

2012

Volume 24
Number 5

**JOURNAL OF** 

# ENVIRONMENTAL SCIENCES





# **CONTENTS**

Aquatic environment	
Immunotoxic potential of aeration lagoon effluents for the treatment of domestic and Hospital wastewaters in the freshwater mussel <i>Elliptio complanata</i> Francçis Gagné, Chantale André, Marlène Fortier, Michel Fournier	781
Spatial distribution of archaeal and bacterial ammonia oxidizers in the littoral buffer zone of a nitrogen-rich lake	/61
Yu Wang, Guibing Zhu, Lei Ye, Xiaojuan Feng, Huub J. M. Op den Camp, Chengqing Yin	790
Accelerated biodegradation of nitrophenols in the rhizosphere of <i>Spirodela polyrrhiza</i>	
Risky Ayu Kristanti, Masahiro Kanbe, Tadashi Toyama, Yasuhiro Tanaka, Yueqin Tang, Xiaolei Wu, Kazuhiro Mori	800
Sorption of 2,4-dinitroanisole (DNAN) on lignin	
Rabih Saad, Zorana Radovic-Hrapovic, Behzad Ahvazi, Sonia Thiboutot, Guy Ampleman, Jalal Hawari	808
Sewage sludge disintegration by high-pressure homogenization: A sludge disintegration model	
Yuxuan Zhang, Panyue Zhang, Boqiang Ma, Hao Wu, Sheng Zhang, Xin Xu	814
Degradation kinetics and mechanism of aniline by heat-assisted persulfate oxidation	
Xiaofang Xie, Yongqing Zhang, Weilin Huang, Shaobing Huang	821
Degradation of some typical pharmaceuticals and personal care products with copper-plating iron doped Cu <sub>2</sub> O under visible light irradiation  Jing An, Qixing Zhou	927
Preparation of high concentration polyaluminum chloride by chemical synthesis-membrane distillation method with self-made hollow fiber membrane	627
Changwei Zhao, Yong Yan, Deyin Hou, Zhaokun Luan, Zhiping Jia	834
Characteristics of gas-liquid pulsed discharge plasma reactor and dye decoloration efficiency	054
Bing Sun, Nyein Nyein Aye, Zhiying Gao, Dan Lv, Xiaomei Zhu, Masayuki Sato	840
Photolysis kinetics and influencing factors of bisphenol S in aqueous solutions	010
Guiping Cao, Jilai Lu, Gongying Wang	846
Comparative study of leaching of silver nanoparticles from fabric and effective effluent treatment	
Aneesh Pasricha, Sant Lal Jangra, Nahar Singh, Neeraj Dilbaghi, K. N. Sood, Kanupriya Arora, Renu Pasricha	852
Atmospheric environment	
Size distribution and chemical composition of secondary organic aerosol formed from Cl-initiated oxidation of toluene	
Mingqiang Huang, Weijun Zhang, Xuejun Gu, Changjin Hu, Weixiong Zhao, Zhenya Wang, Li Fang · · · · · · · · · · · · · · · · · · ·	860
Real-world fuel efficiency and exhaust emissions of light-duty diesel vehicles and their correlation with road conditions	
Jingnan Hu, Ye Wu, Zhishi Wang, Zhenhua Li, Yu Zhou, Haitao Wang, Xiaofeng Bao, Jiming Hao·····	865
Operating condition influences on PCDD/Fs emissions from sinter pot tests with hot flue gas recycling	
Yongmei Yu, Minghui Zheng, Xianwei Li, Xiaolei He · · · · · · · · · · · · · · · · · ·	875
Size distribution of chemical elements and their source apportionment in ambient coarse, fine, and ultrafine particles in Shanghai urban summer atmosphere	2
Senlin Lü, Rui Zhang, Zhenkun Yao, Fei Yi, Jingjing Ren, Minghong Wu, Man Feng, Qingyue Wang ·····	⋯882
Synergistic effects of non-thermal plasma-assisted catalyst and ultrasound on toluene removal	
Yongli Sun, Libo Zhou, Luhong Zhang, Hong Sui·····	891
Absorption characteristics of new solvent based on a blend of AMP and 1,8-diamino-p-menthane for CO <sub>2</sub> absorption	
Sang-Sup Lee, Seong-Man Mun, Won-Joon Choi, Byoung-Moo Min, Sang-Won Cho, Kwang-Joong Oh	897
Terrestrial environment	
Toxicity and subcellular distribution of cadmium in wheat as affected by dissolved organic acids	
Dandan Li, Dongmei Zhou	903
Changes in the sorption, description, distribution, and availability of copper, induced by application of sewage sludge	
on Chilean soils contaminated by mine tailings	
Tatiana Garrido, Jorge Mendoza, Francisco Arriagada	912
Mechanism of lead immobilization by oxalic acid-activated phosphate rocks	010
Guanjie Jiang, Yonghong Liu, Li Huang, Qingling Fu, Youjun Deng, Hongqing Hu	919
Methyl-β-cyclodextrin enhanced biodegradation of polycyclic aromatic hydrocarbons and associated microbial activity in contaminated soil  Mingming Sun, Yongming Luo, Peter Christie, Zhongjun Jia, Zhengao Li, Ying Teng	026
Inhibitory effect of nitrobenzene on oxygen demand in lake sediments	920
Xiaohong Zhou, Xuying Wang, Hanchang Shi	03/
Environmental health and toxicology	754
Endogenous nitric oxide mediates alleviation of cadmium toxicity induced by calcium in rice seedlings	
Long Zhang, Zhen Chen, Cheng Zhu	940
Species-dependent effects of the phenolic herbicide ioxynil with potential thyroid hormone disrupting activity: modulation of its cellular	
uptake and activity by interaction with serum thyroid hormone-binding proteins	
Sakura Akiyoshi, Gobun Sai, Kiyoshi Yamauchi	949
Environmental catalysis and materials	
A screen-printed, amperometric biosensor for the determination of organophosphorus pesticides in water samples	
Junfeng Dou, Fuqiang Fan, Aizhong Ding, Lirong Cheng, Raju Sekar, Hongting Wang, Shuairan Li	956
A GFP-based bacterial biosensor with chromosomally integrated sensing cassette for quantitative detection of Hg(II) in environment	
Himanshu Priyadarshi, Absar Alam, Gireesh-Babu P, Rekha Das, Pankaj Kishore, Shivendra Kumar, Aparna Chaudhari	963
Serial narameter: CN 11-2629/X*1989*m*188*en*P*26*2012-5	





