CO$_2$ absorption rate in semi-aqueous monoethanolamine

Ye Yuan, Gary T. Rochelle *

McKetta Department of Chemical Engineering, The University of Texas at Austin, 200 E Dean Keeton St., Mail code C0400, Austin, TX 78712, United States

HIGHLIGHTS

- CO$_2$ absorbs faster into MEA/NMP (or CARBITOL™)/water than MEA (aq) or PZ (aq).
- CO$_2$ physical solubility and MEA volatility were measured in CO$_2$-MEA-NMP-water.
- A kinetic model was built in MATLAB® to explain the rate behavior.
- Amine/physical solvent/water is promising for CO$_2$ capture.
- The volatility and viscosity of the solvent may limit its usefulness.

ARTICLE INFO

ABSTRACT

Post-combustion CO$_2$ capture using amine scrubbing is the most promising technology to reduce CO$_2$ emissions from coal- or gas-fired power plants. Increasing CO$_2$ absorption rate (k$_g'$) reduces the absorber capital cost, which is the cost center of the capture plant. By partially replacing water with N-methyl-2-pyrrolidone (NMP) in 7 m (30 wt%) aqueous monoethanolamine (MEA), the CO$_2$ absorption rate (k$_g'$) is significantly enhanced because of lower CO$_2$ loading/higher free MEA at the same CO$_2$ partial pressure (P$_{*CO_2}$), greater CO$_2$ physical solubility, and greater MEA activity. At 40 °C, in the operating range of 100–5000 Pa P$_{*CO_2}$, the average k$_g'$ of 7 m MEA in 3 water/1 NMP, 1 water/3 NMP, and 1 water/19 NMP is 1.1 times, 2 times, and 5 times that of 7 m aqueous MEA, respectively. CO$_2$ physical solubility, solvent viscosity, and MEA activity were measured. A kinetic model was built in MATLAB® to better understand the mass transfer of CO$_2$ into semi-aqueous MEA (MEA-NMP-water). The model suggests that the diffusion and reaction of CO$_2$ into aqueous MEA can be approximated by pseudo-first-order (PFO) behavior and adding NMP causes deviation from PFO by the depletion of MEA at the surface. The semi-aqueous solvent provides an excellent rate of CO$_2$ absorption, but the increased viscosity reduces normalized capacity and the volatility of the physical solvent must be addressed.

© 2018 Published by Elsevier Ltd.

1. Introduction

Amine scrubbing using aqueous ethanolamine was first patented in 1930 for the removal of acid gases (CO$_2$ and H$_2$S) from natural gas (Bottoms, 1930). It is the most mature technology for post-combustion carbon capture that can be quickly deployed (Rochelle, 2009). The CO$_2$ absorption rate (k$_g'$) is the most important parameter that determines the cost of the absorber, which is about 30% of the overall capital cost (CAPEX) as estimated by Frailie (2014). Greater k$_g'$ reduces the amount of packing required for the same CO$_2$ removal.

