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Kinetics of reactive absorption of CO_2 using aqueous blend of potassium carbonate, ethylaminoethanol, and N-methyl-2-Pyrollidone (APCEN solvent)

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ABSTRACT

Employing the fall in the CO_2 pressure method, the kinetics of the reactive absorption of CO_2 in the aqueous blend of potassium carbonate, ethylaminoethanol, and N-methyl-2-Pyrollidone (APCEN solvent) is inspected by altering the amine concentration and the absorption temperature. The rate of the absorption of CO_2 and the solubility/diffusivity of CO_2 in the APCEN solvent is ascertained by using a stirred cell reactor. Based on the obtained experimental findings, the order of the absorption for CO_2 in the APCEN solvent is estimated and understood to be of overall second order (1st order with respect to both EAE and CO_2, respectively). The rate of the absorption of CO_2 in the APCEN solvent is observed to be noticeably higher than the APCE solvent (aqueous potassium carbonate promoted by ethylaminoethanol) and numerous other secondary amines. For instance, at 303 K (with EAE concentration equal to 1.5 kmol m^{-3}), the rate of the absorption of CO_2 in the APCEN solvent is 18.8% higher than the APCE solvent. By studying the effect of the absorption temperature, the activation energy for the APCEN solvent is determined and viewed to be equivalent to the APCE solvent. Furthermore, the lumped parameter in case of the APCEN solvent is higher (1.41×10^{-6} $kmol^{1/2}$ $m^{-1/2}$ s^{-1} kPa^{-1}) as compared to the APCE solvent (1.2×10^{-6} $kmol^{1/2}$ $m^{-1/2}$ s^{-1} kPa^{-1}). In total, the rate of absorption of CO_2 in the APCEN solvent is considerably higher than that of the APCE solvent, and other secondary amines such as methylmonoethanolamine (MMEA), propylmonoethanolamine (PMEA), and butylmonoethanolamine (BMEA).

Abbreviations

EAE	Ethylaminoethanol
K_2CO_3	potassium carbonate
MEA	monoethanolamine
NMP	N-methyl-2-pyrolidone
N_2O	nitrous oxide

1. Introduction

1.1. Background

CO_2 is believed to be one of the most harmful greenhouse gases and its capture from industrial off-gases by using solvent-based absorption technique and adsorption using porous materials is very common [1–3]. Some amine-based chemical solvents and their derivatives have been exploited for the reactive absorption of CO_2 [4–14]. In addition to the amine-based solvents, aqueous potassium carbonate (K_2CO_3) is also considered in the industry for CO_2 capture due to the numerous advantages such as high CO_2 solubility, depleted toxicity and loss of solvent, insignificant solvent degradation, the minimal heat of absorption, and negligible formation of heat stable salts.

Even though the aqueous K_2CO_3 solution is advantageous for CO_2 capture, researchers are working comprehensively towards improving the rate of reaction of K_2CO_3 with CO_2 and the liquid side mass transfer. In this regard, monoethanolamine (MEA) [15–18], diethanolamine (DEA) [19,20], methyl diethanolamine (MDEA) [16], ethylaminoethanol [21], piperazine [4,22,23], boric acid [24,25], arginine [26], glycine [27], and others are expended as promoters for the aqueous K_2CO_3 solution. Various experimental set-ups are exercised to experiment the kinetics of absorption of CO_2 in promoted aqueous K_2CO_3 solution, which includes a stirred cell reactor, a rapid mixing approach, a stopped-flow technique, a bubble column reactor, and a wetted wall column.

In our recent investigation [28], we have inspected the kinetics of the absorption of CO_2 in ethylaminoethanol (EAE) promoted aqueous K_2CO_3 (APCE) solvent. The obtained results indicate that

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Nomenclature

(CO_2)	interfacial concentration of CO_2 (kmol m^{-3})
D_{CO_2}	diffusivity of CO_2 in liquid (m^2 s^{-1})
E_i	enhancement factor for an instantaneous chemical reaction
E_A	activation energy (kJ mol^{-1})
EAE	concentration of EAE (kmol m^{-3})
EAE_0	initial concentration of EAE (kmol m^{-3})
H_{CO_2}	Henry's law constant (for CO_2) (kmol m^{-3} kPa^{-1})
H_a	Hatta number
k_2	rate constant for the CO_2 – APCE solvent system (m^3 $kmol^{-1}$ s^{-1})
k_3	rate constant for the CO_2 – APCEN solvent system (m^3 $kmol^{-1}$ s^{-1})
k_{EAE}	rate constant for the reaction of CO_2 with aqueous EAE (m^3 $kmol^{-1}$ s^{-1})
k_{NMP}	rate constant for the reaction of CO_2 with aqueous NMP (m^3 $kmol^{-1}$ s^{-1})
k_L	liquid-side mass transfer coefficient (m s^{-1})
k_{OH^-}	protonation constant for OH^-
(OH^-)	hydroxyl ion concentration (kmol s^{-1})
n	order of the reaction with respect to EAE
P_{CO_2}	partial pressure of CO_2 in bulk gas phase (kPa)
R_{CO_2}	specific rate of absorption of CO_2 (kmol m^{-2} s^{-1})
T	temperature (K)
t	time (s)

the rate of absorption of CO_2 in the APCE solvent is higher than the MEA-promoted aqueous K_2CO_3 solvent. Additionally, the activation energy for the reaction of CO_2 with APCE solvent is also estimated experimentally and observed to be 81.7 kJ/mol.