Journal of Environmental Sciences 2012, 24(5) 897–902

JOURNAL OF **ENVIRONMENTAL SCIENCES** 

ISSN 1001-0742 CN 11-2629/X

www.jesc.ac.cn

# Absorption characteristics of new solvent based on a blend of AMP and 1,8-diamino-p-menthane for CO<sub>2</sub> absorption

Sang-Sup Lee<sup>1</sup>, Seong-Man Mun<sup>2</sup>, Won-Joon Choi<sup>3</sup>, Byoung-Moo Min<sup>4</sup>, Sang-Won Cho<sup>5</sup>, Kwang-Joong Oh<sup>2,\*</sup>

1. Department of Environmental Engineering, Chungbuk National University, Cheongju 361-763, Korea 2. Department of Environmental Engineering, Pusan National University, Busan 609-735, Korea. E-mail: tlossm@pusan.ac.kr 3. Corporate R&D Institute, Fuel Cell System Development Team, Doosan Heavy Industries & Construction, Daejeon 305-811, Korea 4. Greenhouse Gas Research Center, Korea Institute of Energy Research, Daejeon 305-343, Korea 5. Department of Energy and Environment, Korea Polytechnic VII College, Gyeongnam 642-020, Korea

Received 28 April 2011; revised 05 October 2011; accepted 28 October 2011

### Abstract

Aqueous 1,8-diamino-p-menthane (KIER-C3) and commercially available amine solutions were tested for CO<sub>2</sub> absorption. A 2-amino-2-methyl-1-propanol (AMP) solution with an addition of KIER-C3 showed 9.3% and 31.6% higher absorption rate for CO<sub>2</sub> than the AMP solution with an addition of monoethanolamine (MEA) and ammonia (NH<sub>3</sub>), respectively. The reaction rate constant for CO<sub>2</sub> absorption by the AMP/KIER-C3 solution was determined by the following equation:  $k_{2 \text{ AMP/C3}} = 7.702 \times 10^6 \text{ exp} (-2248.03/T)$ . A CO<sub>2</sub> loading ratio of the AMP/KIER-C3 solution was also 2 and 3.4-times higher than that of the AMP/NH<sub>3</sub> solution and the AMP/MEA solution, respectively. Based on the experimental results, KIER-C3 may be used as an excellent additive to increase CO<sub>2</sub> absorption capability of AMP.

**Key words**: carbon dioxide; absorption rate and capacity; 1,8-diamino-p-menthane; 2-amino-2-methyl-1-propanol **DOI**: 10.1016/S1001-0742(11)60788-2

### Introduction

Global warming has become one of the most complicated issues in the world. Carbon dioxide (CO<sub>2</sub>) is recognized as a major greenhouse gas generated in large quantities from various emission sources including fossil-fuel electric power plants, synthetic ammonia industries, steel production works, etc. (Gadalla et al., 2005). Although a number of techniques have been tested for the separation of CO<sub>2</sub> from fossil fuel fired flue gas, an economically viable process is not currently available. Therefore, a more efficient CO<sub>2</sub> recovery process still needs to be developed.

Many studies have been conducted to develop more efficient alkanolamine absorbents for CO<sub>2</sub>. A zwitterion mechanism was proposed for the CO<sub>2</sub> absorption mechanism of the alkanolamine absorbent by Caplow (1968) and Danckwerts (1979). Different from monoethanolamine (MEA), sterically hindered amines form unstable carbamates due to the bulkiness of the carbon groups attached to the amino group. The hydrolysis of carbamates then forms bicarbonate and restores the free amines which can react with additional carbon dioxide (Sartori and Savage, 1983). A representative sterically hindered amine, 2-amino-2methyl-1-propanol (AMP) has therefore a higher CO<sub>2</sub> loading capacity than MEA (Dawodu and Meisen, 1994).

