GHGT-12

Development of Novel Synthetic Amine Absorbents for CO_2 Capture

Firoz A. Chowdhury[1]*, Hidetaka Yamada[1], Yoichi Matsuzaki[2], Kazuya Goto[1],

Takayuki Higashii[1], and Masami Onoda[2]

[1]*Research Institute of Innovative Technology for the Earth (RITE),*
9-2 Kizugawadai, Kizugawa-shi, Kyoto, Japan
[2]*Advanced Technology Research Laboratories, Nippon Steel & Sumitomo Metal Corporation,*
20-1 Shintomi Futtsu, Chiba 293-8511, Japan

Abstract

In the present paper, we investigated five synthetic amine based absorbents, including three formulated solvents. Aqueous solutions of the amines (mass fraction; 30% for single amine and >30% for blended solvents) were used to evaluate the performance for CO_2 capture. Gas scrubbing, vapor-liquid equilibrium (VLE), and reaction calorimetry experiments were conducted in the laboratory to obtain the absorption rate, the amount of CO_2 absorbed, cyclic CO_2 capacity, and heat of reaction for each absorbent. The results of these absorbents were compared with the conventional absorbent monoethanolamine (MEA). Three high performing synthetic absorbents (IPAE, IPAP and IBAE) were found, and these had lower heats of reaction, higher cyclic capacities, and comparable absorption rates compared with MEA. All formulated absorbents showed excellent cyclic CO_2 capacity and keeping moderately good absorption rate and lower heats of absorption. Some blended solvents were already demonstrated with real blast furnace gas at pilot test plants with capacities of 1 ton-CO_2/day and 30 ton-CO_2/day and showed promising results in terms of reducing absorbent regeneration energy.

_____

 * Corresponding author. Tel.: +81-774-75-2360; fax: +81-774-75-2318.
   E-mail address: firoz@rite.or.jp

1. Introduction

Carbon dioxide (CO_2) is a greenhouse gas that contributes to global warming and climate change problems. Carbon capture and storage from large point exhaust sources is promising for mitigation of these problems. Cyclic chemical absorption/regeneration process using an aqueous solution of an amine-based absorbent is the most mature and applied technology for post-combustion CO_2 removal from large stationary sources that emit large amounts of CO_2. To date, amine-based CO_2 capture technology has been widely developed for post-combustion CO_2 removal because of high capture efficiency, high selectivity, and scale-up feasibility. The main obstacle for the application of conventional amine scrubbing technology is the energy requirements for absorbent regeneration. It is estimated that more than half of the capture cost arises from absorbent regeneration. Consequently, for practical application it is essential to reduce absorbent regeneration energy consumption by improving existing absorbents and developing new ones.

Numerous studies on chemical absorption phenomena with alkanolamines such as MEA, DEA, AMP, MDEA, TEA and their related absorbents have been reported.[1-4] Recently, interest in the use of mixed amine absorbents, especially blends of primary and tertiary amines (such as MEA and MDEA) or secondary and tertiary amines (such as DEA and MDEA), has increased. These mixed absorbents combine the higher equilibrium capacity of the tertiary amine with the higher reaction rate of primary or secondary amine, and have been suggested for industrial gas treatment processes.[5-8] Most studies have been limited to MEA-, DEA-, MDEA-, TEA- or MDEA-based single or combined absorbents. There is a very little information available regarding rationally designed new synthetic amines or amino alcohols. Recently, new secondary and tertiary alkanolamines, including some butanol derivatives synthesized by Tontiwachwuthikul and coworkers,[9,10] have been applied to CO_2 capture. These absorbents provided much higher CO_2 absorption and cyclic capacities than the conventional amine MEA. In our previous studies, we
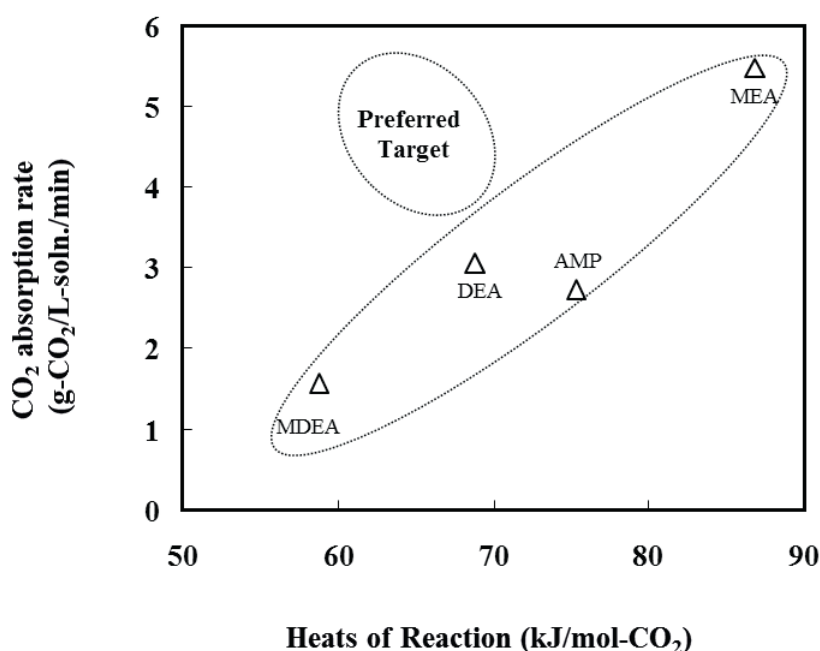

