Potential of Amine-based Solvents for Energy-saving CO\textsubscript{2} Capture from a Coal-fired Power Plant

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The potential of amine-based solvents was investigated by a thermodynamic analysis for low-energy CO\textsubscript{2} capture from the flue gas of a thermal power plant. The solubility of CO\textsubscript{2} into the amine-based solvent was predicted by the vapor-liquid equilibrium model on the basis of absorption reactions between CO\textsubscript{2} and amine. The model was covered for developed and developing amine-based solvents. Considering the energy consumptions of CO\textsubscript{2} capture and compression, the power output of the coal-fired power plant with a post-combustion CO\textsubscript{2} capture was estimated. The results showed that the solvent characteristics of high CO\textsubscript{2} cyclic capacity and low absorption heat had an important effect on reducing the thermal energy requirement for CO\textsubscript{2} capture. In the case of CO\textsubscript{2} capture from a 12\% CO\textsubscript{2}-containing flue gas, the lowest thermal energy requirement was estimated at approximately 2 GJ/t-CO\textsubscript{2}, and the efficiency penalty of power generation was reduced to 7.2\%pt. Also, concerning the impact of CO\textsubscript{2} capture and compression on the power generation system, 1\%pt. of power generation efficiency could be recovered by lowering 0.6 GJ/t-CO\textsubscript{2} of the thermal energy requirement of CO\textsubscript{2} capture. These results mean that the amine-based solvents still have high capability to improve energy performance of post-combustion CO\textsubscript{2} capture. However, lowering the regeneration temperature in the range of 90 °C to 130 °C did not have a significant advantage in reducing energy consumption. This comprehensive analysis for the CO\textsubscript{2} capture and compression integrated with a coal-fired power plant is useful for process evaluation, and the desire will be to extend the analysis to other applications.

Key Words
Chemical absorption, Amine, Amine-based solvent, Vapor-liquid equilibrium, Post-combustion capture

1. Introduction
Mitigation of greenhouse gas emissions is an important issue in establishing a sustainable global system. The main concern is carbon dioxide (CO\textsubscript{2}) emissions from large stationary sources into the atmosphere. One of the promising technologies is carbon dioxide capture and storage (CCS), which has been developed worldwide toward early implementation. CO\textsubscript{2} capture by chemical absorption has already been developed at the commercial technology level, but still the technological and economic advancements have been required to reduce a significant amount of thermal energy for regeneration of a chemical solvent.

Many research studies have been conducted to propose new chemical solvents that could reduce the thermal energy requirement for CO\textsubscript{2} capture. Liang \textit{et al.}\textsuperscript{1} reviewed post-combustion CO\textsubscript{2} capture technology with amine-based solvents and introduced recent progress and
new developments. They concluded that the main challenge of this technology was reduction of energy consumption.

Also a thermal power plant with CO₂ capture is investigated to clarify the impact of CCS on power generation systems from the viewpoint of energy and cost 2) ~ 5). Most notably, the coal-fired power plant has the largest share of the power supply source and the largest CO₂ emission source. It must be the first target for CCS.

Fig. 1 shows the schematic diagram of the coal-fired power plant with CO₂ capture and compression. The CO₂ capture system needs steam for solvent regeneration and electrical energy for solvent circulation. Captured CO₂ is compressed to high pressure for transportation. Because of energy consumption at the capture and the compression processes, the output of the power plant with CO₂ capture decreases. Generally, installation of CO₂ capture and compression into the power plant makes output of the host power plant two-thirds for CO₂ capture using a conventional solvent, such as an aqueous monoethanolamine solution 6). With a state-of-the-art technology for CO₂ capture with new amine alternatives, the efficiency penalty has been estimated lower. However, the performance limit of the amine-based solvents has not been estimated reliably and advanced alternatives have been investigated on a continuing basis.

In this study, we focus on the energy balance of the coal-fired power plant with CO₂ capture and compression. A simple overall evaluation method with a vapor-liquid equilibrium (VLE) model of amine-based solvents is developed to estimate both the energy requirement of CO₂ capture and the energy consumption for post combustion CO₂ capture integrated with the coal-fired power plant. Also, we discuss the potential of amine-based solvents.

2. Methodology
2.1 CO₂ solubility modeled based on CO₂-Amine-H₂O system
The amine-based solvents are commercially used for CO₂ capture from a low partial pressure of CO₂ by a chemical absorption process because they have a high affinity toward CO₂. Amines react with CO₂ to generate several ionic species, and two typical reactions are facilitated in polar environments such as aqueous solutions. The following reactions of CO₂ with amines were approximated by a single equilibrium. One reaction scheme is that an amine reacts with CO₂ to form a protonated cation and a carbamate anion as shown in the following equations (I). The other is a reaction to form a bicarbonate anion (II):

\[
\begin{align*}
2R^1R^2NH + CO_2 &\rightarrow R^1R^2NH_2^+ + R^1R^2NCOO^- \\
R^1R^2NH + CO_2 + H_2O &\rightarrow R^1R^2NH_2^+ + HCO_3^- 
\end{align*}
\]

R¹ and R² represent substituents. A primary or secondary amine has the potential to carry out both reactions, but a tertiary amine reacts with CO₂ through the second reaction only. The reaction (II) can have a higher theoretical capacity of one mole of CO₂ per mole of amine.