Using a single amine can cause relatively fast corrosion and degradation reactions (Choi et al., 2009). Hence more effective and consistent absorption for CO<sub>2</sub> is expected by using a blend of two or more amines (Horng and Li, 2002). A number of studies related to the kinetics of CO<sub>2</sub> absorption into a blend of aqueous amine solutions containing AMP have been conducted (Lee et al., 2008; Aroonwilas and Veawab, 2004; Xu et al., 1991). The blended amine solutions containing showed significant enhancement in the absorption capacity and absorption rate for CO<sub>2</sub> maintaining the characteristics of sterically hindered amines (Li and Chang, 1994).

In this study, KIER-C3 was examined for its possibility as an additive to AMP for CO<sub>2</sub> absorption using a lab-scale reactor. Reactivity of KIER-C3 with CO2 was evaluated comparing with other additives such as MEA and NH3 in terms of CO<sub>2</sub> absorption rate, reaction kinetics and CO<sub>2</sub> loading. Its performance was also tested under various operating conditions.

### 1 Materials and methods

AMP, MEA, NH<sub>3</sub> and 1,8-diamino-*p*-menthane (KIER)

<sup>\*</sup> Corresponding author. E-mail: kjoh@pusan.ac.kr

C3) were used in this study as CO<sub>2</sub> absorbents. We obtained 95% AMP and 70% KIER-C3 from Sigma Aldrich (USA), 99% MEA from Yakuri Pure Chemicals (Japan), and 30% NH<sub>3</sub> from Junsei Chemical (Japan). Each solution was diluted with distilled water to a certain concentration. The purity of CO<sub>2</sub>, N<sub>2</sub> and N<sub>2</sub>O gases in each cylinder was 99.9%.

### 1.2 Apparatus and procedure

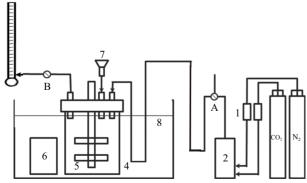
A schematic diagram of the experimental set up is presented in Fig. 1. Absorption experiments were carried out using an agitated glass reactor with an internal diameter of 7.3 cm and a height of 15.1 cm. Each solution of 150 mL was located inside the reactor at 313 K and agitated at 50 r/min.  $N_2$  and  $CO_2$  gases were premixed in the mixing chamber and then injected into the solution. The flow rates of  $N_2$  and  $CO_2$  gases were controlled using mass flow controllers (5850E, Brooks Instruments, USA, accuracy:  $\pm$  1% of full scale) to maintain the  $CO_2$  concentration of 15%. The flow rate of effluent gas from the reactor was determined using a bubble meter. The  $CO_2$  absorption rate was then determined from the difference between the flow rates of the influent and the effluent gas. Each experiment was repeated three times.

The molar flux of  $CO_2$  into each solution j ( $N_j$  kmol/(m<sup>2</sup>·sec)) was determined from the initial absorption rate,  $V(t_1)/t_1$  using the following equation:

$$N_j = \frac{P_{\rm T} - P_{\rm W}^0}{SRT} \frac{V(t_1)}{t_1} \tag{1}$$

where,  $P_{\rm T}$  (kPa) is the atmospheric pressure,  $P_{\rm W}^0$  (kPa) is the vapor pressure, S (cm<sup>2</sup>) is the gas-liquid contact area, R ((L·atm)/(mol·K)) is the gas constant, and T (K) is the temperature.

Another experimental system was constructed to test the amount of  $CO_2$  absorption into each solution at equilibrium as shown in Fig. 2. A reactor with a height of 160 mm was located in a temperature-controlled vessel. Four baffles with 5 mm width were installed inside the reactor. A two-blade impeller (70 mm  $\times$  20 mm) was also installed in the middle of the liquid level. The temperature inside the reactor was measured with a K-type thermocouple with an accuracy of  $\pm$  0.1 K. The stirring speed was limited at no more than 50 r/min to keep the gas-liquid interface



**Fig. 1** Schematic diagram of the agitated vessel. (1) mass flow controller; (2) mixing chamber; (3) soap bubble meter; (4) reactor; (5) impeller; (6) liquid bottle; (7) funnel; (8) water bath.

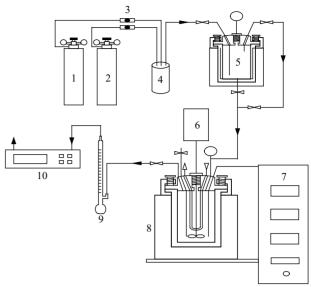


Fig. 2 Schematic diagram of experimental system used to determine  $CO_2$  adsorption capacity. (1)  $N_2$  cylinder; (2)  $CO_2$  cylinder; (3) mass flow controller; (4) mixing chamber; (5) saturator; (6) magnetic drive; (7) controller of temperature and rpm; (8) reactor in a vessel; (9) soap bubble meter; (10) analyzer.