Fig. **1**. The experimental relationship between the CO2 absorption rate and heat of reaction for aqueous solutions of conventional amines (mass fraction 30 %; MEA, AMP, DEA and MDEA) at 40 ºC.

designed and synthesized several secondary and tertiary amino alcohols by modification of the chemical structures, and developed screening methods for finding promising absorbents.[11-15] On the basis of the screening methods, in the

present study, we examined five synthetic and three blended amine based absorbents, including the reference compound MEA, and compared their performance to MEA.

Our previous research has provided useful information on various amine absorbents for CO_2 capture. The CO_2 loading capacities, heats of reaction, and absorption rates of these absorbents were examined, and we found a structure-performance relationship. The relationship between the heat of reaction and CO_2 absorption rate of 30 wt% aqueous conventional amines, as determined experimentally, for primary amines MEA, AMP, a secondary amine DEA and a tertiary amine MDEA are shown in Fig. 1. Figure 1 shows MEA reacts with CO_2 faster than DEA, which reacts faster than AMP and MDEA. Figure 1 also shows that the heat of reaction is lower for MDEA, than DEA, AMP and MEA. This indicates that the heats of reaction and absorption rates of the alkanolamines are dependent on the substituents attached to the N-atom/alkanolamine chain. In aqueous solutions CO_2 and unhindered amines form stable carbamate anions and hindered amines form bicarbonate ions. Low rates of CO_2 absorption, however, make hindered amines difficult to use flue gas cleaning. In this study, firstly we tried to find high performance single-component amine from screening tests then advanced formulated amine absorbents were developed for capturing CO_2 from blast furnace exhaust gases.

2. Experimental

The development of new absorbent materials that efficiently, reversibly, and economically capture CO_2 is very laborious. A tremendous amount of experimental work has to be done on characterizing the new solvents with respect to different properties; for example: rapid and economic synthesis was done by one-pot synthesis with high purity yield, high performance absorbents selection were done by particular chemical structure tuning e.g. changing hydroxyl chain length ethyl to butyl and alkyl substituents e.g. isopropyl, isobutyl, and secondarybutyl around the amino group. Five such secondary amino alcohols were synthesized in our laboratory by the reaction of alkanolamine with their corresponding alkylhalides. These amines were >96% pure and their structures were established by gas chromatography (GC), liquid chromatography-mass spectrometry (LC-MS) and nuclear magnetic resonance (NMR) spectroscopy. Conventional amines MEA, AMP, DEA, and MDEA were purchased from Wako Pure Chemical Industries (Osaka, Japan) and used as received. The details for the investigated amine absorbents are shown in Table 1. Water used in all experiments was purified with water distillation apparatus (RFD240NA, Advantec, Tokyo, Japan) and an ion-exchange apparatus (RFU424CA, Advantec) in series.

