Modelling of liquid-vapor-solid equilibria in the NH₃-CO₂-H₂O system

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Introduction
A thermodynamic model has been developed to describe CO₂ capture processes from ammonia solutions. MultiScale©¹ was used as a basis for the development of both the model and a new process simulation tool. The model consists of (a) components and equilibrium reactions, including mass balances and electro neutrality, (b) a numerical method to solve all the equilibria, (c) thermodynamic relations describing the pressure, temperature and composition dependencies of the ideal system and (d) phase models that describe the non-ideal behavior of the components and phases. The calculations are based on an extended database with salt solubility data, VLE data and thermal properties of the chemical species.

Components and equilibria
The components and main reactions of the system are given in equations (1)-(9). The respective thermodynamic equilibrium expressions were introduced in the model.

\[ \text{CO}_2(g) = \text{CO}_2(aq) \]  \[ K_{\text{H}^{+}(\text{CO}_2)}^{0} = \frac{a_{\text{CO}_2}}{f_{\text{CO}_2}} \]  \[ \text{CO}_2 + \text{H}_2\text{O} = \text{H}^{+} + \text{HCO}_3^{-} \]  \[ K_{\text{H}^{+}(\text{CO}_3)}^{0} = \frac{a_{\text{H}^{+}}a_{\text{HCO}_3}}{a_{\text{CO}_2}a_{\text{H}_2\text{O}}} \]  \[ \text{NH}_3(g) = \text{NH}_3(aq) \]  \[ K_{\text{H}^{+}(\text{NH}_3)}^{0} = \frac{a_{\text{NH}_3}}{f_{\text{NH}_3}} \]  \[ \text{HCO}_3^{-} = \text{H}^{+} + \text{CO}_3^{2-} \]  \[ K_{\text{H}^{+}(\text{CO}_3^{-})}^{0} = \frac{a_{\text{H}^{+}}a_{\text{CO}_3^{-}}}{a_{\text{HCO}_3}} \]  \[ \text{H}_2\text{O}(g) = \text{H}_2\text{O}(aq) \]  \[ f_{\text{H}_2\text{O}} = a_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^{*} \]  \[ \text{NH}_4^{+} = \text{H}^{+} + \text{NH}_3 \]  \[ K_{\text{NH}_4^{+}(\text{NH}_3)}^{0} = \frac{a_{\text{NH}_4^{+}}}{a_{\text{H}^{+}}a_{\text{NH}_3}} \]  \[ \text{H}_2\text{O} = \text{H}^{+} + \text{OH}^{-} \]  \[ K_{\text{H}^{+}(\text{OH}^{-})}^{0} = \frac{a_{\text{H}^{+}}a_{\text{OH}^{-}}}{a_{\text{H}_2\text{O}}} \]  \[ \text{NH}_4^{+} + \text{HCO}_3^{-} = \text{NH}_4\text{HCO}_3(s) \]  \[ K_{\text{NH}_4^{+}(\text{HCO}_3^{-})}^{0} = \frac{a_{\text{NH}_4^{+}}a_{\text{HCO}_3^{-}}}{a_{\text{NH}_4\text{HCO}_3}} \]  \[ \text{NH}_4^{+} + \text{HCO}_3^{-} = \text{NH}_2\text{COO}^{-} + \text{H}_2\text{O} \]  \[ K_{\text{carbonate}}^{0} = \frac{a_{\text{NH}_4\text{HCO}_3}}{a_{\text{NH}_4^{+}}a_{\text{HCO}_3^{-}}} \]  \[ \text{Phase models} \]
There are three possible phases present in the NH₃-CO₂-H₂O system: gas, liquid and solid. Most of the reactions are taking place at low pressure, conditions under which the gas phase may be treated as ideal gas. The SRK equation of state, given by:

\[ P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \]  \[ K_{\text{carbonate}}^{0} = \frac{a_{\text{NH}_4\text{HCO}_3}}{a_{\text{NH}_4^{+}}a_{\text{HCO}_3^{-}}} \]  \[ \text{was included to describe possible non-ideal behavior of the gas phase in sections where the pressure might be high, such as a regenerator operating under high pressure. The aqueous phase is expected to be far from ideal due to high concentrations of dissolved CO₂ and NH₃. The Pitzer semi-empirical equation for the excess Gibbs energy of aqueous, salt-containing systems was used to describe the non-ideal behavior of the aqueous phase. Simplifications of the system were} \]
adopted, thus the only parameters needed are the binary and ternary interaction parameters $\beta_{ij}^0$ and $\tau_{ijk}$, which are expressed through temperature dependent equations.

**Model testing**
The vapor pressure as a function of CO$_2$ concentration when NH$_3$ concentration is kept constant, at various temperatures is given in Figure 1. The total molality of ammonia is in the range 0.5-15 mole/kg H$_2$O and of CO$_2$ up to 15 mole/kg H$_2$O. Simulations were compared to approximately 500 data from the open literature$^{2,3,4,5,6}$. The thermodynamic model is capable of describing reliably the vapor-liquid in the system in a temperature range from 20 to 100°C up to very concentrated solutions.

![Figure 1: Vapour pressure for CO$_2$-NH$_3$-H$_2$O solutions, as a function of CO$_2$ concentration at different temperatures. Symbols are experimental values of vapour pressure, while lines represent the simulations.](image)

**References**
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