Physical absorption is another CO$_2$ capture approach to absorb CO$_2$ under high pressure >2 MPa (Ban et al., 2014). Some widely used physical solvents are dimethylethers (Selexol®), methanol (Rectisol®), N-methyl-2-pyrolidone (NMP), and 2-(2-Ethoxyethoxy)ethanol (CARBITOL™), all of which good CO$_2$ physical solubility (IEA GHG, 2008). Water-lean amines or semi-aqueous amines, consisting of amine, water, and physical solvent, are potentially attractive as they combine the advantages of chemical absorption and physical absorption. MEA in methanol-water (Usubharatana and Tontiwachwuthikul, 2009), MEA in glycerol-water (Shamiri et al., 2016), amines in N-functionalized imidazoles (Bara, 2013), N-methyldiethanolamine (MDEA) in methanol-water (Tamajón et al., 2016), and N-ethylmonoethanolamine (EMEA) in N,N-diethylethanolamine (DEEA) with/without water (Chen et al., 2015) are some recently studied semi-aqueous solvents. In addition, a commercial hybrid solvent developed by Shell containing MDEA, PZ, Sulfolane (as physical solvent), and water has been characterized by pilot plant testing (Nikolic et al., 2009). Heldebrant

```
┌─────────────────────────────────────────────────────────────────────────────────────────────────┐
│  Nomenclature                                                                                      │
│                                                                                                    │
│  α        loading (mol CO₂/mol amine)                    P_CO2,in/out  CO₂ partial pressure going  │
│  aᵢ       activity of a component (mol/m³)                             in/out of the WWC (Pa)       │
│  Cᵢ       concentration of a component (mol/m³)           Pᵢ          the initial pressure of the   │
│  D_CO2    diffusivity of CO₂ in the solution (m²/s)                   total pressure apparatus (Pa) │
│  D_MEA    diffusivity of MEA in the solution (m²/s)       P_f         the final pressure of the     │
│  H_CO2    Henry's constant of CO₂ at infinite dilution                total pressure apparatus (Pa) │
│           in water (Pa ∗ m³/mol)                          P_MEA       partial pressure of MEA (Pa)  │
│  H_N2O    Henry's constant of N₂O at infinite dilution    V_M         molar volume of an ideal gas  │
│           in water (Pa ∗ m³/mol)                                      (L/mol)                       │
│  H_MEA    Henry's constant MEA at infinite dilution       V_l         volume of the liquid (ml)     │
│           in water (Pa ∗ m³/mol)                          V_total     volume of the total pressure  │
│  k'_g     liquid film mass transfer coefficient                       apparatus (L)                 │
│           (mol/s ∗ Pa ∗ m²)                               N_CO2       flux of CO₂ in the WWC        │
│  K_G      overall mass transfer coefficient                           (mol/(s ∗ m²))                │
│           (mol/s ∗ Pa ∗ m²)                               Q_liquid/gas liquid/gas flow rate         │
│  k_g      gas film mass transfer coefficient                          (ml/s or l/s)                 │
│           (mol/s ∗ Pa ∗ m²)                               t_c         contacting time in the WWC (s)│
│  k₃       third order rate constant between amine         ρ           density (kg/ m³)              │
│           and CO₂ (m⁶/s ∗ mol²)                           h           height of the annulus in the  │
│  Keq      equilibrium constant                                        WWC (m)                       │
│  m        molality, mole per kg of solvent                d           diameter of the annulus in    │
│           (water + NMP/CARB) (mol/kg solvent)                         the WWC (m)                   │
│  P*_CO2   CO₂ equilibrium partial pressure (Pa)           Sᵢ          sensitivity of k'_g to         │
│                                                                       different parameters          │
│                                                           γᵢ          activity coefficient of a     │
│                                                                       component                     │
│                                                           μ           viscosity (cP)                │
│                                                           ΔC_solν     CO₂ cyclic capacity (mol      │
│                                                                       CO₂/kg total solvent)         │
│                                                           ΔC_μ        CO₂ cyclic capacity           │
│                                                                       normalized by viscosity (mol  │
│                                                                       CO₂/kg total solvent)         │
└─────────────────────────────────────────────────────────────────────────────────────────────────┘
```

Nomenclature

α	loading (mol CO_2/mol amine)
a_i	activity of a component (mol/m³)
C_i	concentration of a component (mol/m³)
D_{CO2}	diffusivity of CO_2 in the solution (m²/s)
D_{MEA}	diffusivity of MEA in the solution (m²/s)
H_{CO2}	Henry's constant of CO_2 at infinite dilution in water (Pa $*$ m³/mol)
H_{N2O}	Henry's constant of N_2O at infinite dilution in water (Pa $*$ m³/mol)
H_{MEA}	Henry's constant MEA at infinite dilution in water (Pa $*$ m³/mol)
k'_g	liquid film mass transfer coefficient (mol/s $*$ Pa $*$ m²)
K_G	overall mass transfer coefficient (mol/s $*$ Pa $*$ m²)
k_g	gas film mass transfer coefficient (mol/s $*$ Pa $*$ m²)
k_3	third order rate constant between amine and CO_2 (m⁶/s $*$ mol²)
Keq	equilibrium constant
m	molality, mole per kg of solvent (water + NMP/CARB) (mol/kg solvent)
P^*_{CO2}	CO_2 equilibrium partial pressure (Pa)
$P_{CO_2,in/out}$	CO_2 partial pressure going in/out of the WWC (Pa)
P_i	the initial pressure of the total pressure apparatus (Pa)
P_f	the final pressure of the total pressure apparatus (Pa)
P_{MEA}	partial pressure of MEA (Pa)
V_M	molar volume of an ideal gas (L/mol)
V_l	volume of the liquid (ml)
V_{total}	volume of the total pressure apparatus (L)
N_{CO2}	flux of CO_2 in the WWC (mol/(s $*$ m²))
$Q_{liquid/gas}$	liquid/gas flow rate (ml/s or l/s)
t_c	contacting time in the WWC (s)
ρ	density (kg/ m³)
h	height of the annulus in the WWC (m)
d	diameter of the annulus in the WWC (m)
S_i	sensitivity of k'_g to different parameters
γ_i	activity coefficient of a component
μ	viscosity (cP)
$\Delta C_{sol\nu}$	CO_2 cyclic capacity (mol CO_2/kg total solvent)
ΔC_μ	CO_2 cyclic capacity normalized by viscosity (mol CO_2/kg total solvent)

et al. (2017) reviewed water-lean solvent and demonstrated that replacing water could increase k'_g, but most organic solvents are much more volatile than MEA and cannot be used in current amine scrubbing designs due to their high volatility.