Several fundamental experiments of synthesized amines were performed in our laboratory to evaluate their CO_2 capture performance. For example, 30 wt% aqueous synthesized amines were used for gas scrubbing test, vapor-liquid equilibrium test and reaction calorimetric measurements. Among these experiments solvent characteristics such as CO_2 absorption capacity, absorption-regeneration rate, cyclic CO_2 loading, and heats of absorption were obtained. A similar study of conventional alkanolamine (MEA) was also conducted at the same time under similar conditions for comparisons. The blended solvents (A, B and C) were formulated on the basis of solvent concentration, rich CO_2 loading, lean CO_2 loading and cyclic CO_2 loading. Other solvent issues like foaming tendency, crystallization, density, viscosity also considered. The detailed equipment and experimental procedures of the above mentioned tests were explained in our previous work.

Table **1**. Investigated amine absorbents

| Synthesized and blended absorbents	Conventional absorbents
1. 2-(isopropylamino)ethanol (**IPAE**)	**9**. 2-aminoethanol (**MEA**)
2. 3-(isopropylamino)propanol (**IPAP**)	**10**. 2-amino-2-methyl-1-propanol (**AMP**)
3. 4-(isopropylamino)butanol (**IPAB**)	**11**. Diethaholamine (**DEA**)
4. 2-(isobutylamino)ethanol (**IBAE**)	**12**. Methyldiethanolamine (**MDEA**)
5. 2-(sec-butylamino)ethanol (**SBAE**)	
6. Solvent-**A**	
7. Solvent-**B**	
8. Solvent-**C**	
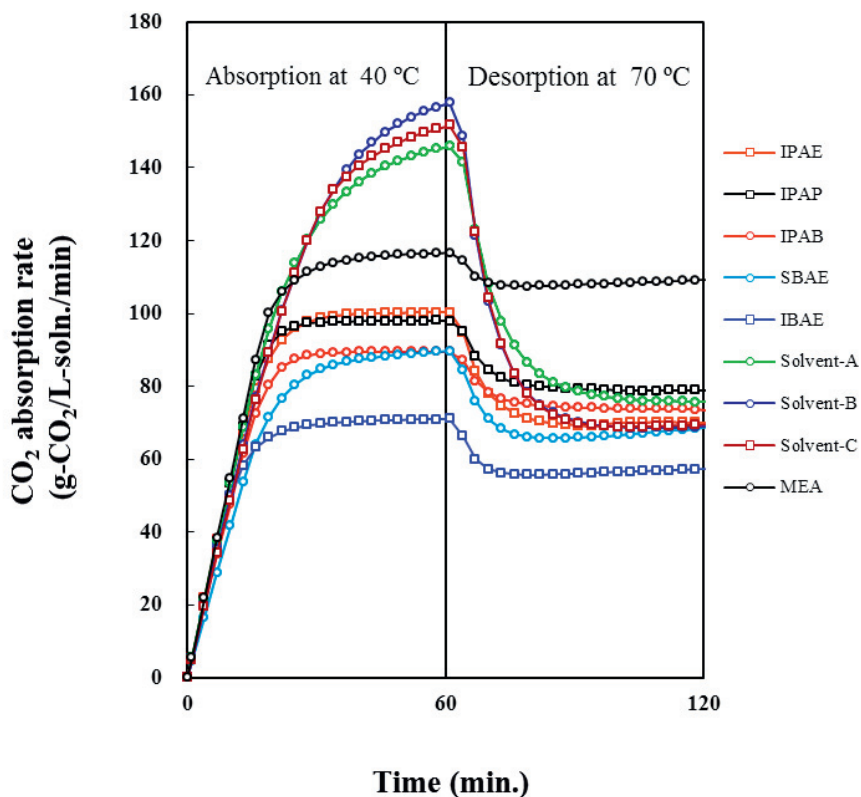
Fig. 2. Experimental CO_2 absorption-regeneration profiles for 5 synthetic amines (IPAE, IPAP, IPAB, SBAE, and IBAE), and 3 blended solvents (A, B and C) compared with conventional amine MEA. (mass fraction 30wt% for single amine and >30wt% for blended solvents).

3. Results and Discussion

The experimental CO_2 absorption-regeneration profiles obtained in this work for the five single synthetic amine and three blended amine based solvents are compared with the conventional absorbent MEA in Fig. 2. The amount of absorbed CO_2 in the aqueous amine solution (CO_2 loading) was calculated from the measured CO_2 concentration in the outlet gas flow. As shown in Fig. 2, the CO_2 loading increased with time at 40 °C and then decreased at 70 °C. The gradient of the curve at 50 % of the 60 min CO_2 loading was defined as the absorption rate. The absorption rate is not the chemical reaction rate but the apparent CO_2 transfer rate from the gas to liquid phase. This reference index was used to compare the behavior of the aqueous amine solutions. The reproducibility of the experiments was checked, and the error in all of the experimental measurements was less than 3 %. Figure 2 show that all synthetic amine had a higher desorption amount of CO_2 and keeping similar absorption rate except SBAE compared with MEA. All blended solvents in Fig. 2 shows higher CO_2 absorption-desorption characteristics and keeping similar absorption rate than that of MEA.