planar and smooth. Each solution of 300 mL was located in the reactor, and its absorption capacity was determined with a CO<sub>2</sub> partial pressure in the range of 0–600 kPa at 313 and 383 K, respectively. The CO<sub>2</sub> partial pressure in the reactor was recorded using a pressure data logging system (PR2000, Madgetech, USA). The CO<sub>2</sub> loading of each solution was calculated according to the following Eqs. (2)–(4):

$$n_{\text{object gas}} = [(P_{N_2 + \text{object gas}} - P_{\text{eq}})V]/RT$$
 (2)

$$P_{\text{object gas}} = (P_{\text{eq}} - P_{\text{N}_2}) \tag{3}$$

$$\alpha = n_{\text{object gas}}/\text{mole of amine}$$
 (4)

where,  $n_{\text{object gas}}$  is the amount of object gas,  $P_{\text{object gas}}$  is the partial pressure of object gas,  $P_{\text{eq}}$  is the equilibrium pressure,  $P_{\text{N}_2}$  is initial pressure and  $\alpha$  is the CO<sub>2</sub> loading ratio.

### 2 Results and discussion

### 2.1 Solubility

 $CO_2$  is physically soluble in an aqueous alkanolamine solution without chemical reaction. The physical solubility of  $CO_2$  was determined from the solubility of  $N_2O$  in each solution because  $CO_2$  reacts with the amine solution. Each KIER-C3 solution with different concentrations of 0.05, 0.10, 0.15 and 0.20 kmol/m³ was added into a 2 kmol/m³ AMP solution. Henry's constant (H) for  $N_2O$  on each AMP solution with an addition of KIER-C3 was determined at various temperatures of 293, 303, 313 and 323 K and then converted to the constant for  $CO_2$  in the solution using Eq. (5).

$$(H_{\rm CO_2})_{\rm amine} = (H_{\rm N_2O})_{\rm amine} \times (H_{\rm CO_2}/H_{\rm N_2O})_{\rm water}$$

As shown in Fig. 3, Henry's constant decreased with

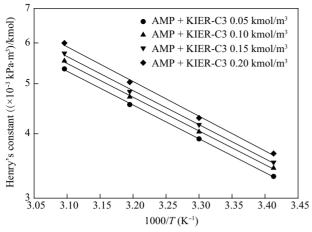


Fig. 3 Henry's constants for  $CO_2$  in AMP/KIEP-C3 solution with different KIER-C3 contents as a fuction of temperature.

increasing temperature and the concentration of KIER-C3 in the AMP/KIER-C3 solution. Therefore, the solubility of  $CO_2$  in the AMP/KIER-C3 solution was found to increase with an increase in the concentration of KIER-C3.

### 2.2 Diffusivity

Diffusivity ( $D_A$ ) of CO<sub>2</sub> in the AMP/KIER-C3 solution was also obtained from determining diffusivity of N<sub>2</sub>O in the solution at the temperatures of 293, 303, 313 and 323 K by using Eq. (6).

$$(D_{\text{CO}_2})_{\text{amine}} = (D_{\text{N}_2\text{O}})_{\text{amine}} \times (D_{\text{CO}_2}/D_{\text{N}_2\text{O}})_{\text{water}}$$
(6)

Detailed information on the wetted wall column used to determine the diffusivity is found in our previous publication (Choi et al., 2009). As shown in Fig. 4, diffusivity of  $CO_2$  in the AMP/KIER-C3 solution decreased with increasing KIER-C3 content for all tested temperatures. This may be attributed to the increase in the viscosity of the solution with increasing KIER-C3 content.

### 2.3 Absorption rate

The  $CO_2$  absorption rate was determined for AMP, MEA, NH<sub>3</sub> and KIER-C3 with various concentrations of 0.5, 1.0, 1.5 and 2.0 kmol/m<sup>3</sup> at the temperature of 313 K and

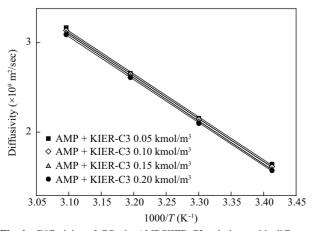
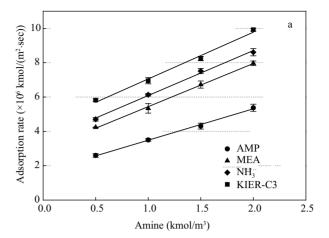


Fig. 4 Diffusivity of  $CO_2$  in AMP/KIER-C3 solutions with different KIER-C3 contents at  $2 \; \text{kmol/m}^3$  AMP as a function of temperature.



