Abstract

Piperazine is an amine which is used both as an activator or promoter, but also as active component in CO₂ capture solvents. High concentrations are being formulated to draw benefit of the PZ properties. This results in a risk of precipitation of PZ and other solid phases during capture. It could be a benefit to the capture process, but it could also result in unforeseen situations of potential hazardous operation, clogging, equipment failure etc.

Security of the PZ process needs to be in focus. Flow assurance requires additional attention, especially due to the precipitation phenomenon. This entails all parts of the streams, but also during formulation and transport of the solvent.

In this work the extended UNIQUAC thermodynamic model is presented with the addition of piperazine (PZ or PIPH₂) in combination with the potassium ion of mixtures with CO₂ in equilibration with KOH-KHCO₃-K₂CO₃. Phase boundaries are laid out which shows the concentration regions of solid formation. A special focus will be given to the boundary where precipitations occur.

The model is a generic. It builds on consistent parameters of the extended UNIQUAC model previously published. It allows for accurate vapor liquid equilibrium (VLE) calculation, heat capacity determination, and similar thermodynamic properties. It especially allows for determination of solid liquid equilibria (SLE) and heat of absorption/heat of desorption which are core variables in the determination of energy requirements for CO₂ capture.

In this work the typical phase behavior will be shown for the PZ solvent with potassium (K₂CO₃/KHCO₃) for CO₂ capture. Conclusions are given on a solvent compositions resulting in low heat requirements using the predictive nature of the extended UNIQUAC model. Concentration of a PZ/K₂CO₃ solvent is suggested with a heat of absorption/desorption of 40 kJ/mol.

Keywords: Solid Precipitation, Piperazine, Potassium carbonate, Phase boundaries of slurry, Heat of absorption and desorption, thermodynamic modelling

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1. Introduction

Sustainable power production is a vital ingredient in keeping the economy fit and the environment free from green house gasses. The world’s coal reserves are a competing energy resource compared to renewable energy processes. It is being used presently, and due to low production costs, it will be used in the future.

Currently several CO₂ capture technologies exist, some are emerging and others have been used on a smaller scale in the oil and gas industry for some time now. The mature solvent based CO₂ absorption/desorption technique is the focus of this study. There is a potential to innovate the existing solvents, especially to limit their critical characteristics regarding degradation, emissions, and hazardous nature.

Piperazine (PZ) is a solvent being suggested as a potential candidate for developing the CO₂ capture technology. It attacks some of the mentioned issues. It was used as a promoter or activator of amine solutions in order to improve the CO₂ reaction kinetics. Recently it has been used in much higher concentrations as active capture component.

Precipitation is a key issue in the use of PZ. The solubility is a limiting factor.

The aim of this work is to present the extended UNIQUAC model applied to the piperazine system containing potassium and CO₂. The model is used for calculating phase diagrams. These will indicate the boundary at which solid formation will occur. This allows for design of a process where solid can actively be used in the optimization and increase of the capture capacity, but it certainly can also become a road map for safe operation in order to prevent solid formation.

The extended UNIQUAC model is generic in the sense that it allows for calculation of related consistent thermodynamic properties using one set of parameters for all properties.

In this work the extended UNIQUAC is used in the prediction of phase behavior. It is additionally used in the determination of the heat of desorption. The model is actively applied in order to predict a solvent composition with a low heat requirement.

2. The Extended UNIQUAC model for the PZ-KOH-K₂CO₃-KHCO₃-H₂O system

The extended UNIQUAC model is a Gibbs excess model which applies the thermodynamic \( \gamma \Phi \) convention, indicating that the extended UNIQUAC model is used for the liquid phase and the SRK equation for the gas phase. For the typical CO₂ capture system the gas phase is often close to ideal and only minor correction is observed from the SRK equation in the gas phase. The extended UNIQUAC model is the well known UNIQUAC model plus a Debye-Hückel–term to correct for the electrostatic interaction between the ions in the liquid phase.