CO_2 absorption involves multiple electrolyte reactions in a liquid phase, but only the overall reaction was considered. The heats of reaction (ΔH_r) of each aqueous amine solution during CO_2 absorption was acquired using a differential reaction calorimeter. ΔH_r means the enthalpy difference between fresh aqueous amine solution and CO_2-loaded solution. ΔH_r were measured at 40 °C. Generally, ΔH_r values depend on the CO_2 loadings. Consequently, we expressed the ΔH_r values as the differential (average) enthalpies in the range of the absorbent loading. Our results are summarized in Fig. 3. Figure 3 also shows that the heat of reaction for all investigated absorbents is much lower than the conventional MEA absorbent.
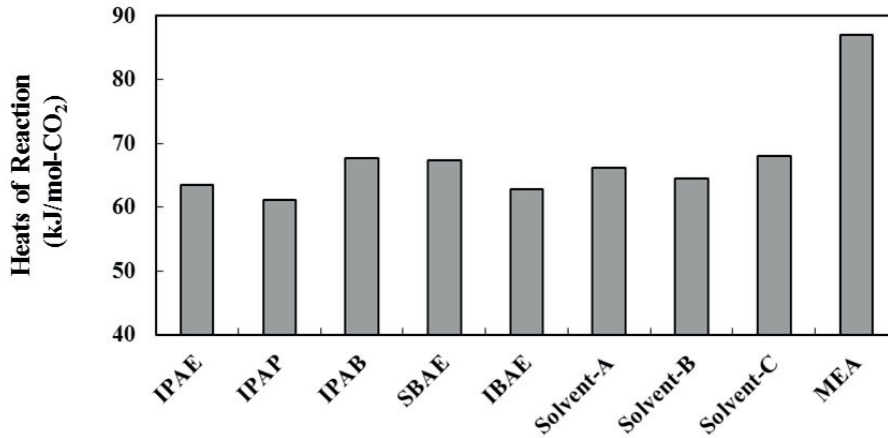
Fig. **3**. Heats of reaction of this work absorbents compared with conventional absorbent (MEA).

To reduce the energy requirements of the capture process, absorbents with high absorption rates, high cyclic capacities, and low heats of reaction are needed. In Figure 4, the CO_2 absorption rates for single-component amines and formulated absorbents (A, B and C) are plotted against the heats of absorption values. As mentioned for Figure 1, there was a trade-off between the heat of reaction and absorption rate for primary, secondary and tertiary amines. However, the results in Figure 1 showed that synthetic and formulated absorbents were plotted at outside of the

Heats of Reaction (kJ/mol-CO₂)
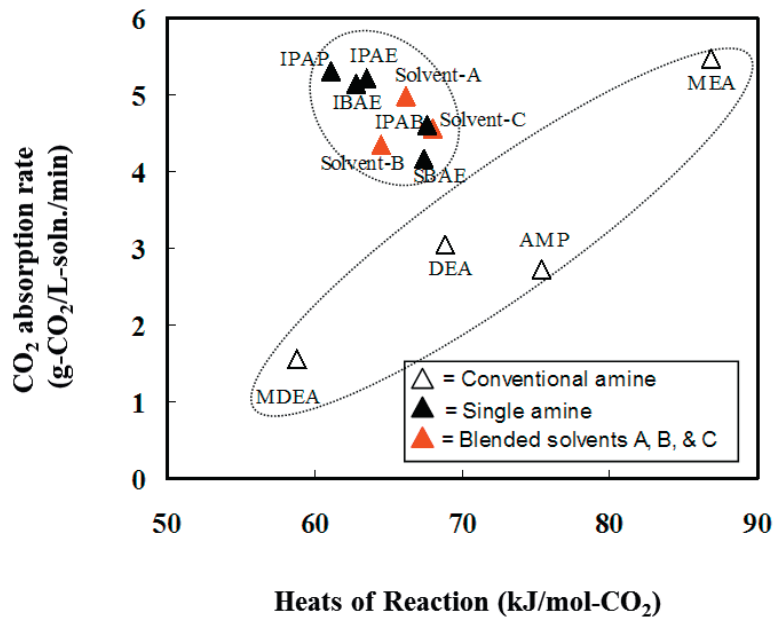
Fig. **4**. Five synthetic and three blended solvents preliminary screening results compared with conventional amines.