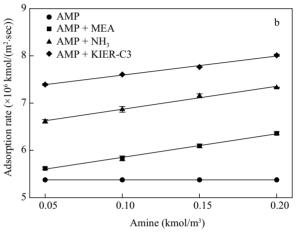


Fig. 5 Absorption rates of the  $CO_2$  into (a) aqueous AMP, MEA, NH<sub>3</sub> and KIER-C3 and (b) AMP/amine solutions as a function of the concentration of each amine solution at 313 K.

the CO<sub>2</sub> partial pressure of 15 kPa. Figure 5a shows the absorption rate as a function of the concentration of each solution. The absorption rate increased with increasing concentration of each solution. This is caused by enhanced mass transfer in the gas-liquid interfacial area with increasing concentration. The absorption rate of CO<sub>2</sub> into 2 kmol/m<sup>3</sup> KIER-C3 solution was found to be 84.7%, 24.6% and 15.2% higher than that into 2 kmol/m<sup>3</sup> AMP, MEA and NH<sub>3</sub>, respectively. As hydrolysis of carbamate, which is created via reaction of KIER-C3 and CO<sub>2</sub>, is accelerated, and CO<sub>2</sub> within carbamate is converted to bicarbonate, the concentration of carbamate gets lower. However, since concentration of the reactant amine increases, those will be involved in absorption reaction of CO<sub>2</sub>, and stimulates absorption to adjust lower concentration of carbamate and higher amine to equilibrium concentration, which leads to a higher reaction rate.

Figure 5b shows the  $CO_2$  absorption rates of 2 kmol/m<sup>3</sup> AMP with different concentrations of additives at 313 K. The absorption rates were found in the range of  $5.62 \times 10^{-6}$  to  $8.01 \times 10^{-6}$  kmol/(m<sup>2</sup>·sec). The absorption rate of the solution with an addition of KIER-C3 was 9.3%–31.6% higher than the absorption rates of other solutions with MEA and NH<sub>3</sub>. Therefore, KIER-C3 showed the highest absorption rate for  $CO_2$  and the best performance as an additive into AMP out of the absorbents tested in this study.



# 2.4 Effect of the KIER-C3 concentration on CO<sub>2</sub> absorption

The adsorption of  $CO_2$  in AMP solution with an addition of KIER-C3 was tested at different temperatures. In addition to the total absorption rate of the AMP/KIER-C3 solution, the absorption rates of the AMP portion and the KIER-C3 portion in the AMP/KIER-C3 solution were determined respectively as presented in Fig. 6.

It was observed from Fig. 6 that the absorption rates into the KIER-C3 portion ( $N_{\rm KIER-C3}$ ) increased from  $1.28\times10^{-6}$  to  $4.12\times10^{-6}$  kmol/(m<sup>2</sup>·sec) and  $1.96\times10^{-6}$  to  $6.52\times10^{-6}$  kmol/(m<sup>2</sup>·sec) with increasing KIER-C3 concentration at the temperature of 293 and 323 K, respectively. But the absorption rate into the AMP portion ( $N_{\rm AMP}$ ) decreased with increasing KIER-C3 concentration. As a result,  $N_{\rm KIER-C3}$  was as much as 55.7% of the total absorption rate ( $N_{\rm total}$ ) at the KIER-C3 concentration of 0.2 kmol/m<sup>3</sup>.

### 2.5 Reaction kinetics

Reaction rate constants ( $k_2$ ) for the absorption of CO<sub>2</sub> into AMP and AMP/KIER-C3 were determined by plotting overall reaction rate constant ( $k_{ov}$ , m<sup>3</sup>/(kmol·sec)) with the absorbent concentration at 293, 303, 313 and 323 K. By using Eq. (7),  $k_{ov}$  can be calculated as follows:

$$k_{\rm ov} = k_{mn} = (N_{\rm A} H_{\rm A}^{(m+1)/2} / P_{\rm A}^{(m+1)/2} / D_{\rm A}^{1/2})^2$$
 (7)

where,  $N_A$  (m³/(kmol·sec)) is the overall absorption rate,  $H_A$  ((kPa·m³)/kmol) is the Henry's constant,  $P_A$  (kPa) is the partial pressure,  $D_A$  (m²/sec) is the diffusivity of CO<sub>2</sub>, m is the order of reaction with respect to species A, and n is the order of reaction with respect to CO<sub>2</sub>.

The reaction of  $CO_2$  with the AMP/KIER-C3 solution can be classified as a fast pseudo first-order reaction. We confirmed the reaction order by plotting Eq. (7) with the concentration of KIER-C3 in the solution. Figure 7 shows straight lines with a slope of 1. In addition, the  $k_{ov}$  value increased linearly with increasing the temperature and the concentration of KIER-C3 in the solution. This may be

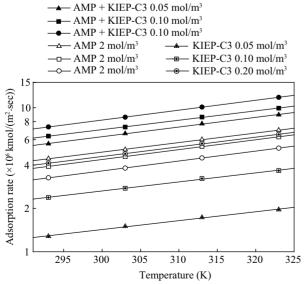


Fig. 6 Absorption rate of  ${\rm CO_2}$  into the AMP/KIER-C3 solution at different temperatures.

attributed to the increased diffusion at the gas-liquid interface with increasing the temperature and concentration.

