

CO₂ absorption by borate-promoted carbonate solution: Promotion mechanism and vapor liquid equilibrium



Shufeng Shen^{a,b,*}, Yanan Yang^a, Shaofeng Ren^a

^a School of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang 050018, China

^b Hebei Research Center of Pharmaceutical and Chemical Engineering, Shijiazhuang 050018, China

ARTICLE INFO

Article history:

Received 9 August 2013

Received in revised form 4 January 2014

Accepted 23 January 2014

Available online 31 January 2014

Keywords:

Carbon dioxide absorption

Potassium carbonate (K₂CO₃)

Boric acid

Vapor–liquid equilibrium

Borate

ABSTRACT

Carbonate-based solvents have advantages over amines for capturing CO₂ from fossil fuel-fired power stations. However, due to slow reaction kinetics, boric acid has been proposed as rate promoter in carbonate-based solvents for reducing CO₂ emission. In this work, borate promotion mechanism has been validated and vapor liquid equilibrium for 35 wt% carbonate solutions with 1 wt%, 3 wt% boric acid was investigated at 323 K, 333 K and 343 K. Based on complexation reaction with mannitol, results show that the tetrahydroxy borate ion, B(OH)₄[−], is considered as a reactive specie toward carbon dioxide absorption. Effect of boric acid and temperature on equilibrium CO₂ partial pressures was discussed in the investigated CO₂ loading range.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

It is widely accepted that post-combustion carbon capture, storage and utilization (CCSU) is one of promising routes to reduce carbon dioxide (CO₂) emissions from fossil-fired power generation in the near-term. The development of solvent absorption processes remains a key step toward the large-scale implementation of CO₂ capture technology [1,2]. Absorption happens by contacting solvent to gases in an absorber column to capture CO₂. Then the CO₂-rich absorbent is fed to a high temperature regenerator to strip out CO₂ by energy input for storage or utilization, and the lean solvent is sent back to the absorber for reuse [3].

The chemical absorption of CO₂ into potassium carbonate (K₂CO₃)–bicarbonate (KHCO₃) solutions is a widely known process in the 1950s and has seen renewed attention in recent years due to its advantages over amine-based solvents such as low absorption heat, low cost, no thermal and oxidative degradation, without the formation of heat-stable salts [2–10]. However, a key limitation

associated with using K₂CO₃ is the slow reaction rate of absorption. Main reactions can be described as follows [2,7–10]:



Rate promoters have been intensively studied to improve the reaction rate with CO₂. Additives, such as arsenites [4,11,12], piperazine and amine derivatives [5–7,13], boric acid (B(OH)₃) [8,9,14–17], carbonic anhydrase [18,19] and amino acids [10,20–27], have been proved to enhance greatly the absorption rate in carbonate solutions. Of these, B(OH)₃ is relatively benign, tolerant to oxidative and thermal conditions, and does not have unexpected reaction with other minor components in flue gas mixtures [8,9,15,17]. Boric acid also behaves as a Lewis acid and can convert to borate ion, B(OH)₄[−], in the alkaline solutions. The extent of conversion is difficult to ascertain due to the rapid formation of polyborates. Therefore, promotion mechanism involved is not well understood and active form of boron species is uncertain as well. In recent literature, it has been preliminary reported that B(OH)₄[−] is considered as an active boron specie using a stopped flow pH indicator technique [16]. Thymol blue and 4-nitrophenol indicators were used, which were monitored the UV/visible absorbance. The authors have proposed the borate-catalyzed hydration of CO₂ via

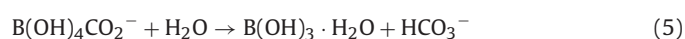
* Corresponding author at: School of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang 050018, China. Tel.: +86 311 88632183; fax: +86 311 88632183.

E-mail addresses: shufengshen@gmail.com, sfshen@hebust.edu.cn (S. Shen).

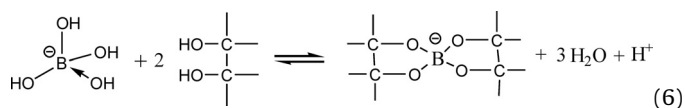
Table 1
Description of chemical samples used in this study.

