Contents lists available at ScienceDirect



International Journal of Greenhouse Gas Control

journal homepage: www.elsevier.com/locate/ijggc



Understanding the vapour–liquid equilibrium of CO₂ in mixed solutions of potassium carbonate and potassium glycinate



Andrew Lee, Kathryn A. Mumford*, Yue Wu, Nathan Nicholas, Geoff W. Stevens

Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC), Peter Cook Centre for CCS Research, Particulate Fluids Processing Centre, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia

ARTICLE INFO

Article history: Received 29 September 2015 Received in revised form 26 November 2015 Accepted 4 February 2016 Available online 20 February 2016

Keywords: Carbon dioxide capture Potassium carbonate Potassium glycinate Model

1. Introduction

Potassium carbonate exhibits strong potential for widespread implementation in solvent based carbon dioxide (CO₂) capture processes. Numerous reasons exist for this including: extensive industrial knowledge of the system based on widespread use of the Benfield Process in the chemical industries over many years (Mumford et al., 2015), relative low costs (Mumford et al., 2012) and comparatively low environmental impacts compared to amine solutions which are the market leader (Anderson et al., 2014). Currently, application of this technology in the major CO₂ emitting facilities, i.e. the power generation sector, is inhibited by the slow reaction kinetics of the CO₂ absorption process at the prevailing low temperatures (45-65 °C) and pressures (approximately atmospheric), which are the typical conditions of flue gas streams in Pulverised Coal Combustion plants. To address this limitation, many researchers have investigated potential additives that may be used to increase the CO₂ absorption rate, commonly known as promoters. Additives investigated have included: inorganic acids (Smith et al., 2012), alkanolamines (Thee et al., 2012), piperazine (Cullinane and Rochelle, 2006) and amino acids (Shen et al., 2013). Whilst much work has been conducted to identify suitable promoters and quantify their enhancement effect, minimal work has

* Corresponding author. *E-mail address*: mumfordk@unimelb.edu.au (K.A. Mumford).

http://dx.doi.org/10.1016/j.ijggc.2016.02.005 1750-5836/© 2016 Elsevier Ltd. All rights reserved.

ABSTRACT

A thermodynamic model was developed to describe the absorption of CO_2 into a glycine promoted potassium carbonate solution. It was found that the model could effectively predict vapour–liquid equilibrium of CO_2 and solubility of hydrated potassium carbonate and potassium bicarbonate in glycine promoted K_2CO_3 solutions over a range of temperatures. Both simulation and experimental results showed CO_2 partial pressure decreased with the addition of glycine, indicating a good potential to improve CO_2 absorption efficiency in potassium carbonate solution.

© 2016 Elsevier Ltd. All rights reserved.

been conducted to understand other potentially significant effects on the solvent capture system performance. These effects include: changes to physical properties, i.e. density and viscosity and their flow on impact to diffusivity and additionally the vapour–liquid equilibria (VLE) of the system. This work follows the previous analysis of the impact of the addition of the amino acid, potassium glycine to potassium carbonate on the VLE of the solvent system (Lee et al., 2015). This work indicated that the VLE of the system improved with the addition of potassium glycine due to an apparent additional mode of CO₂ sequestration within the solution. It was postulated that this mode was due to formation of stable potassium carbamate. In this work we develop appropriate thermodynamic models that may be used to verify this conclusion.

2. Model development

The reaction mechanism for CO_2 absorbed into potassium carbonate and potassium glycine may be described by the following reaction sequence. Reaction (1) presents the self-ionisation of water, and Reaction (2) shows CO_2 absorbed into aqueous carbonate solutions where it reacts with H_2O to form HCO_3^- and H_3O^+ ions. In Reaction (3), the presence of carbonate within the system acts to buffer the pH changes due to the absorption of CO_2 :

$$2H_2O_{(l)} = H_3O^+_{(aq)} + OH^-_{(aq)}$$
(1)