The details of the equations system and derived properties of the Gibbs excess model were described by Thomsen et al. [1]. The method for performing VLSE calculations were outlined by Thomsen and Rasmussen [2]. A description of how parameter fitting is performed, the framework surrounding it, and the possibilities using the model, is given in detail by Thomsen [3]. It has been applied in several process related challenges like geological research, scaling, corrosion, high pressure gas hydrate precipitation, ion exchange etc. Recently it has been applied in a number of works related to CO₂ capture. Amino acids, typical amines have been studied. It was optimized by Darde et al. [4] for the chilled ammonia process (CAP) on calculation of kinetics, simulation, optimization, and integration.

The model uses ion/species specific model parameters. The system containing piperazine potassium and CO₂, contains the following 13 ions/species: H₂O(l), CO₂(aq), K⁺(aq), H⁺, OH⁻, HCO₃⁻, CO₃²⁻, PZ(aq), PZCO₂⁻(aq), PZCO₂⁻, PZ(CO₂)₂²⁻, PZH⁺, PZH₂²⁺. Piperazine has the tendency to form at least
three carbamate reaction products. An uncharged zwitter ionic type \( \text{PZCO}_2 \) and additional two carbamates. These have either one or two \( \text{CO}_2 \) molecules incorporated, ie. \( \text{PZCO}_2 \) and \( \text{PZ(CO}_2)_2 \). since piperazine has two active nitrogen groups which attracts \( \text{CO}_2 \). Piperazine can be titrated like any other base and it has two protolytic steps which entails the components \( \text{PZH}^+ \) and \( \text{PZH}_2^{2+} \). The speciation in the liquid phase is very complex, as outlined by the following used reaction scheme:

\[
\begin{align*}
H_2O & \rightarrow H^+ + OH^- \\
HCO_2^- + OH^- & \rightarrow CO_3^{2-} + H_2O \\
PZ(aq) + H^+ & \rightarrow PZH^+ \\
PZH^+ + H^+ & \rightarrow PZH_2^{2+} \\
PZCOO^- + H^+ & \rightarrow PZH^+COO^- \\
PZ(aq) + HCO_3^- & \rightarrow PZCOO^- + H_2O \\
PZCOO^- + HCO_3^- & \rightarrow PZ\left(\text{COO}^-\right)_2 + H_2O
\end{align*}
\]

Several solid phases may precipitate in addition to ice. The solid phases of the potassium system are \( \text{K}_2\text{CO}_3 \cdot 6\text{H}_2\text{O} \), Sesquihydrate \( \text{K}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O} \), bicarbonate \( \text{KHCO}_3 \), and the double salt \( \text{K}_2\text{CO}_3 \cdot 2\text{KHCO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O} \). Piperazine forms a number of solid components which are \( \text{PZ} \cdot 6\text{H}_2\text{O} \), hemihydrate \( \text{PZ} \cdot \frac{1}{2}\text{H}_2\text{O} \), and anhydrous, \( \text{PZ(s)} \). There are indications of a possible potassium piperazine carbamate solid which may precipitate, but the data material for this component is still scarce [5].

The Extended UNIQUAC model has parameters in order to describe the ions and the interaction between molecules. These are found through data reduction by fitting to experimental measured properties. A well described consistent framework is used for the parameters and not all interaction parameters are used in the model [6,7]. For example the interaction between \( \text{PZ(aq)} \) and \( \text{PZH}_2^{2+} \) is known and fixed to no-interaction since they will never be present in the same solution, due to the acid/base nature of their presence.

The parameters of the \( \text{CO}_2 \)-\( \text{KHCO}_3 \)-\( \text{K}_2\text{CO}_3 \)-\( \text{H}_2\text{O} \) system originate from the work of Thomsen and Rasmussen [2]. During the previous modeling approximately 700 data points were used in the fitting process. For the present study on piperazine, an additional 1200 data points were used. It should be noted that several sources of literature on piperazine are of questionable quality, making the modelling difficult. These were of course not prioritised during the correlation. The data resides in the CERE electrolyte data bank [8], from which 140,000 data points are available to the CERE consortium members.

3. Model validation

It is a long cumbersome process to reach an acceptable parameter scheme for the piperazine process. During the steps in the parameter development the performance of the model is constantly evaluated in order to establish the accuracy of the fit. The current correctness is validated in the following plots.