The reaction rate constants  $(k_2)$  were then determined for the absorption of CO<sub>2</sub> into AMP and AMP/KIER-C3 at different temperatures and shown in Table 1. The values of  $k_2$  were found to be 530.98– 1323.81 m<sup>3</sup>/(kmol·sec) for AMP and 3939.53-7347.65  $m^3/(kmol \cdot sec)$  for AMP/KIER-C3. Hence the  $k_2$  values for a blend of AMP and KIER-C3 were five to six times higher than that for AMP without KIER-C3. This result shows that the reactivity of AMP is significantly enhanced with an addition of KIER-C3. Therefore, KIER-C3 is considered to be an effective activator in the AMP solution. This may be attributed that KIER-C3 has two amine groups which have characteristic of sterically hindered amine. While primary amine forms stable carbamate, sterically hindered amine forms more instable cabarmate. The reduction in stability promotes hydrolysis of carbamate and CO<sub>2</sub> absorption. Because KIER-C3 has two sterically hindered amine groups, KIER-C3 may act as an effective activator in the AMP solution.

Figure 8 shows the correlation between reaction rate constant  $(k_2)$  and temperature using the results in Table 1. From a linear regression analysis  $(r^2 = 0.99)$ , the following equations were obtained for the relationship between  $k_2$  and temperature.

$$k_{2,\text{AMP}} = 1.079 \times 10^7 \exp(-2909.16/T)$$
 (8)

$$k_{2\text{-AMP/C3}} = 7.702 \times 10^6 \exp(-2248.03/T)$$
 (9)

From the exponents in the Arrhenius equations, activation energies for the reaction of CO<sub>2</sub> with AMP and

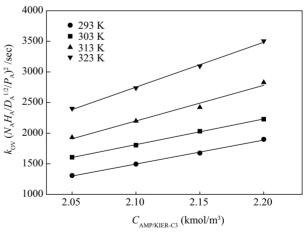


Fig. 7 Pseudo first-order overall reaction rate constant for the reaction of  $CO_2$  with AMP/KIER-C3 solution at different temperatures.

 $\begin{array}{ll} \textbf{Table 1} & \text{The second-order reaction rate constant calculated for the } \\ \text{reaction of CO}_2 & \text{into aqueous AMP and 2 kmol/m}^3 & \text{AMP/KIER-C3} \\ & & \text{solutions as a function of temperature} \\ \end{array}$ 

Temperature (K)	AMP (m <sup>3</sup> /(kmol·sec))	$AMP + KIER-C3$ $(m^3/(kmol \cdot sec))$
293	530.98	3939.53
303	730.53	4146.09
313	992.78	5976.13
323	1323.81	7347.65
		~ . 0

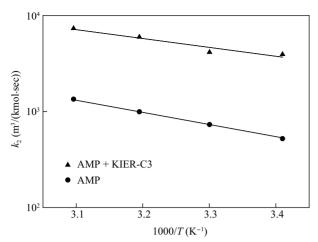


Fig. 8 Arrhenius plot for the correlation between reaction rate constant and temperature.

AMP/KIER-C3 were determined to be 24.2 and 18.7 kJ/mol, respectively. The lower activation energy for AMP/KIER-C3 also indicates that the reactivity of AMP for CO<sub>2</sub> is enhanced with an addition of KIER-C3.

### 2.6 Absorption equilibrium

The reaction of  $CO_2$  with the primary amino group can produce three possible reactions: the formation of carbamate and bicarbonate, the reversion of carbamate to bicarbonate, or the formation of the carbonate ion (Yih et al., 1988).

$$CO_2(g) + 2RNH_2 \longleftrightarrow RNH_3^+(aq) + RNHCOO^-(aq)$$
(10)

$$RNHCOO^{-} + H_2O \longleftrightarrow RNH_2 + HCO_3^{-}$$
 (11)

The equilibrium loading capacities of primary and secondary amines are limited by stoichiometry (0.5 mol of  $CO_2/mol$  of amine) of Eq. (10). The zwitterions mechanism originally proposed by Caplow (1968) and reintroduced by Danckwerts (1979) is generally accepted

as the reaction mechanism for Eq. (10) (Blauwhoff et al., 1983).

$$CO_2 + RNH_2 \longleftrightarrow RNH_2^+ COO^-$$
 (12)

$$RNH_2^+COO^- + B' \longleftrightarrow RNHCOO^- + B'H^+ \tag{13}$$

where, B' is amine,  $OH^-$  or  $H_2O$ . The carbamates formed from primary and secondary amines are quite stable. If the carbamate ion is unstable, as in the case of a hindered amine, it undergoes the formation of bicarbonate ion as in Eq. (11). This reaction means that 1 mol of hindered amine allows loading of  $CO_2$  up to 1 mol.

The CO<sub>2</sub> loading ratio is the most basic factor to evaluate the performance of absorbents. CO<sub>2</sub> loading in each 2 kmol/m³ solutions of AMP, MEA, NH<sub>3</sub> and KIER-C3 was determined respectively with increasing CO<sub>2</sub> partial pressure at 313 K. The highest CO<sub>2</sub> loading in the AMP, MEA, NH<sub>3</sub> and KIER-C3 solution was 0.72, 0.82, 0.93 and 2.88 mol CO<sub>2</sub>/mol absorbent, respectively, in the range of CO<sub>2</sub> partial pressure as shown in Fig. 9a. Hence KIER-C3 was found to have three to four times higher CO<sub>2</sub> loading than other solutions. The higher CO<sub>2</sub> loading in KIER-C3 may be attributed that KIER-C3 has two nitrogen compounds which have characteristics of sterically hindered amine. In addition, the CO<sub>2</sub> loading of more than 2 mol CO<sub>2</sub>/mol absorbent indicates that intermediate products formed during the reaction act as the absorbents for CO<sub>2</sub>.