Nomenclature	
ΔH	heat of reaction, kJ/mol
Κ	equilibrium constant
Patm	atmospheric pressure, Pa
$p_{\rm CO_2}$	partial pressure of CO ₂ , Pa
$p_{\rm H_2O}$	partial pressure of water vapour, Pa
T	temperature, K
Greek la α α _Α γ τ	etters ENRTL binary interaction non-randomness factor loading in terms of CO ₂ absorbed, mol CO ₂ absorbed/mol K ⁺ activity coefficient ENRTL binary interaction energy parameter
Superso ref	cripts reference state

$$CO_{2(aq)} + 2H_2O_{(l)} \Rightarrow H_3O^+_{(aq)} + HCO^-_{3(aq)}$$
 (2)

$$HCO_{3(aa)}^{-} + H_2O_{(l)} \rightleftharpoons H_3O_{(aa)}^{+} + CO_{3(aa)}^{2-}$$
(3)

In aqueous solutions, glycine can be present in three main forms including protonated (Gly⁺), zwitterionic (⁻Gly⁺) and anionic (⁻Gly). As solutions suitable for CO₂ absorption have pH greater than the pK_a of the amino group in glycine (c.a. 9.6 (Izatt et al., 1992)), the concentration of the protonated form (Gly⁺) present is assumed negligible. The protonation of the anionic form of glycine (glycinate) to the zwitterionic form is described using Reaction (4). Aqueous CO₂ can also react with the glycinate (⁻Gly) to form an unstable zwitterion (⁻Gly⁺·COO⁻), which rapidly loses a proton to form a stable carbamate (⁻Gly·COO⁻). This two-step mechanism can be combined into a single overall reaction, which is shown in Reaction (5). This carbamate (⁻Gly·COO⁻) can then undergo hydrolysis to form a bicarbonate ion whilst regenerating the glycinate ion, as shown in Reaction (6):

$${}^{-}\operatorname{Gly}_{(aq)} + \operatorname{H}_{3}\operatorname{O}_{(aq)}^{+} \rightleftharpoons {}^{-}\operatorname{Gly}_{(aq)}^{+} + \operatorname{H}_{2}\operatorname{O}_{(l)}$$

$$\tag{4}$$

$${}^{-}\text{Gly}_{aq} + \text{CO}_{2(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons {}^{-}\text{GlyCOO}_{(aq)}^{-} + \text{H}_3\text{O}_{(aq)}^{+}$$
(5)

$${}^{-}\operatorname{GlyCOO}_{(aq)}^{-} + \operatorname{H}_{2}\operatorname{O}_{(l)} \rightleftharpoons {}^{-}\operatorname{Gly}_{(aq)} + \operatorname{HCO}_{3(aq)}^{-}$$
(6)

Additionally, there is the possibility that potassium salts or solid glycine may be precipitated at higher concentrations (Smith et al., 2013). In this case, the salts considered were hydrated potassium carbonate ($K_2CO_3 \cdot 1.5H_2O$) and potassium bicarbonate (KHCO₃), as shown in Reactions (7) and (8). The multiple salt, potassium sesquicarbonate, and potential precipitates of glycine were not included as they were not observed under the experimental conditions studied:

$$K_2 CO_3 \cdot 1.5 H_2 O_{(s)} \rightleftharpoons 2K_{(aq)}^+ + CO_{3(aq)}^{2-} + 1.5 H_2 O_{(l)}$$
(7)

$$\operatorname{KHCO}_{3(s)} \rightleftharpoons \operatorname{K}_{(aq)}^{+} + \operatorname{HCO}_{3(aq)}^{-} \tag{8}$$