Chemical name	Source	Purity (mass fraction)	Purification method
Boric acid	Tianjin Yongda reagent	≥99.5%	None
K ₂ CO ₃ (anhydrous)	Tianjin Yongda reagent	≥99.0%	None
KHCO ₃	Tianjin Hongyan Chemical Reagent Factory	≥99.5%	None
D-Mannitol	Tianjin Yongda reagent	≥99.5%	None
CO ₂	Shijiazhuang Xisanjiao oxygen generation station	99.995% (v/v)	None
N ₂	Shijiazhuang Xisanjiao oxygen generation station	99.99% (v/v)	None
Water			Distilled

the carbonic anhydrase mechanism, expressed using the following equations:



However, the potential mechanism that B(OH)₄⁻ undergoes direct reaction and chemically binds with CO₂ needs to be further validated. In the field of boron chemistry, it is believed that tetrahedral borate ions can react with diols or polyols (e.g. mannitol, sorbitol) to form stable borate complexes in a substantially alkaline solution [28–34].



In this work, rates of CO₂ absorption were investigated in unpromoted/promoted carbonate solvents. Upon adding mannitol (a kind of polyols), it is expected that a stable borate complex, *bis* (D-mannitol) 3,4:3'4'-borate form, which is confirmed on the basis of ¹¹B and ¹³C NMR measurements [28,29,31]. The formation of borate esters will result in decreasing active borate ion concentration in the absorbents. Therefore, CO₂ absorption rate is expected

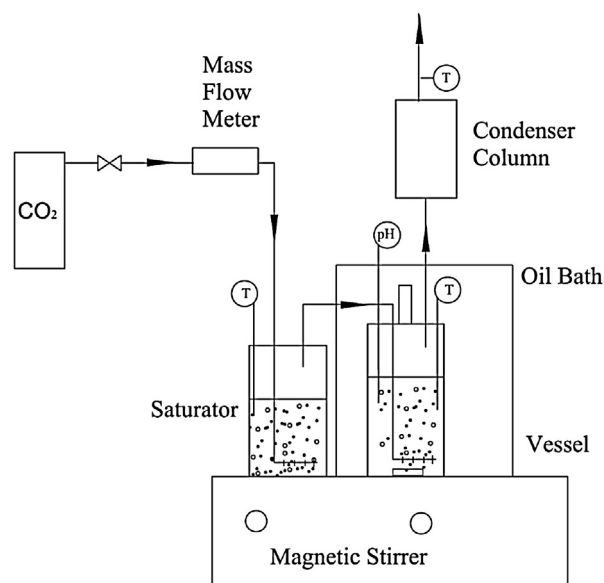


Fig. 1. CO₂ absorption experimental apparatus.

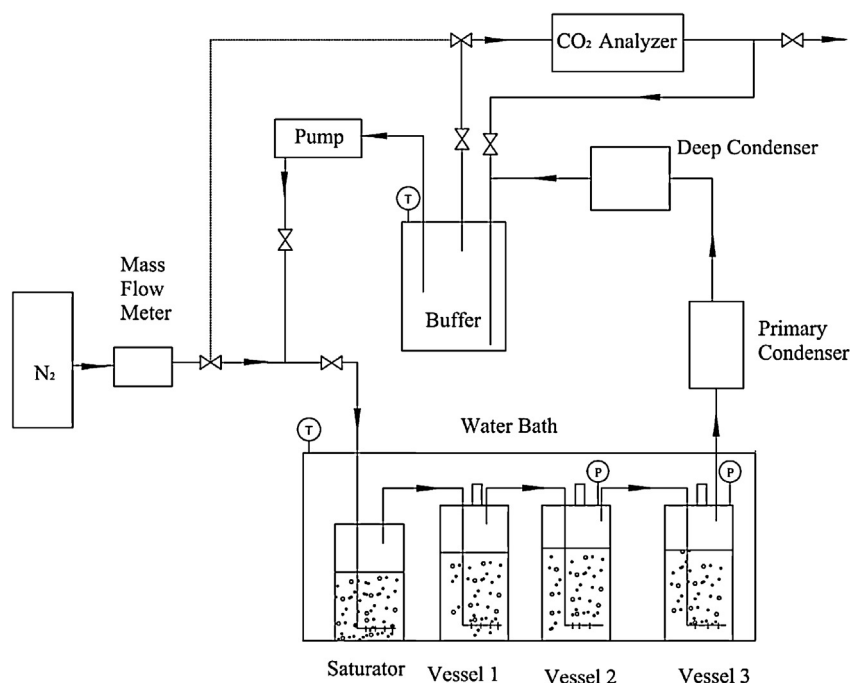


Fig. 2. A schematic diagram of experimental apparatus for vapor–liquid equilibrium measurement.

Download English Version:

<https://daneshyari.com/en/article/200947>

Download Persian Version:

<https://daneshyari.com/article/200947>

[Daneshyari.com](https://daneshyari.com)