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Effect of piperazine on solubility of carbon dioxide using aqueous diethanolamnie

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ABSTRACT

Experimental results of vapor–liquid equilibrium of this study for CO_2 capture in solutions of activated diethanolamine (DEA) are presented at temperatures ranging from 313.15 to 353.15 K. Piperazine (PZ), which is used as an activator in this study, its concentration ranged from 0.01 to 0.1 M. Total alkalinity of the solution was kept 2 M. The partial pressure of CO_2 varied from 0.01 to 100 kPa. A thermodynamic model is developed to predict the vapor liquid equilibrium of CO_2 in aqueous mixtures of DEA/PZ. For $CO_2 + H_2O$ + DEA + PZ system, the e-NRTL model is used to develop the VLE model, which defines equilibrium behavior of the solution. Model is validated using data generated from this work as well as data available in literature. Results of the current model are in an acceptable degree of agreement with the experimental data of CO_2 solubility of this work as well as of those stated in literature. The species concentration, activity coefficients, pH of the CO_2 loaded solutions, and the model predicts amine volatility. Addition of PZ to DEA, as an activator, has increased the solubility of CO_2 under a specific range of CO_2 partial pressure.

1. Introduction

Importance of removal of acid gases like carbon dioxide (CO_2) and hydrogen sulfide (H2S) using amines cannot be denied [1]. The maturity of amine solvents surrounds monoethanolamine (MEA), methyldiethanolamine (MDEA) and diethanolamine (DEA) for acid gas absorption. MEA solutions are known for their high reactivity with CO_2, low hydrocarbons solubility, low cost and ease in reclamation [2]. Stability of carbamate plays a vital role in CO_2 solubility using amines. Due to the formation of stable carbamates, CO_2 loading for primary and secondary amines is about 0.5 mol of CO_2/mole of amine [3,4]. Tertiary amines, like MDEA has higher CO_2 loading capacity (about 1.0 mol of CO_2/mole of amine) and lower enthalpy of reaction. MDEA is also attractive due to lower regeneration energy. However, the slow rate of reaction of MDEA with CO_2 limits its usage.

Solutions of two or more amines improve the CO_2 absorption rate and may reduce the solvent regeneration energy when blended together because of combined properties of their constituent amines [5]. One of the frequently investigated solvent at present is piperazine. Piperazine is a cyclic diamine, which has fast rate of reaction with CO_2, higher CO_2 capture capacity, and resistance to degradation [6–10].

Literature reports about the effect of addition of PZ on the rate of CO_2 absorption when blended with amines like AMP, MDEA, TIPA, MEA, AEP, DAB etc. [11–15]. However, a limited literature is available in public domain on CO_2 solubility in aqueous mixtures of DEA and PZ. Mondal [16] investigated the solubility of CO_2 in aqueous solutions of PZ and DEA. The molar ratio of PZ ranged from 0.01 to 0.2 in total amine concentration of 1–4 mol/l and CO_2 partial pressure was up to 20.265 kPa. However, Mondal did not take into account the presence of carmabate species in the liquid phase, such as diethanolamine carbamate (DEACOO-), piperazine dicarbamate PZ(COO-)2 and protonated piperazine carbamate (H + PZCOO-). Even though, formation of carbamates species is reported for PZ and DEA in other studies [17–19].

In this work, effect of addition of PZ on solubility of CO_2 using aqueous DEA is investigated. Concentration and temperature of solutions are varied. An additional, CO_2 solubility data is also provided to extend the existing experimental database of the mixture. The data includes not only equilibrium of CO_2 loading, but also corresponds information on the pH of the loaded solvents. In order to estimate the loss of solvent during CO_2 absorption and stripping,

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Nomenclature

D	dielectric constant
d_s	density of mixed solvent (kg/m^3)
e	electron charge (1.60219×10^{-19}) (C)
G^{ex}	excess Gibbs Energy
H_{CO_2}	Henry's coefficient of CO_2 (kPa)
K	equilibrium constant
k	Boltzman constant (1.38065×10^{-23}) (J/K)
M	molarity ($kmol/m^3$)
N_A	Avogadro's number (6.02205×10^{23}) (mol^{-1})
N	number of moles
P_t	total pressure (kPa)
P°	saturation pressure (kPa)
P_{CO_2}	equilibrium CO_2 partial pressure (kPa)
R	gas constant (8.314) (J/mol.K)
r	Born radius (m)
T	Solution temperature (K)
υ_i	partial molar volume (m^3/kmole)
x	mole fraction in liquid phase
y	mole fraction in vapour phase
z_i	charge number of ion i
α_{CO_2}	mole loading, (mole CO_2/mole alkalinity)
γ	activity coefficient
ρ	closest approach parameter
$\varnothing^{\upsilon}$	vapor phase fugacity coefficient