The rate-increasing mechanism of semi-aqueous amines is not fully understood. Since the system is highly non-ideal, the kinetics should be activity-based rather than concentration-based. Also, as in solution at the interface increases with the organic content and the diffusivity of amine decreases due to higher viscosity, the amine at the interface might be lower than in the bulk liquid. Hence the pseudo-first-order (PFO) approximation may not be accurate for semi-aqueous systems. In addition, adding non-aqueous solvent (except methanol) increases the viscosity, which reduces the heat transfer coefficient of the heat exchanger.

Systematic study of the rate behavior in semi-aqueous amine was done by both experimental and modeling efforts. The effect of viscosity, CO_2 physical solubility (Henry's constant), and amine activity on rate were explored.

NMP was selected as the organic physical solvent in this study for the following properties:

1. Good CO_2 physical solubility (IEA GHG, 2008)
2. Miscibility with water and low viscosity (Tan et al., 2015). which increases the heat transfer coefficient and reducing the heat exchanger size.
3. Low vapor pressure of 31.6 Pa at 20 °C (Aim, 1978), compared to 13 kPa of Methanol (Gibbard and Creek, 1974) and 133 Pa of DEEA (U.S. Department of Transportation, 1990) at 20 °C.
4. Good thermal stability with maximum operating temperature is of 200 °C (Tan et al., 2015).

To demonstrate that NMP is not the only physical solvent that could increase k'_g, the absorption rate in MEA in 2-(2-Ethoxyethoxy) ethanol (CARBITOL™) and water was also measured.

2. Experimental methods

2.1. Materials

The solvent was prepared by mixing chemicals gravimetrically. Initial chemical species are listed in Table 1. Molality (m) was used for the convenience of keeping MEA weight percent (wt.%) to be 30%. 7 m MEA in 3 NMP/1 water means 7 mol MEA is mixed with 750 g NMP and 250 g water, and MEA is exactly 30 wt%. To achieve each loading condition, CO_2 was added by bubbling gaseous CO_2 (99.99%, Matheson Tri-Gas) into the solvent. The CO_2 loading was checked by total inorganic carbon (TIC) analysis, described previously in Freeman et al. (2010).

2.2. Viscosity measurement

Viscosity was measured at 40 °C using a Physica MCR 300 cone-and-plate rheometer. The method was described in detail by Freeman et al. (2010).

2.3. CO₂ solubility and absorption rate by the wetted wall column (WWC)

k'_g and CO_2 solubility (P^*_{CO2}) were measured simultaneously using the WWC. The method is exactly identical to that used by Chen and Rochelle (2011), Li et al. (2013), and Du et al. (2016), and can approximate real packing hydrodynamics to allow direct scale-up.

As shown in Fig. 1, the amine solvent counter-currently contacts N_2/CO_2 on the surface of a stainless rod with known surface area. The solvent rate (Q_{liquid}) was approximately 4 ml/s. The total gas flow rate (Q_{gas}) was 5 standard liters/minute. Liquid and gas were controlled at 40 °C using oil baths. The outlet CO_2 was measured continuously by an infrared CO_2 analyzer (Horiba 2000 series). The inlet CO_2 was measured by bypassing the WWC chamber to the CO_2 analyzer.

The CO_2 flux was obtained using Eq. (1). V_M is the molar volume of an ideal gas at standard condition; A is the total gas-liquid contact area.

$$N_{CO2} = \frac{(P_{CO_2,in} - P_{CO_2,out})}{P_{tot}} \cdot Q_{gas} \cdot \frac{1}{V_M \cdot A} \tag{1}$$

Six measurements with variable inlet P_{CO_2} were made for each CO_2 loading, with three for absorption and three for desorption. The operating time of absorption/desorption was less than 3 min. The CO_2 flux was relatively small compared to the amount of solvent in the system, and NMP volatility was relatively low. The