Reaction kinetics of carbon dioxide and hydroxide in aqueous glycerol

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HIGHLIGHTS

- CO_2 absorption into aqueous glycerol/NaOH was measured in a wetted wall column.
- Glyceroxide reacts with CO_2 7 times faster than hydroxide.
- In concentrated aqueous glycerol, glyceroxide is depleted at the interface.

ARTICLE INFO

ABSTRACT

The reaction kinetics of carbon dioxide and sodium hydroxide (nominally 0.1 N and 0.3 N) in aqueous glycerol were measured in a wetted wall column (WWC) at 20, 30, and 40 °C. Glycerol was added at 0–89 wt% to achieve a liquid viscosity (μ_L) of 0.89–65 cP. Compared to pure aqueous alkaline solution, the absorption rate (k_g') initially increased by 30% and then decreased rapidly by 75% with increasing glycerol. Based on the measured k_g', a model was developed to calculate the overall reaction rate constant (k_{Alk}), which resulted from the competing effects of CO_2/NaOH (k_{OH^-}) and CO_2/glyceroxide ($k_{Glycerol^-}$) reactions. The $k_{Glycerol^-}$ was 6–7 times faster than k_{OH^-}. The non-monotonic trend of k_g' was the combined effect of k_{Alk} increasing and diffusivity (D_{CO_2}) decreasing when glycerol increased. The effect of alkalinity depletion at the gas/liquid interface has been included in the kinetic model. The average depletion for 0.1 N NaOH is 4% for water and 20% for 89 wt% glycerol. Average depletion was less than 3% for 0.3 N NaOH. The addition of 0.05 N sodium carbonate has an insignificant effect on k_g'.

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1. Introduction

Mass transfer in viscous liquids such as electrolyte solutions, crude oil, and ionic liquid is important for many industrial processes. One example is post-combustion CO_2 capture with aqueous amine solutions, which have typical viscosities 5–15 times greater than water (Dugas, 2009). The increased viscosity will impede mass transfer in the absorber and stripper by slowing down the diffusion of CO_2 and loaded amine to the bulk liquid, the diffusion of free amine to the liquid-gas interface, and reducing liquid turbulence on the packing surface. Unlike conventional gas/liquid contactors which are usually limited by gas-film mass transfer, the limiting mechanism of mass transfer in the absorber will usually vary from diffusion with fast reaction to diffusion of reactants and products, requiring k_La; the stripper will also be limited by diffusion, requiring k_La (Rochelle et al., 2001). A good prediction of mass transfer rate in the viscous liquid can help prevent inefficient or insufficient contactor design; however, a literature review

showed that existing k_L (k_La) correlations do not provide satisfactory predictions (Song et al., 2014).

A research plan was proposed to systematically investigate the effect of μ_L on mass transfer for packed columns in a previous paper (Song et al., 2014). Glycerol was chosen as the liquid viscosity enhancer for its complete solubility and Newtonian behavior in water. The CO_2/NaOH/H_2O system has been used to determine the effective mass transfer area (a_e) of packed columns (Tsai et al., 2011; Zakeri et al., 2011; Wang et al., 2013) because of its well-established reaction kinetics (R1) and (R2).

$$CO_2 + OH^- \xrightarrow{k_{OH^-}} HCO_3^- \tag{R1}$$

$$HCO_3^- + OH^- \rightleftharpoons H_2O + CO_3^{2-} \tag{R2}$$

Since R2 is a proton transfer reaction, the rate constant of the forward reaction was estimated to be 6×10^6 m³/mol·s at 20 °C (Eigen, 1963), which is several orders of magnitude greater than R1 in basic solution. As the rate-governing reaction, R1 is practically irreversible with its rate constant described by Eq. (1).

