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Kinetics of the reaction of carbon dioxide with aqueous sodium and potassium carbonate solutions

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ABSTRACT

Kinetics for CO_2 absorption into 5–30 wt-% sodium carbonate solutions and 5–50 wt-% potassium carbonate solutions up to 70 °C were studied in a string of discs apparatus under conditions, in which the reaction of CO_2 could be assumed pseudo-first-order. The experimental data were evaluated based on the use of activities in the reaction rate expressions. The second order kinetic constant for the CO_2 reaction $CO_2+OH^- \leftrightarrow HCO_3^-$ at infinite dilution is discussed and an expression for it is obtained up to 70 °C.

The difference between the activity and concentration based kinetic constants were found to be small at low concentrations, where the apparent Henry's law constant is close to that at infinite dilution in water. However, at high concentrations (high apparent Henry's law constants), the difference was bigger. Using the activity based approach, the second order kinetic constant was calculated, compared to the second order kinetic constant in infinite dilution and found to be independent of both carbonate concentration and the cation present in the solution.

1. Introduction

When CO_2 is absorbed into aqueous carbonate solutions, the overall reaction can be written as

$$CO_2 + CO_3^{2-} + H_2O \leftrightarrow 2HCO_3^- \quad (1)$$

This is normally divided into the following two reactions

$$CO_2 + OH^- \leftrightarrow HCO_3^- \quad (2)$$

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \quad (3)$$

Hydration of CO_2, Eq. (2), is second order, i.e. first order with respect to both CO_2 and OH− ions. Reaction Eq. (2) is rate determining, since reaction Eq. (3) is a proton transfer reaction, and has a very much higher rate constant than reaction Eq. (2) (Hikita et al., 1976).

The reaction rate constant for reaction Eq. (2) has previously been published based on concentrations (Kucka et al., 2002; Pohorecki and Moniuk, 1988; Pinsent et al., 1956)

$$r = k_{OH^-}[OH^-][CO_2] \quad (4)$$

For electrolyte solutions, the kinetic constant is typically expressed as a function of ionic strength (Astarita et al., 1983)

$$\log k_{OH^-} = \log k_{OH^-\ \mathrm{inf}} + bI \quad (5)$$

In Eq. (5), $k_{OH^-\ \mathrm{inf}}$ is the infinite dilution reaction rate constant, I the ionic strength, and b is a solution dependent constant. In Pohorecki and Moniuk (1988), concentrations instead of ionic strength were used. The infinite dilution kinetic constant in equation

$$k_{OH^-\ \mathrm{inf}} = A\exp(E_A/RT) \quad (6)$$

where A is a pre-exponential factor and E_A is the reaction activation energy.

Since both OH^- and CO_2 concentrations have a direct effect on the reaction rate kinetics, correct modeling/measurement of them is important. The concentration of CO_2 at the interface is normally found via solubility models as the Schumpe (1993) model or earlier versions of it, like the models of Danckwerts (1970) or Van Krevelen and Hoftijzer (1948).

When sodium/potassium carbonate solutions are used, the concentration, or activity if an activity based model is used, of OH^- must be modeled because of the low concentrations of OH^- compared to CO_3^{2-} in the solution (Benedetti-Pichler et al., 1939; Kloosterman et al., 1987; Savage et al., 1980). The used model should of course be consistent with the Henry's law constants used to calculate the free liquid phase CO_2 concentrations.

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When using concentration based kinetic expressions, the kinetic constants are not real constants at a given temperature, but will depend on the concentration level of the ions in solution (see Eq. (5)) as well as on the type of ions (Pinsent et al., 1956; Pohorecki Moniuk, 1988). In an activity based kinetic expression like

$$r = k^{\gamma}_{OH^-}[OH^-]_{\gamma}[CO_2]_{\gamma}\gamma_{CO_2}\gamma_{OH^-} \tag{7}$$

the kinetic constant, $k^{\gamma}_{OH^-}$, should be independent of the concentration level of ions in solution and only be an Arrhenius type temperature function. The activities of the reactants should take care of the possible changes in reaction rate with composition.

2. Previous work

Pinsent et al. (1956) measured the reaction rate constant of Eq. (4) in the temperature range 0–40 °C. The experiments were based on absorption of CO_2 in sodium and potassium hydroxide solutions. They concluded that the kind of cation present in the solution had an influence on the rate constant of reaction (2). The kinetic constant at infinite dilution was also presented. Savage et al. (1980) measured CO_2 absorption and desorption rates in 25 wt-% potassium carbonate solutions. Using the film theory, they developed a correlation to calculate the kinetic constant of reaction Eq. (2), as expressed by Eq. (4) up to 110 °C.

Pohorecki and Kusharski (1991) studied desorption of potassium carbonate with a wetted wall column. They developed a correlation to describe the desorption rates for loaded potassium carbonate systems.