Figure 1 to 3 illustrates the core performance of the model in the \( \text{CO}_2 \)-\( \text{KHCO}_3 \)-\( \text{K}_2\text{CO}_3 \)-\( \text{H}_2\text{O} \) system as established during 1999 [2]. Figure 1 shows a small subsection of the used VLE data originating from Tosh et al. [9]. There is a good resemblance between the data and the model, all the way from low pressure to high pressure at these temperatures. Figure 2 illustrates the performance of the \( \text{K}_2\text{CO}_3 \) SLE correlation. On adding \( \text{K}_2\text{CO}_3 \) to water, ice is formed at a low temperature while freezing. This is up to a concentration of 38 wt% (4.4 molal). Hereafter various hydrates of \( \text{K}_2\text{CO}_3 \) precipitate. At approximately 50-60 wt% no more \( \text{K}_2\text{CO}_3 \) will dissolve and the SLE curve increases abruptly as function of temperature. Figure 3 validates the SLE correlation in the ternary \( \text{KHCO}_3 \)-\( \text{K}_2\text{CO}_3 \)-\( \text{H}_2\text{O} \) system. There seem to be a
slight under-prediction of the KHCO$_3$ solubility as function of K$_2$CO$_3$, but at the same time it should be noted that this is the only isotherm available for this system and only one author have determine this kind of property. The dataset could easily be extended adding more isotherms in the future. This would guarantee the accuracy of both the modeling and experimental data.

The piperazine modeling is validated in figure 4 to 10. Figure 4 illustrates the vapor pressure over pure PZ. PZ is a crystalline chemical at room temperature and it attracts water, but melts at approximately 111°C. Figure 4 represents the vapor pressure over liquid PZ(l). There is a good representation of the selected data [10,11]. What the figure does not show is that the model was fitted accurately up to even higher temperatures using additional data. Heat capacity data were also used in the modeling of PZ.

**Fig. 1.** Extended UNIQUAC correlation of the CO$_2$ partial pressure in the aqueous K$_2$CO$_3$ system

**Fig. 2.** Extended UNIQUAC correlation of the SLE data of the aqueous K$_2$CO$_3$ system
PZ dissolves easily in water, but bound so tightly that the emitted vapor pressure is very low, as indicated in figure 5(left). There is a good representation of both PZ and water partial pressure as shown in the figure. At this PZ concentration of 2.5 molal, solid is formed below 30 °C. The experimental data are not available in the presence of solid. Here a small selection of the Hilliard data [5] is shown. There is a similar good representation of pressures at other conditions.

The precipitation phenomenon in the aqueous PZ system was recently studied in detail by Fosbøl et al. [12]. Figure 6 summarizes a section of the findings. The modeling of the system is accurate and represents all the possible PZ solid phases in this system. PZ has an interesting behavior. While added to water at 40 °C it will dissolve until approximately 34 wt% where it starts precipitating as PZ·6H2O. Adding more PZ cause a strange phenomenon, PZ will suddenly re-dissolve at 54 wt% and become one
liquid phase. Finally at 63 wt% it solidifies as \( \text{PZ} \cdot \frac{1}{2} \text{H}_2\text{O} \). Above 90 wt% it becomes a mixture of solid \( \text{PZ} \cdot \frac{1}{2} \text{H}_2\text{O} \) and anhydrous PZ(s). It is important to note these intermediate “holes” in the phase diagram does exist and it is known behavior of other chemicals. Aqueous PZ has two eutectic points \( \text{E}_1 \) and \( \text{E}_2 \) plus a peritectic point \( \text{P}_1 \). The diagram shows that PZ is completely solid below -1°C. Note that only 12.4 wt% (1.6 molal) will dissolve at 20°C.

Fig. 5. (left) extended UNIQUAC correlation of PZ pressure from a random dataset of aqueous PZ; (right) The same as left for water partial pressure. Notice the large difference in pressures left/right and the observed scatter in the data.