trade-off relationship formed by the conventional absorbents. In this study, (synthetic and formulated) absorbents were unique in that they had low heats of reaction and maintained moderately high absorption rate. Solvents with low heat of absorption might benefit from regeneration below atmospheric pressure and at low temperatures.

Solvents that showed superior performance (higher absorption rate, and lower reaction heat) from screening tests were selected for the evaluation of their vapor-liquid equilibrium (VLE) property. Four synthetic amines IPAE, IPAP, IBAE, SBAE and three formulated solvents (A, B & C) along with the reference solvent MEA was selected for the evaluation of their VLE property. For each absorbent, measurements under conditions with two temperatures, 40, and 120 °C and partial pressures of CO_2 20 and 100 kPa were conducted. The experimental results are given in Table 2-9.

Table **2**. VLE solubility of CO_2 in 30wt% MEA aqueous solution

40 ℃		120 ℃		$\Delta\alpha$
P_{CO2}	α	P_{CO2}	α	**(40-120)** ℃
[kPa]	[g-CO_2/ L-soln.]	[kPa]	[g-CO_2/ L-soln.]	[g-CO_2/ L-soln.]
20	117.4	20	55.5	61.9
100	129.8	100	80.2	49.6

Table **3**. VLE solubility of CO_2 in 30wt% IPAE aqueous solution

40 ℃		120 ℃		$\Delta\alpha$	$\Delta\alpha$
P_{CO2}	α	P_{CO2}	α	**(40-120)** ℃	Difference
[kPa]	[g-CO_2/ L-soln.]	[kPa]	[g-CO_2/ L-soln.]	[g-CO_2/ L-soln.]	(%)
20	93.9	20	10.6	83.3	35
100	108.3	100	27.2	81.1	64

Table **4**. VLE solubility of CO_2 in 30wt% IPAP aqueous solution

40 ℃		120 ℃		$\Delta\alpha$	$\Delta\alpha$
P_{CO2}	α	P_{CO2}	α	**(40-120)** ℃	Difference
[kPa]	[g-CO_2/ L-soln.]	[kPa]	[g-CO_2/ L-soln.]	[g-CO_2/ L-soln.]	(%)
20	102.2	20	16.7	85.5	38
100	111.1	100	42.2	68.9	39

Table **5**. VLE solubility of CO_2 in 30wt% IBAE aqueous solution

40 ℃		120 ℃		$\Delta\alpha$	$\Delta\alpha$
P_{CO2}	α	P_{CO2}	α	**(40-120)** ℃	Difference
[kPa]	[g-CO_2/ L-soln.]	[kPa]	[g-CO_2/ L-soln.]	[g-CO_2/ L-soln.]	(%)
20	70.6	20	9.4	61.2	-1
100	77.3	100	42.2	53.4	8

Table **6**. VLE solubility of CO_2 in 30wt% SBAE aqueous solution

40 ℃		120 ℃		$\Delta\alpha$	$\Delta\alpha$
P_{CO2}	α	P_{CO2}	α	**(40-120)** ℃	Difference
[kPa]	[g-CO_2/ L-soln.]	[kPa]	[g-CO_2/ L-soln.]	[g-CO_2/ L-soln.]	(%)
20	89.4	20	10.0	79.4	28
100	105.0	100	24.4	80.6	63

Table **7**. VLE solubility of CO_2 in Solvent-A aqueous solution

40 ℃		120 ℃		$\Delta\alpha$	$\Delta\alpha$
P_{CO2}	α	P_{CO2}	α	**(40-120)** ℃	Difference
[kPa]	[g-CO_2/ L-soln.]	[kPa]	[g-CO_2/ L-soln.]	[g-CO_2/ L-soln.]	(%)
20	140.9	20	8.4	132.5	114
100	172.7	100	22.8	149.9	202