The performance of solvents used for CO₂ capture is generally described in terms of their loading, i.e. moles of CO₂ sequestered in pure unit solvent. Here loading (α_A) is defined as the molar increase in CO₂ content per mole K⁺ from fresh solvent to loaded solution, where CO₂ content is determined via strong acid titration. The definition of loading in this work is illustrated through Eqs. (9) and (10):

$$\alpha_E = \frac{[\text{CO}_2]_{evolved}}{[\text{K}^+]} \tag{9}$$

$$\alpha_{A} = \frac{[\text{CO}_{2}]_{evolved} - [\text{CO}_{3}^{2^{-}}]_{unloaded}}{[\text{K}^{+}]} = \alpha_{E} - \frac{[\text{CO}_{3}^{2^{-}}]_{unloaded}}{[\text{K}^{+}]}$$
(10)

In this work, all the potassium ions K^+ exist in the solution due to potassium carbonate salts and potassium glycinate salts. So the ratio of unloaded carbonate ions over potassium ions can be directly calculated using stoichiometry, which is shown in Eqs. (11) and (12) (Lee et al., 2015):

$$[K^+] = 2 \times [CO_3^{2-}]_{unloaded} + [Glycine]_{total}$$
(11)

$$\frac{[CO_3^{2-}]_{unloaded}}{[K^+]} = \frac{[K^+] - [Glycine]_{total}}{2[K^+]}$$
(12)

Based on Eq. (12), the defined loading (Eq. (10)) can be modified, which is shown in Eq. (13). It should be noted that the range of defined loading α_A is not normalised to be within 0 and 1 (as is commonly used), and the maximum theoretical loading varies between 0.5 (no glycine) to 1 (full glycine).

$$\alpha_A = \alpha_E - \frac{1}{2} \times \left(1 - \frac{[\text{Glycine}]_{total}}{[\text{K}^+]} \right)$$
(13)

3. Thermodynamic modelling

Equilibrium and solubility constants for potassium carbonate, potassium bicarbonate and potassium glycine, K_i , were described by the temperature dependent functions shown in Eq. (14) and the van't Hoff equation (Eq. (15)):

$$\ln K_i = A_i + \frac{B_i}{T} + C_i \ln T + D_i T$$
(14)

$$\ln K_i = -\frac{\Delta H_i}{R} \left(\frac{1}{T} - \frac{1}{T^{\text{ref}}}\right) + \ln K_i^{\text{ref}}$$
(15)

With respect to activity models, aqueous solutions of K₂CO₃ and KHCO₃, have been observed to exhibit noticeable deviations from ideal behaviour (Hilliard, 2005), although similar observations for the glycine system have not been made. Therefore it is necessary to include an activity coefficient model when modelling the vapour–liquid–solid equilibria (VLSE) behaviour of the K₂CO₃ and the KHCO₃ systems with limited requirement for the glycine components.

For this work the electrolyte non-random two-liquid (Chen and Evans, 1986) activity coefficient model with the Redlich-Kwong equation of state (ENRTL-RK) was implemented in Aspen Plus® (Aspen Plus, 2011). A detailed description of the model and its derivation can be found in Chen and Evans (1986). Briefly, the ENRTL model represents activity coefficient for each species, γ_i , as a combination of long range electrostatic interactions and short ranged local interactions between different species. The long range interactions were modelled using the Pitzer-Debye-Hückel equation which has no fitted parameters, whilst the short range interactions were modelled using a number of asymmetric binary interaction energy parameters $(\tau_{i,i})$ and symmetric binary nonrandomness factors ($\alpha_{i,i}$). The temperature dependency of the binary interaction energy parameters for salt-salt and neutral molecule-salt pairs was modelled using Eq. (16), whilst the nonrandomness factor was assumed to be temperature independent:

$$\tau_{ij} = C_{ij} + \frac{D_{ij}}{T} + E_{ij} \left[\frac{T^{\text{ref}} - T}{T} + \ln\left(\frac{T}{T^{\text{ref}}}\right) \right]$$
(16)

The binary interaction parameters for neutral moleculemolecule pairs were modelled using Eqs. (17) and (18):

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + e_{ij} \ln T + f_{ij}T$$
(17)

$$\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15) \tag{18}$$

Download English Version:

https://daneshyari.com/en/article/1742861

Download Persian Version:

https://daneshyari.com/article/1742861

Daneshyari.com