Subscripts and superscripts

∞	infinite dilution
a, $\acute{a}$	anion
c, $\acute{c}$	cation
i,j,k	species index
m	molecule
s	solvent
w	water

the volatilities of amines are undertaken into account. A thermodynamic framework is used to model amine solution VLE with minimal experimental effort to investigate the feasibility of the electrolyte nonrandom two-liquid (e-NRTL) model. The data of CO_2 loading in aqueous solutions is collected over a CO_2 partial pressure of 0.01–100 kPa, at 40–80 °C.

2. Experimental

2.1. Chemicals and sample preparation

Following chemicals (mentioned in Table 1) were used in this study.

Required amounts of both amines were dissolved in degassed and deionized water in a volumetric flask, and water was poured until the required volume was achieved. Amine concentration was verified titrating a fixed amount of amine solution with 1 N HCl. Throughout the investigation, oxygen free nitrogen and high purity CO_2 (99.8%) were used as the reaction gases.

2.2. Apparatus and experimental procedure

The Fig. 1 is the schematic diagram of the experimental setup used for this study. The system has a double-jacketed reactor, stirred cell resistant glass reactor with a volume of 250 ml. A pressure transducer, a thermocouple, a magnetic stirrer, and a pH meter were fitted with the reactor, which were linked to a data acquisition system. A water saturator at a constant temperature using a water bath was connected with the system in order to keep the temperature uniform. The reaction temperature was adjustable by changing the temperature of the bath using the aforementioned setup.

For a typical run, an aliquot sample of 150 ml of the amine solution was put into the reactor for ten minutes at a predefined temperature. Gas mixture of N_2 and CO_2, were mixed in a desired proportion, and were fed into the reactor through a sparger using Brooks mass flow controller. Prior feeding the reaction gas into the reactor, it was passed through a water saturator placed in the water bath. This was to ensure that the reaction gas is saturated and is at the reaction temperature, in order to avoid any change in the concentration of the solution. Change in pH of the solution during reaction was observed. On achieving the equilibrium observed through pH, the flow of the gas was stopped.

The CO_2 loading (moles of CO_2/mole alkalinity), was verified by titration. A 5 ml (V_{sample}), of the loaded amine solution was reacted with excess volumes of 0.5 N $BaCl_2$ and 0.5 N NaOH for 3 h at 70 °C and atmospheric pressure. White, fine crystals of $BaCO_3$ were then formed and were allowed to settle. Later, which were separated from the clear liquid by filtration. In order to remove the traces of NaOH from the crystals, they were washed with distilled water. The crystals in water were then titrated with 1.0 N HCl using a PC controlled metrohm 716 DMS titrino auto titrator. The set method for titration was DET (Dynamic Equivalence point Titration) for the determination of the endpoint. Thus, the key for the determination of concentration of solution was the volume of HCl consumed to neutralize the crystals. Eq. (1) was used to determine CO_2 loading of carbonated solutions.

$$\alpha = \frac{V_{HCl}}{V_{sample}\,2M} \tag{1}$$

Where,

α: CO_2 loading in moles of CO_2 per mole alkalinity
V_{HCl}: Volume of HCl in ml needed to neutralize the basic species
M: Alkalinity of amine solution in moles per liter

Table 1
List of chemicals used in this study.

Chemical	Molecular weight	Purity (%)/Concentration (N)	Supplier
Piperazine flakes	86.14	99%	Across
Diethanolamine	105.14	99.5%	Merck Millipore
sodium hydroxide	40	1.0 N	J.T.Baker® Chemicals
Hydrochloric Acid	37.5	1.0 N	J.T.Baker® Chemicals
Barium chloride dihydrate	208.23	99%	Merck Millipore