Fig. 6. SLE diagram of the aqueous PZ system. Precipitation of ice, \( \text{PZ} \cdot 6\text{H}_2\text{O} \), \( \text{PZ} \cdot \frac{1}{2} \text{H}_2\text{O} \), and PZ(s) are shown.
While formulating a highly concentrated piperazine solvent at room conditions, it is important to mix in small amounts of PZ at a time. If more than 1.6 molal is needed, then it is advisable to heat the solution to above 45 °C to prevent precipitation. This way it is possible to mix a solution to 65 wt% (21.6 molal). Further heating will not increase the solubility drastically as seen in the figure.

![Graph showing CO2 loading vs. CO2 partial pressure for different piperazine concentrations and temperatures.](image1)

![Graph showing CO2 loading vs. total pressure for different piperazine concentrations and temperatures.](image2)

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The extended UNIQUAC model is also accurate in the modeling of CO2 VLE phase boundaries in the PZ systems. This is shown in figure 7 and 8 comparing the calculated and experimental pressure of some of the used data sets [5,13,14]. Figure 7 indicates the precision obtained in the CO2-PZ-H2O system, both at low and high temperatures, low and high concentration, and low and high pressure. Figure 8 shows that this is also obtained in the quaternary CO2-PZ-K2CO3-H2O system. The amount of available VLE data in the last system is limited and could be further extended.
The speciation is extremely complex as noted in the presented reaction scheme above. Even though, several experimental studies have examined the nature of the reaction chemistry. Figure 9 gives an example of the accuracy of the speciation compared to the data of Hilliard [5]. During the measurements it is impossible through the NMR technique used to distinguish the groups of chemicals from each other. This is why the sum of $PZ + PZH^+ + PZH_{2}^{2+}$ are one group, and $PZCO^{-} + PZCO_{2}$ are another group. Here a fairly high temperature and concentration is shown. An equally well representation is observed in all the other experimental data.

![Graph 9](image9.png)

Fig. 9. Comparison of the extended UNIQUAC towards speciation data.

Heat of absorption was also used in the extended UNIQUAC fitting process. The comparison towards experimental data is shown for one of the more complex systems in figure 10. It contains both $PZ$ and $PZCO_{2}$.

![Graph 10](image10.png)

Fig. 10. Comparison of the extended UNIQUAC model towards heat of CO$_2$ absorption data.
K$_2$CO$_3$ [5]. It is worthwhile noticing that these data are often scattered and reproduction from one set to another is difficult. The total average relative deviation is 14.7% which is good under these circumstances. This plot shows one of the better representations of the comparison. The evaluation to the newly published data by Liu et al. [15] gives an equally good representation which can be characterized as prediction since they were not used in the fitting of the parameters.

![Graph](image)

Fig. 11. (left and right) Predicted phase behavior of the PZ SLE as function of the CO$_2$ content.

![Graph](image)

Fig. 12. Blue lines, predicted extended UNIQUAC isotherms of phase boundaries for precipitation of PZ as function of PZ and CO$_2$ content. Grey dotted line from left to right indicates loadings of 0.2, 0.4, 0.6, 0.8, and 1.
It can be concluded that the extended UNIQUAC model performs very well for the property calculation in the PZ-CO$_2$-K$_2$CO$_3$-KHCO$_3$-H$_2$O system. It acceptably correlates and predicts thermodynamic properties. An MS Excel® module has been created which allows for easy calculation of equilibrium composition in the very complex chemical system. The model is also implemented in an Aspen Plus® user module similar to Darde et al. [16,17] available to the CERE consortium.

4. Slurry formation and solid precipitation

One of the purposes for this study was to apply the extended UNIQUAC model in a predictive manner. Taking the model and using it in order to forecast what the effect of temperature, CO$_2$ content, and solvent composition has on the stability and solid formation in the PZ-CO$_2$-K$_2$CO$_3$-KHCO$_3$-H$_2$O system.