Table **8**. VLE solubility of CO_2 in Solvent-B aqueous solution

40 ℃		120 ℃		$\Delta\alpha$	$\Delta\alpha$
P_{CO2}	α	P_{CO2}	α	**(40-120)** ℃	Difference
[kPa]	[g-CO_2/ L-soln.]	[kPa]	[g-CO_2/ L-soln.]	[g-CO_2/ L-soln.]	(%)
20	158.0	20	5.0	153.0	147.0
100	221.2	100	15.0	206.2	316.0

Table **9**. VLE solubility of CO_2 in Solvent-C aqueous solution

40 ℃		120 ℃		$\Delta\alpha$	$\Delta\alpha$
P_{CO2}	α	P_{CO2}	α	**(40-120)** ℃	Difference
[kPa]	[g-CO_2/ L-soln.]	[kPa]	[g-CO_2/ L-soln.]	[g-CO_2/ L-soln.]	(%)
20	155.8	20	6.7	149.1	141
100	198.4	100	19.4	179.0	261

The experimental results of the selected seven promising absorbents (IPAE, IPAP, IBAE, SBAE, and formulated solvents A, B, and C) compared to MEA at various conditions are presented in Table 2-9. The $\Delta\alpha$ is the absorption capacity differences between the rich and lean solvent under equilibrium condition was obtained from VLE experiment. The $\Delta\alpha$ CO_2 loading, is a key index that determines the net cyclic capacity in the CO_2 industrial capture

system. From the experimental results all tested absorbents have better performance than MEA and seemed to be effective solvent for CO_2 capture. In Table 2-9 the absorption capacity $\Delta\alpha$ compared with MEA at various operating conditions are higher by (35~64)% for IPAE, (38~39)% for IPAP, (-1~8)% for IBAE, (28~63)% for SBAE, (114~202)% for solvent A, (147~316)% for solvent B, and (141~261)% for solvent C. This means, these seven absorbents absorb more CO_2 and release more CO_2 off at high temperature. Good VLE property will reduce liquid flow rate and steam required for CO_2 recovery. This advantage can result in lowering solvent regeneration cost for gas treating process thereby making it more economically feasible.
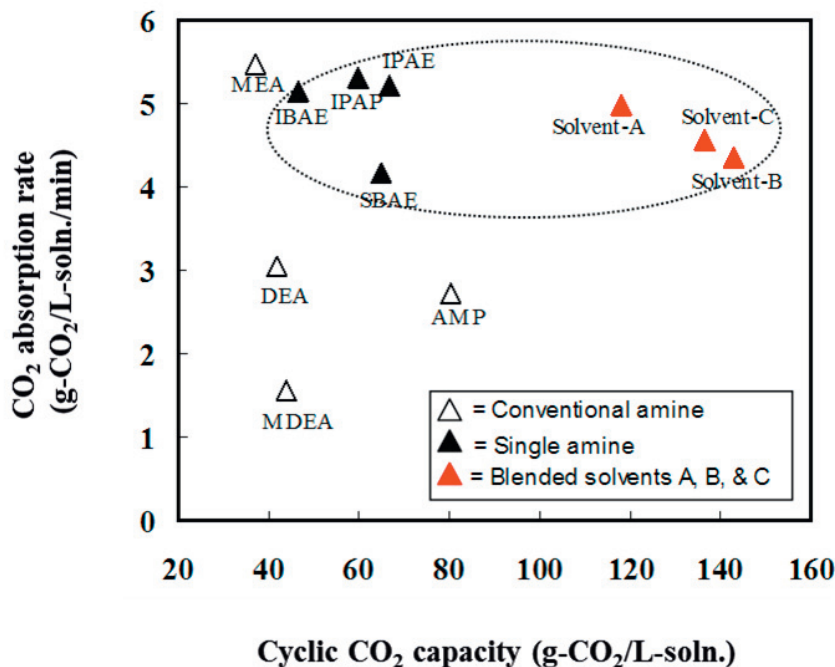

Fig. **5**. Four synthetic and three blended solvents CO_2 absorption rates verses equilibrium cyclic CO_2 capacities compared with conventional MEA. Cyclic CO_2 capacity = difference between lean and rich CO_2 loading at 40 ℃ (20kPa) and 120 ℃ (100kPa) under equilibrium condition obtained from VLE experiment.