Pohorecki and Moniuk (1988) measured absorption rates to calculate the reaction rate constants for reaction Eq. (2) in different electrolytes up to 41 °C. The OH^- concentrations were determined using the Warder and Winkler (Benedetti-Pichler et al., 1939) methods and Henry's law constants were calculated with the model of Danckwerts (1970)

$$\log\frac{H^{app}_{CO_2}}{H^{\infty}_{CO_2}} = -\Sigma I_i h_i \tag{8}$$

$$h_i = h_+ + h_- + h_{gas} \tag{9}$$

where $H^{app}_{CO_2}$ is an apparent Henry's law constant for CO_2 in the electrolyte solution and $H^{\infty}_{CO_2}$ is Henry's law constant for CO_2 in water at infinite dilution. The h_+, h_- and h_g are contributions of cations, anions, and the gas, respectively.

A general correlation between the reaction rate constant for reaction Eq. (2) and the ionic strength and type of anion and cation in the aqueous electrolyte solutions was presented. The kinetic constant for infinite dilution was given as

$$\log k^{\infty}_{OH^-} = 11.895 - 2382/T \tag{10}$$

Himmelblau and Babb (1958, 1959) measured the kinetic constant for reaction Eq. (2), using sodium carbonate–bicarbonate buffers at temperatures 0–20 °C with a radioactive tracer technique. The system was operated at chemical equilibrium, but at isotopic non-equilibrium. Under controlled conditions, tracer in the form of $NaH^{14}CO_3$ was injected into the closed reaction vessel containing sodium carbonate–bicarbonate buffer solution. By taking samples from the vessel at periodic intervals the rate of reaction Eq. (2) could be followed by analyses of the percentage of tracer in the solution in the form of $C^{14}O_2$. They calculated the kinetic constant for reaction Eq. (2) based on the activity. The rate constants of Himmelblau and Babb (1958, 1959) are approximately 50 times higher than any other data available.

In the paper of Kucka et al. (2002), the kinetics of sodium and potassium hydroxide solutions were studied in a stirred cell at temperatures of 20–50 °C. In the paper, the kinetic constant of an infinite solution for reaction Eq. (2), as expressed by Eq. (4), was obtained as

$$k_{OH^-\ \mathrm{inf}} = 3.2789\times10^{13}\exp(-54{,}971/RT) \tag{11}$$

The results agree well with the model of Pohorecki and Moniuk (1988).

In a recent paper, Haubrock et al. (2007) studied the applicability of using activities in the kinetic expressions. In the paper, the kinetics of the reaction between CO_2 and sodium hydroxide with different additives were studied at 25 °C in a stirred cell reactor. The kinetic constants were first calculated based on experimental concentrations of OH^- and CO_2. The CO_2 concentrations were determined from Henry's law constant based on the model of Schumpe (1993). Then the concentration based kinetic constants were transferred to activity based kinetic constants. The activities were modeled using the Pitzer model (Pitzer, 1973). The model was only partly validated with experimental data, and the consistency with the Henry's law constant was not considered.

3. Experimental apparatus

The kinetic measurements with sodium and potassium carbonate solutions were in this work done in a string of discs apparatus, as shown in Fig. 1. A more detailed description of the apparatus can be found in Ma'mun et al. (2007) and Hartono et al. (2009). The string of discs contactor was operated in a counter current mode with the liquid entering at the top. The liquid is removed at the bottom through a small tube formed as a funnel. The gas enters from the bottom with long enough distance from the first disc to establish the gas flow pattern. The liquid and gas flows were independently adjusted with a liquid pump and gas blower.

The concentration of CO_2 in the gas entering the system was controlled by using Bronkhorst Hi-Tec mass flow controllers and the concentration of CO_2 in the circulating gas, and thereby in the constant pressure bleed, was monitored by an IR Rosemount Binos 100 online CO_2 analyzer. The set-up was equipped with K-type thermocouples at the inlet and outlet of both the gas and liquid phases.

Absorption rates of CO_2 into sodium carbonate solutions from 5 to 30 wt-% and potassium carbonate solutions from 5 to 50 wt-% were measured at temperatures from 25 to 70 °C. The solutions were prepared by mixing potassium carbonate (> 98% pure from VWR) and sodium carbonate (> 99.9% pure from VWR) with deionized water. The CO_2 analyzers were calibrated once a day by using calibrated mass flow controllers (Bronkhorst Hi-Tec) for CO_2 and N_2 with at least 4–5 different concentrations covering the whole range of interest. CO_2 (99.9992 % pure by mole), N_2 (99.999% pure by mole) were supplied by AGA Gas GmbH.

An unloaded sodium or potassium carbonate solution was passed through the column with a flow rate of ~51 mL/min. For every concentration and temperature, it was confirmed that this flow rate was high enough, so that the absorption flux was independent of the liquid flow rate. The same procedure was used as in Hartono et al. (2009). After the column reached the desired temperature level, a known mixture of CO_2 and N_2 was fed into the column. When the temperatures and CO_2-analyzer showed constant values for 10–25 min, the process was deemed to be in steady state and all the data were collected in the computer, using Field Point and LabVIEW data acquisition systems. Average values