Figure 11 to 15 outlines the obtained results of predicting the solid-liquid phase boundary. Figure 6 gives an overview of how the trend is in the pure solvent without CO$_2$. While adding CO$_2$ there has been speculations of how the solid-liquid lines would move. Figure 11 suggest a quantitative development of it. Typical loadings in this system are in the order of 0.3 for a lean solvent and 0.9 for a rich solvent. At constant loadings in mol CO$_2$/mol PZ, the figure shows it requires a high loading to secure that solid is not formed. In a PZ solvent of 0 to 10 molal (45 wt%), a lean loading of 0.5 is needed in order to prevent precipitation at room conditions. Cold climate or freezing can not be accepted. It should be noted that the ice line is unaffected by the addition of CO$_2$. While formulating a PZ solvent, loading it by CO$_2$, will help to prevent PZ precipitation. A solvent loaded to 0.3 can be mixed to 3.2 molal PZ at 20 °C and still not form a slurry.

The information presented in figure 12 represents the same as figure 11, but additional conclusions can be made. The lines are now isothermal boundaries instead of constant loadings. The grey dotted lines are constant loadings. For concentrations above the blue lines there will be PZ precipitation. It can be concluded that for temperatures above -5 °C, a loading of 0.6 can be used in order to prevent solid formation. Approximately 0.4 in loading will not result in precipitation at 25 °C. The isotherm at 40 °C deliberately increases abruptly at high PZ concentration above 12.3 molal. PZ·6H$_2$O precipitate until 1.4 molal CO$_2$ in a 12.3 molal PZ solvent where after PZ·1½H$_2$O precipitate at a much higher PZ concentration. This behavior is equivalent to the bulges and holes observed in figure 6 and 11.

![Fig. 13. (Left) Extended UNIQUAC predictions of SLE phase behavior. 1 molal KOH, as function of PZ and CO$_2$ amount; Blue, PZ boundary. Orange, KHCO$_3$ boundary (right) Zoom of left. Green: capture relevant. Dotted line: loading of 0.2, 0.4, 0.6, 0.8, and 1.](image-url)
It becomes complicated on adding potassium to the system. Now KHCO₃ may also precipitate. Figure 13 shows a scheme equivalent to the previous picture. The green area depicts concentrations which could be observed in a CO₂ capture equipment. The left horizontal part are extremely lean solutions, the right leaning part are very rich solutions with a maximum of 1 mol CO₂/(mol PZ + K₂CO₃). Above the blue lines PZ or ice will precipitate to the right of the orange lines KHCO₃ will precipitate. The figure shows that below -5°C only a narrow band exists where a liquid phase can be guaranteed. This is indicated by reddish color. At higher temperatures the band expands and above 40 °C almost only the KHCO₃ remains. Note that the KHCO₃ boundary is less affected by temperature and only moves slightly towards the right. The orange KHCO₃ boundaries stop in the middle of the diagram at approximately 2 to 4 molal PZ. This is consistent with the trend of the KHCO₃ solubility shown in figure 14.

Fig. 15. (Left) Extended UNIQUAC predictions of SLE phase behavior at 7.5 molal KOH as function of PZ and CO₂ amount. Blue, PZ boundary. Orange, KHCO₃ boundary; (right) Zoom of left. Green area: capture relevant. Dotted line: loading of 0.2, 0.4, 0.6, 0.8, and 1.
Figure 14 shows the solubility of KHCO$_3$ in pure water without PZ. At -5°C the solubility is 2 molal. Since figure 13 is plotted for 1 molal KOH, a concentration of 2 molal KHCO$_3$ can not be reached for any CO$_2$ content. This is why KHCO$_3$ does not precipitate at low PZ concentrations. PZ indeed has an influence on the KHCO$_3$ SLE, since it provokes the precipitation of it. This may be related to the speciation scheme where PZ has the tendency to increase the activity/concentration of HCO$_3^-$.

At high potassium concentration the picture is slightly different, see figure 15. Still a narrow band of liquid exists at -5°C, indicated by the reddish area. The potassium concentration is readily high to make the orange KHCO$_3$ boundary continue all the way to the x-axis of zero PZ concentration. There is a high risk of KHCO$_3$ precipitation inside the green area which depict typical CO$_2$ concentrations, even for very small concentration of PZ. At 40 °C which is a typical temperature of a rich solvent in the bottom of the absorber it is unlikely that PZ will precipitate, but KHCO$_3$ will almost definitely precipitate.

