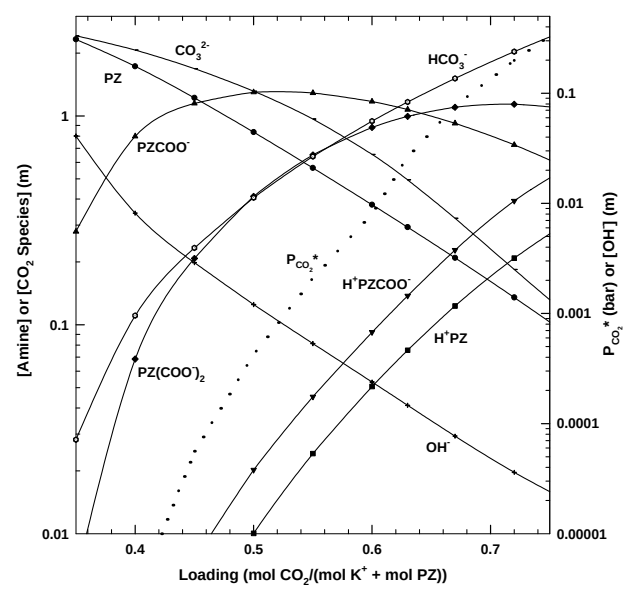


**Figure 1.** Electrolyte NRTL Prediction of Speciation of 5.0 m $K^+$/2.5 m PZ at 60°C

The results of VLE experiments for various $K^+$/PZ solvents at 60°C are shown in Figure 2. The addition of 3.6 m $K^+$ to 1.8 PZ solutions depresses the $P_{CO2}$* by as much as a factor of 20. As the solution becomes more concentrated in $K^+$ and PZ the $P_{CO2}$* line becomes less steep as evidenced by 5.0 m $K^+$/2.5 m PZ, showing that the equilibrium behavior approaches that of 7 m MEA solutions. Model predictions are shown to be within 30% of experimental findings.

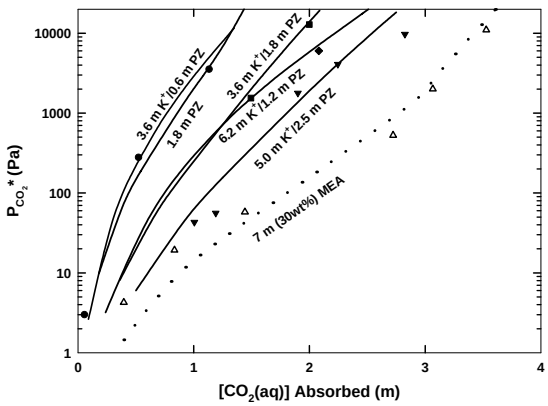


**Figure 2.** Vapor-Liquid Equilibrium of $CO_2$ in $K^+$/PZ at 60°C. Points: Experimental Data. Lines: Model Predictions.

The VLE model was used to predict $P_{CO2}$* at various temperatures, allowing estimations for the heat of absorption ($\Delta H_{abs}$) of $CO_2$ at 3000 Pa (Figure 3). The $\Delta H_{abs}$ shows a strong dependence on the ratio of PZ to $K^+$. At low ratios, the value of $\Delta H_{abs}$ approaches 8 kcal/mol. With more PZ the heat of absorption increases and approaches a value typical of amine-based solvents (~22 kcal/mol). The 1.8 m PZ solution also has a lower $\Delta H_{abs}$, ~16 kcal/mol, due to protonation of the amine at the high $CO_2$ partial pressure.

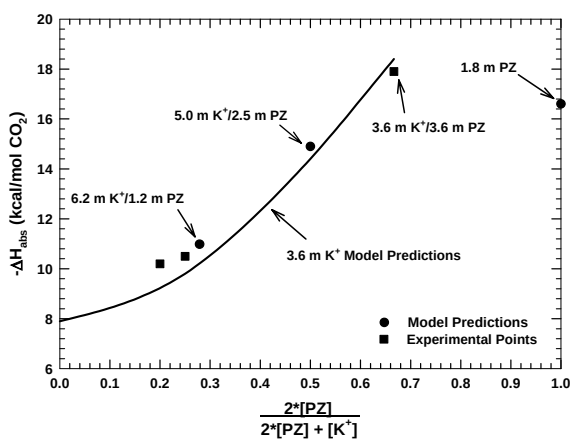


**Figure 3**. Heat of Absorption of $K^+$/PZ Mixtures. Model Predictions and Experimental Data at T = 60°C, $P_{CO2}$* = 3000 Pa

The dependence of $\Delta H_{abs}$ on PZ:$K^+$ reflects a strong dependence on the reaction stoichiometry relevant at given conditions. This behavior is reflected in Figure 4 for 5.0 m $K^+$/2.5 m PZ. At loading less than 0.4, the reaction of $CO_2$ with hydroxide has a significant effect. With increasing loading, the absorption of $CO_2$ is dominated by the formation of $H^+$PZ and $HCO_3^-$, reducing the $\Delta H_{abs}$. At even higher loading, the formation of carbamates becomes more prevalent at 60 and 80°C, increasing the $\Delta H_{abs}$. At 40°C, a decline in $\Delta H_{abs}$ occurs throughout the range of loading as protonation of the amine becomes more important. Temperature has a marked effect, shifting equilibrium and changing reaction stoichiometry at given loading. It appears that the protonation of PZ becomes more important at higher temperatures as the carbamate stability decreases.

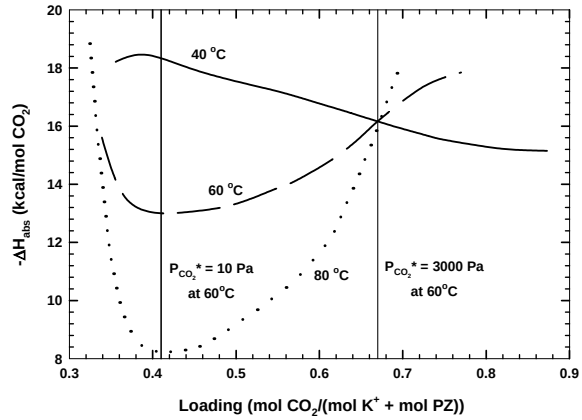


**Figure 4.** Electrolyte NRTL Model Predictions of the Heat of Absorption of 5.0 m $K^+$/2.5 m PZ.

## Conclusions

The addition of $K^+$ to aqueous PZ yields significant advantages in both speciation and $P_{CO2}$* behavior. Large amounts of carbonate/bicarbonate buffer the solution at high pH, reducing loss of the free amine to protonation. Concentrated solutions reduce the vapor pressure of $CO_2$ over solvents at equivalent loadings. Data has been used to create a robust, thermodynamic model of the solvent applicable over wide ranges of temperature and concentration.

Behavioral differences are reflected positively in the $\Delta H_{abs}$ of mixtures. The cost of regenerating the solvent in the stripper could be lowered by 10 to 30% over MEA-based processes with the reduction in $\Delta H_{abs}$, resulting in a more economical process for $CO_2$ capture.

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