In this paper, we have focused on improving the CO_2 absorption capacity of APCE by adding N-methyl-2-pyrolidone (NMP) as an activator (forming APCEN solvent). NMP is cheaply available and utilized in refinery industry (Purisol process). Also, NMP is also used in the past as the physical solvent for improving the absorption capacity of aqueous amines [29]. In this investigation, the kinetics of the absorption of CO_2 in the aqueous potassium carbonate (20%) promoted by EAE and NMP is explored and compared with APCE and multiple secondary amines. The rate of the absorption of CO_2 and kinetic rate constants for the APCEN solvent are determined using the stirred cell reactor. Furthermore, the effect of reaction temperature on the activation energy associated with the reactive absorption of CO_2 in the APCEN solvent is also estimated.

1.2. Kinetic measurements

The kinetic equations associated to, a) CO_2-aqueous K_2CO_3 and b) CO_2-aqueous EAE absorption systems are already explained in our previous studies [28,29]. In case of the CO_2-APCE absorption system [28], the CO_2-EAE reaction runs parallel with the reaction of CO_2 with K_2CO_3. Likewise, the overall reaction in case of the CO_2-APCEN absorption system is considered as the reaction of CO_2 with EAE in parallel with CO_2-K_2CO_3 and CO_2–NMP reactions. Therefore, the kinetic measurement equations related to the CO_2-APCE and CO_2-APCEN absorption systems can be elucidated as follows:

CO_2-APCE absorption system:

$$R_{CO_2} = (CO_2)\sqrt{D_{CO_2}[k_{EAE}(EAE) + k_{OH^-}(OH^-)]} \quad (1)$$

$$R_{CO_2} = (CO_2)\sqrt{D_{CO_2}[k_2(EAE)]} \quad (2)$$

where,

$$k_2 = k_{EAE} + \frac{k_{OH^-}(OH^-)}{(EAE)} \quad (3)$$

CO_2-APCEN absorption system:

$$R_{CO_2} = (CO_2)\sqrt{D_{CO_2}[k_{EAE}(EAE) + k_{OH^-}(OH^-) + k_{NMP}(NMP)]} \quad (4)$$

$$R_{CO_2} = (CO_2)\sqrt{D_{CO_2}[k_3(EAE)]} \quad (5)$$

where,

$$k_3 = k_{EAE} + \frac{k_{OH^-}(OH^-)}{(EAE)} + \frac{k_{NMP}(NMP)}{(EAE)} \quad (6)$$

As explained earlier [28], the rate of the absorption of CO_2 in the APCE and APCEN solvents can be stated as:

$$R_{CO_2} = (CO_2)\sqrt{D_{CO_2}k_2(EAE)_o^n} \quad \text{(APCE solvent)} \quad (7)$$

$$R_{CO_2} = (CO_2)\sqrt{D_{CO_2}k_3(EAE)_o^n} \quad \text{(APCEN solvent)} \quad (8)$$

Eqs. (7) and (8) can be re-stated as:

$$\log\left\{\frac{R_{CO_2}}{(CO_2)(D_{CO_2})^{1/2}}\right\} = \left\{\frac{1}{2}\log(k_2)\right\} + \left\{\frac{n}{2}\log(EAE)_o\right\} \quad \text{(APCE solvent)} \quad (9)$$

$$\log\left\{\frac{R_{CO_2}}{(CO_2)(D_{CO_2})^{1/2}}\right\} = \left\{\frac{1}{2}\log(k_3)\right\} + \left\{\frac{n}{2}\log(EAE)_o\right\} \quad \text{(APCEN solvent)} \quad (10)$$

By using Eqs. (9) and (10), the order of the CO_2 absorption reaction (concerning EAE concentration) and kinetic rate constants for both CO_2-APCE and CO_2-APCEN absorption systems are estimated. The expressions for Hatta number (H_a), enhancement factor (E_i) and the essential circumstance for the satisfaction of the fast reaction regime are acquired from previous investigations [30,31].

2. Experimental

2.1. Materials

Ethylaminoethanol (99% purity), anhydrous K_2CO_3, and N-methyl-2-pyrolidone (98% purity) used in this study were purchased from Merck Co. and S. D. Fine Chemicals. The gas cylinders containing CO_2, N_2O, and N_2 individually (~99.5% purity) are procured from Inox Air Products Ltd. By using distilled water, the aqueous solvents of EAE, NMP, and K_2CO_3 are prepared.

2.2. Determination of absorption rate

The experiments allied with the study of the kinetics of the reaction for both CO_2-APCE and CO_2-APCEN absorption system are performed using a stirred cell reactor [28,29] as shown in Fig. 1 and by employing the fall in CO_2 pressure technique. The details of the experimental set-up are as follows: diameter = 97 mm, height = 187 mm, design pressure = 202.6 kPa, volume of the reactor = 1450 ml, and the interfacial surface area = 7.4×10^{-3} m^2.

The experimental set-up is first tested by performing the CO_2 – aqueous MEA kinetic experiments and the obtained results are compared with the previous studies to verify the experimental method. The kinetic rate constants for the CO_2 – aqueous MEA absorption system studied by us are matching very well with the data reported by Hikita et al. [32] and Versteeg and van Swaaij

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