In the full-scale CO<sub>2</sub> separation process using alkanolamine solutions, CO<sub>2</sub> absorption and stripping systems may be operated at the temperature range of 310–320 K and 380–400 K, respectively. To examine CO<sub>2</sub> loadings in blended amines at the absorption and stripping temperatures, each AMP solution with different additives was tested at 313 and 383 K. As shown in Fig. 9b, AMP/KIER-C3 shows much higher CO<sub>2</sub> loading at 313 K and similar CO<sub>2</sub> loading as the other absorbents at 383 K. Hence, AMP/KIER-C3 shows 2 and 3.4-times higher difference in CO<sub>2</sub> loading compared to AMP/NH<sub>3</sub> and AMP/MEA,

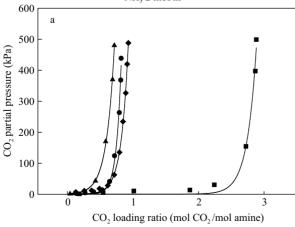
AMP + MEA 0.20 kmol/m³ (313 K)
 AMP + NH<sub>3</sub> 0.20 kmol/m³ (313 K)

AMP + KIER-C3 0.20 kmol/m3 (313 K)

AMP + MEA 0.20 kmol/m<sup>3</sup> (383 K)

□ AMP + NH<sub>2</sub> 0.20 kmol/m<sup>3</sup> (383 K)

- ▲ MEA 2 mol/m³
- AMP 2 mol/m<sup>3</sup>
- KIER-C3 2 mol/m³
- ♦ NH<sub>3</sub> 2 mol/m<sup>3</sup>



A AMP + KIER-C3 0.20 kmol/m³ (383 K)

700

600

500

100

0.0

0.2

0.4

0.6

0.8

1.0

1.2

1.4

Fig. 9 CO<sub>2</sub> loading in AMP, MEA, NH<sub>3</sub> and KIER-C3 with increasing CO<sub>2</sub> partial pressure at 313 K (a) and in AMP with different additives at 313 K and AMP 2 kmol/m<sup>3</sup> (b).

respectively. This suggests that KIER-C3 can be used as an excellent additive to AMP in the CO<sub>2</sub> separation process.

### **3 Conclusions**

Absorption of CO<sub>2</sub> into AMP/KIER-C3 was tested using a stirred batch tank reactor with different concentrations and reaction temperatures. The absorption rate into the aqueous KIER-C3 solution were 84.7%, 24.6% and 15.2% higher than that into aqueous AMP, MEA and NH3 solution at 313 K, respectively. Also, the CO<sub>2</sub> absorption rate on the addition of KIER-C3 into 2 kmol/m<sup>3</sup> AMP solutions increased by 9.3% to 31.6% compared to the addition of MEA and NH<sub>3</sub> solution, respectively. This may be ascribed to the increase in diffusion and contact between the CO<sub>2</sub> and KIER-C3. KIER-C3 showed the best performance as an additive to increase CO<sub>2</sub> absorption rate of AMP. The calculated reaction rate constant for the reaction of CO2 into aqueous AMP and AMP/KIER-C3 solution was determined to be  $k_{2,AMP} = 1.079 \times 10^7 \exp(-2909.16/T)$  and  $k_{2,\text{AMP/C}3} = 7.702 \times 10^6 \exp(-2248.03/T)$ , respectively. In addition, activation energies of AMP and AMP/KIER-C3 were found to be 24.16 and 18.62 kJ/mol, respectively. The reactivity of AMP was enhanced with an addition of KIER-C3. CO<sub>2</sub> loading in a KIER-C3 solution was three to four times higher than other solutions such as AMP, MEA and NH<sub>3</sub>. Also, CO<sub>2</sub> loading in the AMP/KIER-C3 solution was 2 and 3.4-times higher than that of the AMP/NH<sub>3</sub> solution and the AMP/MEA solution, respectively. Therefore, KIER-C3 may be used as an excellent absorbent or additive to AMP for the separation of CO<sub>2</sub> from flue gases.

### Acknowledgments

This research was financially supported by the Brain Korea 21 Project in 2012 and by the Energy Efficiency & Resources of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (No. 2006CCD11P011A -21-3-010).