For example in these systems an absolute maximum which can be reached is 1 mol CO$_2$ / (mol PZ + mol K$_2$CO$_3$). At a rich loading of 0.75 mol CO$_2$/ (mol PZ + mol K$_2$CO$_3$) in a 1 molal PZ + 3.75 molal K$_2$CO$_3$ solution (7.5 molal KOH + 3.75 molal CO$_2$ from K$_2$CO$_3$), there will be 3.325 molal CO$_2$ + 3.75 molal present from K$_2$CO$_3$. This is a total of 7.08 molal CO$_2$. According to figure 15(right) at 40°C, KHCO$_3$ starts precipitating at 5.75 molal CO$_2$ which correspond to a loading of (5.75-3.75)/(1+3.75)=0.42 mol CO$_2$/ (mol PZ + mol K$_2$CO$_3$). The same conclusion can be reached by using the grey dotted lines. It can be concluded for this simple example that precipitation would have occurred just after a minor loading of the lean solvent. For the 2 molal PZ+ 3.75 molal K$_2$CO$_3$ 40 °C solution, precipitation starts at a loading of 0.49 mol CO$_2$ / (mol PZ + mol K$_2$CO$_3$). Making the same calculation for PZ precipitation at 20°C shows that in a 2 molal PZ + 3.75 molal K$_2$CO$_3$ solution, PZ starts precipitating at 0.15 mol CO$_2$ / (mol PZ + mol K$_2$CO$_3$). Instead of performing the calculations, the grey dotted lines can be used instead.

General conclusions on precipitation: In a pure aqueous PZ solvent, precipitation of highly concentrated solutions can be expected to form solid PZ below a loading of 0.5 at room temperature. In the system containing potassium, precipitation of PZ can be expected to occur at very lean concentrations at low temperature. At 20 °C and 2 molal PZ, it would be approximately 0.15 to 0.2 mol CO$_2$ / (mol PZ+K$_2$CO$_3$) and below. This is independent of potassium concentration. Precipitation of KHCO$_3$ will occur at intermediate loadings and above; and intermediate temperature. This is noteworthy since it will be a typical problem in the bottom of the absorber. It could also be used actively to increase the capacity of the solvent. For the sodium system (Na$^+$), the mentioned problems are expected to be even more profound since NaHCO$_3$ has a lower aqueous solubility compared to KHCO$_3$.

5. Heat requirements

Much has been said qualitatively on the heat requirements. Many have tried to estimate the energy requirements. The experimental data shown previously tells the true, but scatted picture. It may not tell the whole truth since the experimental work is time consuming. Here the extended UNIQUAC model is used in order to predict the heat of absorption, also known as the heat of desorption. The calculation is performed equivalent to the experiment. The energy is obtained by the addition/removal of CO$_2$ from the solution.
The energy consumption in the reboiler is very much linked to the energy it requires to strip CO₂, but also the unfortunate side effect of water evaporation. In this study the energy requirement to desorb CO₂ is in focus.

Figure 16 and 17 shows the prediction of the values correlated in figure 10 of heat of absorption at desorber condition. This value is the negative value of heat of desorption. The left part of figure 16 is based on pure aqueous PZ. There seem to be little effect of changing the concentration from 0.3 to 3 molal. On the other hand the K₂CO₃ content has a large effect as shown in figure 16, right. Heat of desorption range from 20 kJ/mol to 65 kJ/mol in the concentration range 0.5 molal to 6 molal K₂CO₃.

Note the step observed in the 6 molal curve at 0.42 loading due to precipitation of KHCO₃. The curve should be discontinuous since the formation of KHCO₃ is a discrete phenomenon. As solid appears the enthalpy of the system increases by the amount of the solid contribution. The formation is exothermic. In this case it is not beneficial to have KHCO₃ formed since it requires additional energy to re-dissolve. The same can be observed in Figure 17.