$$r = k_{OH^-}[CO_2][OH^-] \tag{1}$$

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Nomenclature

A	surface area of wetted wall column, 38.52 cm^2		k_L	liquid phase mass transfer coefficient, m/s
c	concentration, mol/L		N	molar flux, mol/m^2·s
D	diffusion coefficient, m^2/s		Q	volumetric liquid flow rate, m^3/s
D^0	infinite dilution diffusivity of ion in water, m^2/s		R	gas constant, 8.314 J/K·mol
D_{ij}^0	infinite dilution diffusivity for component i present in trace amount in component j, m^2/s		r	chemical reaction rate, mol/L·s
			T	temperature, K
d	hydraulic diameter of WWC reaction camber, 0.44 cm		t	defined in Eq. (22)
E	reaction activation energy, kJ/mol		u	liquid velocity, m/s
E_∞	enhancement factor for instantaneous reactions		u_s	liquid velocity at the surface of the liquid, m/s
F	Faraday's constant, 96,500 C/mol		W	wetted wall column circumference, 3.96 cm
g	gravitational acceleration, 9.81 m/s^2		z	ion charge number
H	Henry's constant, atm·L/mol		δ	thickness of the liquid film flowing down the wetted-wall column, m
h	wetted wall column height, 0.091 m			
k	reaction rate constant, L/mol·s		μ	viscosity, cP
K	defined in Eqs. (23) and (24)		ρ	density, kg/m^3
$K_{b,Glycerol}$	equilibrium constant of R3, mol/L		Ha	Hatta number, defined in Eq. (28)
K_G	overall mass transfer coefficient expressed in gas unit, mol/m^2·Pa·s		Sc	Schmidt number, $\mu/\rho D$
			Sh	Sherwood number, kd/D
k_G	gas phase mass transfer coefficient, mol/m^2·Pa·s		Re	Reynolds number, $u\rho d/\mu$
k_g'	liquid phase mass transfer coefficient with chemical reactions expressed in gas unit, mol/m^2·Pa·s			

The value of k_{OH^-} has been extensively studied (Faurholt, 1924; Pinsent et al., 1956; Nijsing et al., 1959; Pohorecki and Moniuk, 1988; Kucka et al., 2002). A thorough review of k_{OH^-} is given by Haubrock et al. (2005).

CO_2 reacts with metal alkoxide faster than with hydroxide in an aqueous environment. Faurholt (1927a) investigated competing reactions with a limited amount of CO_2 between hydroxide and methoxide. The rates of the reactions were demonstrated by the relative ratio of the end products carbonate and methylcarbonate, which were determined by adding barium chloride. Heston et al. (1943) extended Faurholt's measurement to greater methanol concentrations. Metal alkoxide was also shown to enhance CO_2 absorption in a metal-organic framework (Stergiannakos et al., 2015) and organic solutions (Darensbourg et al., 1987; Tsuda and Saegusa, 1972). Though few direct data were found in literature of the reaction rate between CO_2 and glyceroxide, Fairbourne et al. (1930, 1931) did prove the formation of glyceroxide in the strong basic environment.

Since the addition of glycerol to the system CO_2/NaOH/H_2O may affect the kinetics because glyceroxide will be formed, it is necessary to investigate the absorption rate of CO_2 into the alcoholic alkaline solution prior to any a_e measurement in the pilot-scale packed column (Tsai et al., 2011; Wang, 2015).

In this work, a model of reaction kinetics for CO_2/NaOH/H_2O-glycerol was built based on experimental k_g' obtained from the bench-scale wetted wall column (WWC).

2. Experimental methods

Fig. 1 shows the wetted wall column (WWC) (Dugas, 2009; Chen, 2011; Li, 2015) used to measure k_g' for CO_2/NaOH/H_2O-glycerol. White et al. (1977) used this WWC to measure k_g' for CO_2/NaOH/H_2O. Inside the 2.54 cm O.D. glass tube reaction chamber was a stainless-steel tube of 1.26 cm O.D. and 9.1 cm height. Liquid was pumped by a Cole-Parmer Micropump from a 1000 cm^3 stainless steel solvent tank to the top of the tube and
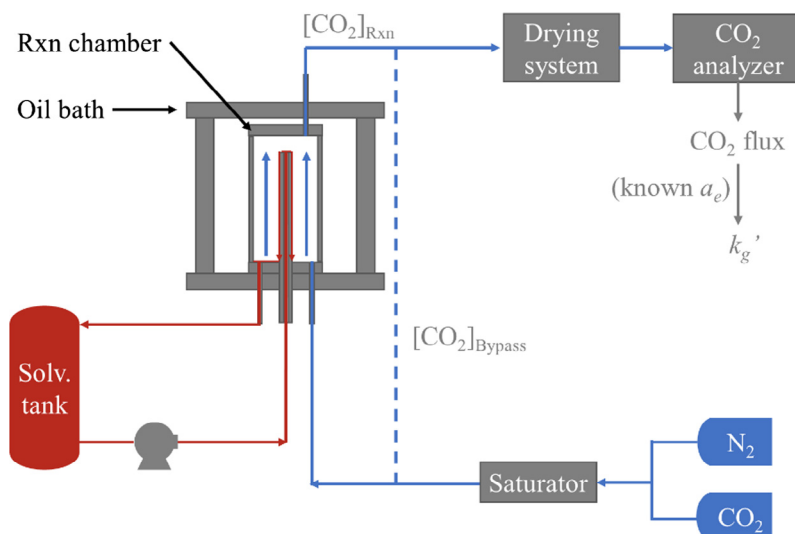

Fig. 1. Wetted wall column (WWC).