Figure 5 showed the performance comparison of this work absorbent with conventional absorbents in terms of absorption rate versus cyclic CO_2 capacity. All formulated absorbents (A, B and C) showed excellent cyclic CO_2 capacity and keeping moderately good absorption rate compared with conventional amines (Fig. 5). Two synthetic absorbents (IPAE and IPAP) showed high cyclic capacity compared to MEA, DEA and MDEA and moderate compared to AMP. It should be noted that 30 wt% aqueous AMP contains more amine molecules (3.37 mol amine/kg solvent) than 30 wt% aqueous IPAE and IPAP (2.91 and 2.56 mol amine/kg solvent), which should be an advantage for AMP in terms of its CO_2 capacity.

4. Conclusions

In the present paper we investigated five synthetic amine based absorbents with particular chemical structure tuning e.g. changing hydroxyl chain length ethyl to butyl and alkyl substituents e.g. isopropyl, isobutyl, and secondarybutyl around the amino group. Placement of functional groups within the N-atom/alkanolamine chain affects CO_2 absorption-regeneration performance. Gas scrubbing, VLE and reaction calorimetry experiments were conducted to obtain the absorption rates, CO_2 loadings, cyclic capacities and heats of reaction for the absorbents. The results were compared with those for the conventional absorbent absorbents. Three high performing synthetic

absorbents (IPAE, IPAP and IBAE) were found, and these had lower heats of absorption and comparable absorption rates and cyclic capacities compared with conventional amine absorbents. All formulated absorbents showed excellent cyclic CO_2 capacity and keeping moderately good absorption rate and lower heats of absorption. Some blended solvents were already demonstrated with real blast furnace gas at pilot test plants with capacities of 1 ton-CO_2/day and 30 ton-CO_2/day and showed promising results in terms of reducing absorbent regeneration energy.

Acknowledgements

References

(1) Idem, R.; Wilson, M.; Tontiwachwuthikul, P.; Chakma, A.; Veawab, A.; Aroonwilas, A.; Gelowitz, D. *Ind. Eng. Chem. Res.* **2006**, *45*, 2414.
(2) Oyenekan, B. A., Rochelle, G. T. *AIChE Journal*. **2007**, *53*, 3144.
(3) Huttenhuis, P. J. G.; Agrawal, N. J.; Solbraa, E.; Versteeg, G. F. *Fluid. Phase Equilib*. **2008**, *264*, 99.
(4) Ma'mun, S; Nilsen, R; Svendsen, H.F.; Juliussen O. *J. Chem. Eng. Data* **2005**, *50*, 630.
(5) Bishnoi, S.; Rochelle, G. T. *Fluid Phase Equilib*. **2000**, *168*, 241.
(6) Li, Y.-g.; Mather, A. E. *Ind. Eng. Chem. Res.* **1996**, *35*, 4804.
(7) Dubois, L.; Thomas, D. *Chem. Eng. Technol*. **2012**, *35*, 513.
(8) Kumar, G.; Mondal, T. K.; Kundu, M. *J. Chem. Eng. Data* **2012**, *57*, 670.
(9) Zhu D; Fang, M; Lv, Z; Wang, Z; Luo, Z. *Energy Fuels* **2012**, *26*, 147.
(10) Li, J.; You, C.; Chen, L.; Ye, Y.; Qi, Z.; Sundmacher, K. *Ind. Eng. Chem. Res.* **2012**, *51*, 12081.
(11) Chowdhury, F. A; Yamada, H.; Higashii, T.; Goto, K.; Onoda, M. *Ind. Eng. Chem. Res.* **2013**, *52*, 8323-8331.
(12) Chowdhury, F. A; Okabe, H.; Yamada, H.; Onoda, M; Fujioka, Y. *Energy Procedia*, **2011**, *4*, 201.
(13) Goto, K.; Okabe, H.; Chowdhury, F. A; Shimizu, S.; Fujioka, Y.; Onoda, M. *Int. J. Greenhouse Gas Control*, **2011**, *5*, 1214.
(14) Yamada, H; Chowdhury, F. A; Goto, K.; Higashii, T. *Int. J. Greenhouse Gas Control*, **2013**, *17*, 99-105.
(15) Matsuzaki, Y; Yamada, H; Chowdhury, F. A; Higashii, T.; Onoda, H. *J. Phys. Chem. A* **2013***, 117, 9274−9281*.