It can be concluded that it may be preferred to use a high PZ concentration or a low K₂CO₃ concentration. When mixing PZ and K₂CO₃ creates unexpected conditions. Figure 17 indicates the findings. The left part shows that using a PZ concentration of 1 molal, results in a fairly high energy requirement. On average 60 kJ/mol and in worst case, of high K₂CO₃ concentration, 90 kJ/mol.

Decreasing the PZ concentration is preferred. It should be used as originally intended, as a promoter or activator with a concentration of 0.3 molal. It opens up the opportunity of decreasing the energy requirements for CO₂ stripping by 30 to 40% (from 60 to 40 kJ/mol). The right part of figure 17 shows that using a K₂CO₃ concentration of 3 molal or lower, 40 kJ/mol can be expected for the CO₂ stripping. Notice that a minimum can be reached. Using a low K₂CO₃ concentration of 1 molal results in a lower heat requirement of 30 kJ/mol compared to conditions at 0.5, 3, and 6 molal. While investigating the model it can be determined that a minimum is reached at 1.1 molal K₂CO₃ and 0.3 molal PZ. Of cause this would require an increased amount of pumping and there is a risk of also increasing the water evaporation. Further studying the model, it can be noticed that it is feasible to use 2.5 molal K₂CO₃ at 0.3
molal PZ because the relative change in energy requirement is small compared to the added solvent concentration/capacity.

These results are shown at 120 °C but the results are more or less identical at 100 °C.

There has recently been an ongoing discussion whether a high or a low heat of absorption would be preferred. It can be stated that heat of absorption at 40°C is a property related to the bond energies between CO2 and the solvent. A high heat of absorption would indicate a high bond energy and low heat of absorption, a low bond energy. Likewise, a high bond energy would suggest a high driving force to attract CO2. Therefore it is often stated that a high heat of absorption would be preferred. But, the CO2 has to come off the solvent again. Every time one mole of CO2 will be desorbed, the heat of desorption have to be paid. It can be concluded that the solvent needs to have a temperature tendency which favors these conditions. In conclusion a high heat of absorption and a low heat of desorption are to be preferred.

6. Conclusions

It can be concluded that an accurate electrolytic thermodynamic model has been presented for the PZ-K2CO3-KHCO3-H2O system based on previously published parameters of the extended UNIQUAC model. The study entailed approximately 1200 data points collected from the open literature.

It is used in this study to predict the phase behavior with respect to solid formation and the precipitation of PZ and KHCO3. Guideline for mixing the PZ with potassium solvent is given. Adding CO2 in order to increase PZ solubility is a viable method. Be aware that potassium content may have an opposite effect, decreasing solubility.

![Fig. 17. Extended UNIQUAC prediction of 120°C heat of CO2 desorption from aqueous PZ-K2CO3 (left) high PZ content; (right) low PZ content.](image-url)
In the pure aqueous PZ system it was found that PZ will precipitate at room temperature for high PZ concentrations, especially for lean loadings, below 0.5.

For systems containing potassium, it was found that PZ generally precipitate from lean solutions at low temperature. It was surprisingly found that KHCO₃ will precipitate from capture relevant solutions identical to absorber mid to absorber bottom conditions.

There are indications that KHCO₃ precipitate above a loading of 0.5 mol CO₂ / (mol PZ + K₂CO₃) at 40 °C for the studied solutions. The situation becomes worse, the lower the temperature and the higher the loading is. Detailed figures and examples are given, of how to predict KHCO₃ precipitation.

Finally the thermodynamic model was used in order to predict energy requirements on heat of absorption/stripping of CO₂. It can be concluded that in order to reach a low heat of absorption of approximately 40 kJ/mol, 0.3 molal PZ and up to 2.5 molal K₂CO₃ should be used. This is independent of stripper temperature.

The developed model can be used in a broader perspective to accurately simulate the capture process using PZ. The process can be optimized for thermodynamic properties. Solvent composition is a core variable which can be optimized, benefitting from the knowledge of solid formation.

The model is available to the CERE consortium as a MS Excel® and Aspen Plus® plug in. The CERE consortium members are allowed favorable conditions.

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References