### References

- Aroonwilas A, Veawab A, 2004. Characterization and comparison of the CO<sub>2</sub> aborption performance into single and blended alkanolamines in a packed column. *Industrial & Engineering Chemistry Research*, 43(9): 2228–2237.
- Blauwhoff P M M, Versteeg G F, van Swaaij W P M, 1983. A study on the reaction between CO<sub>2</sub> and alkanolamines in aqueous solutions. *Chemical Engineering Science*, 38(9): 1411–1429.
- Caplow M, 1968. Kinetics of carbamate formation and breakdown. *Journal of the American Chemical Society*, 90(24): 6795–6803.
- Choi W J, Min B M, Seo J B, Park S W, Oh K J, 2009. Effect of ammonia on the absorption kinetics of carbon dioxide into aqueous 2-amino-2-methyl-1-propanol solutions. *Industrial & Engineering Chemistry Research*, 48(8): 4022–4029.
- Dawodu O F, Meisen A, 1994. Degradation of alkanolamine blends by carbon dioxide. *The Canadian Journal of Chemical Engineering*, 74(6): 960–966.
- Danckwerts P V, 1979. The reaction of CO<sub>2</sub> with ethanolamines. *Chemical Engineering Science*, 34(4): 443–446.
- Gadalla M A, Olujic Z, Jansens P J, Jobson M, Smith R, 2005. Reducing CO<sub>2</sub> emissions and energy consumption of heat-integrated distillation systems. *Environmental Science & Technology*, 39(17): 6860–6870.
- Horng S Y, Li M H, 2002. Kinetics of absorption of carbon dioxide into aqueous solutions of monoethanolamine + triethanolamine. *Industrial & Engineering Chemistry Research*, 41(2): 257–266.
- Lee D H, Choi W J, Moon S J, Ha S H, Kim I G, Oh K J, 2008. Characteristics of absorption and regeneration of carbon dioxide in aqueous 2-amino-2-methyl-1-propanol /ammonia solutions. *Korean Journal of Chemical Engineering*, 25(2): 279–284.
- Li M H, Chang B C, 1994. Solubilities of carbon dioxide in water + monoethanolamin + 2-amino-2-methyl-1-propanol. *Journal of Chemical & Engineering Data*, 39(3): 448–452.
- Sartori G, Savage D W, 1983. Sterically hindered amines for CO<sub>2</sub> removal from gases. *Industrial & Engineering Chemistry Fundamentals*, 22: 239.
- Xu S, Wang Y W, Otto F D, Mather A E, 1991. Rate of absorption of carbon dioxide in a mixed solvent. *Industrial & Engineering Chemistry Research*, 30(9): 1213–1217.



## JOURNAL OF ENVIRONMENTAL SCIENCES

### **Editors-in-chief**

Hongxiao Tang

**Associate Editors-in-chief** 

Nigel Bell Jiuhui Qu Shu Tao Po-Keung Wong Yahui Zhuang

**Editorial board** 

R. M. Atlas Nigel Bell Alan Baker Tongbin Chen

University of Louisville The University of Melbourne Imperial College London Chinese Academy of Sciences

United Kingdom China USA Australia

Maohong Fan Jingyun Fang Lam Kin-Che Pinjing He University of Wyoming Peking University The Chinese University of Tongji University

Wyoming, USA China Hong Kong, China China

Chihpin Huang Jan Japenga David Jenkins Guibin Jiang

"National" Chiao Tung University Alterra Green World Research University of California Berkeley Chinese Academy of Sciences

Taiwan, China The Netherlands China

K. W. Kim Clark C. K. Liu Anton Moser Alex L. Murray

Gwangju Institute of Science and Technical University Graz University of Hawaii University of York Technology, Korea USA Austria Canada

Yi Oian Jiuhui Ou Sheikh Raisuddin Ian Singleton

Tsinghua University Chinese Academy of Sciences Hamdard University University of Newcastle upon Tyne

China China India United Kingdom

Yasutake Teraoka Hongxiao Tang Shu Tao Chunxia Wang

Chinese Academy of Sciences Peking University Kyushu University Chinese Academy of Sciences

China China China Japan

Brian A. Whitton Rusong Wang Xuejun Wang Po-Keung Wong

Chinese Academy of Sciences Peking University University of Durham The Chinese University of

China China United Kingdom Hong Kong, China

Zhifeng Yang Hanqing Yu Zhongtang Yu Min Yang

Chinese Academy of Sciences Beijing Normal University University of Science and Ohio State University

China China Technology of China USA

Yongping Zeng Qixing Zhou Lizhong Zhu Yahui Zhuang

Chinese Academy of Sciences Chinese Academy of Sciences Zhejiang University Chinese Academy of Sciences

China China China China

**Editorial office** 

Qingcai Feng (Executive Editor) Zixuan Wang (Editor) Sugin Liu (Editor) Zhengang Mao (Editor)

Christine J Watts (English Editor)

### Journal of Environmental Sciences (Established in 1989)

Vol. 24 No. 5 2012

Chinese Academy of Sciences Supervised by Published by Science Press, Beijing, China Sponsored by Research Center for Eco-Environmental Elsevier Limited, The Netherlands Sciences, Chinese Academy of Sciences Distributed by Edited by Editorial Office of Journal of Domestic Science Press, 16 Donghuangchenggen Environmental Sciences (JES) North Street, Beijing 100717, China P. O. Box 2871, Beijing 100085, China Local Post Offices through China Tel: 86-10-62920553; http://www.jesc.ac.cn Foreign Elsevier Limited

E-mail: jesc@263.net, jesc@rcees.ac.cn http://www.elsevier.com/locate/jes

Editor-in-chief Printed by Beijing Beilin Printing House, 100083, China Hongxiao Tang

CN 11-2629/X Domestic postcode: 2-580 Domestic price per issue RMB ¥ 110.00