The VLE model in this study was based on an assumption of parallel reactions of (I) and (II), and CO₂ physical absorption following Henry’s Law. The equilibrium vapor pressure of CO₂ can be calculated as

\[
p_{CO_2} = K \cdot \left( \frac{1 - n}{1 - (2 - n)n} \right) \cdot a_1^{1-n} \cdot a_2 \cdot a_3^{1-n}
\]

where, a₁ is an overall amine molar concentration, and α is the molar ratio of CO₂ to amine (CO₂ loading), n is the molar ratio of CO₂ absorbed as bicarbonate anion to the total CO₂ absorbed. Namely, it is the probability of reaction (II) occurring and was set as a constant for each amine. Further information on deriving the Eq. (I) is explained in Appendix A.

Regarding a reaction equilibrium constant, it is possible to use equilibrium constant values at different temperatures to calculate using the Arrhenius type equation (Eq. 2).

\[
K = A \exp \left( - \frac{B}{RT} \right)
\]
If \( B \) is considered as a change in the standard enthalpy during absorption, Eq. (2) means the Van’t Hoff equation, which was utilized in previous studies. In this study, a wide range of CO\(_2\) absorption conditions shown in Table 1 were investigated to simulate various solvents with different VLE characteristics.

### 2.2 Estimation of energy consumption

#### 2.2.1 Thermal energy requirement of CO\(_2\) capture

Fig. 2 illustrates the process flow of chemical absorption for CO\(_2\) capture. The flue gas (CO\(_2\)-containing gas) and the amine-based solvent are contacted with counter-current flow at the absorber. The CO\(_2\)-absorbed rich solvent flows from the bottom of the absorber to the top of the regenerator via a rich-lean heat exchanger. The temperature of the rich solvent rises by ascending vapor from the bottom of the regenerator. After CO\(_2\) desorption from the solvent in the regenerator occurs, the lean solvent is recirculated to the absorber. Chemical absorption requires a significant amount of thermal energy during regeneration of the solvent. The reduction of the thermal energy requirement at the reboiler is currently the main challenge in the developments of novel CO\(_2\) capture technology.

Generally, steam is supplied to a reboiler, an indirect heat exchanger, as the thermal energy for regeneration. The thermal energy is used for three purposes, such as the sensible heat of the solvent, heat of desorption, and vapor latent heat. Therefore, the thermal energy can be represented as follows.

\[
Q_{\text{cap}} = Q_{\text{sen}} + Q_{\text{des}} + Q_{\text{vap}} \tag{3}
\]

Their terms of heat consumptions were estimated by Eq. (4) ~ Eq. (6).

\[
Q_{\text{sen}} = C_{\text{ps}} W \Delta T_s \tag{4}
\]

\[
Q_{\text{des}} = \frac{\Delta H_{\text{des}}}{M_{\text{CO2}}} \tag{5}
\]

\[
Q_{\text{vap}} = \frac{p_{\text{H2O}} - p_{\text{CO2}}}{p_{\text{CO2}}} \Delta H_{\text{vap}} \tag{6}
\]

Table 2 is a summary of parameters to calculate the thermal energy requirement in a thermodynamic analysis of the CO\(_2\) capture process. Heat loss from a capture plant can be ignored because CO\(_2\) capture capacity for CCS will be ten times greater than a conventional plant operated by industry.

#### 2.2.2 Electrical energy consumptions of CO\(_2\) capture and compression

The electrical energy consumption for CO\(_2\) capture and compression is the other energy consumption at CCS equipment. By reference to the energy calculation presented by Okabe et al., energy consumption of a blower, a solvent circulation pump and a compressor were considered.

The electrical energy consumptions of a blower and a solvent circulation pump were calculated by Eq. (7) and Eq. (8), respectively.

\[
P_{\text{blow}} = \frac{n_\text{EB}}{3600} \left( \rho g h + \rho_{\text{in}} v_{\text{in}} - \rho_{\text{out}} v_{\text{out}} \right) q_s \eta_{\text{EB}} \tag{7}
\]

\[
P_{\text{pump}} = \frac{N \gamma p_{\text{in}} (\gamma - 1)/\gamma}{\eta_{\text{EP}}} \tag{8}
\]

The electrical energy consumption of a compressor was calculated by Eq. (9). Here, \( \eta_{\text{EC}} \) is the adiabatic efficiency of compression.

\[
P_{\text{comp}} = \frac{N \gamma}{\eta_{\text{EC}}} \left( \frac{P_{\text{out}}}{P_{\text{in}}} \right)^{(\gamma - 1)/\gamma} - 1 \right] \frac{1}{3600} \tag{9}
\]

Table 3 is a summary of parameters to calculate the electrical energy consumption in energy analysis of the CO\(_2\) capture and compression.

### 2.3 Coal-fired power plant with CO\(_2\) capture and compression

As mentioned in the previous review, the efficiency penalty refers to the power generation loss by installing
CCS in a power plant and is generally considered the difference in thermodynamic performance between power plants with and without CCS. The CO₂ capture and compression processes require both thermal energy and electrical energy, and these result in a decrease in power output. In this regard, the efficiency penalty could be considered an index for evaluating whether a power plant with CCS is energy efficient.

Fig. 1 shows a schematic diagram of a coal-fired power plant with CO₂ capture and compression processes that obtain their energy for operation from the host power plant. The net power output is expressed with Eq.(10).

\[
E_{\text{net}} = E_{\text{gross}} - E_{\text{aux}} - (E_{\text{cap,Q}} + E_{\text{cap}} + E_{\text{comp}}) \tag{10}
\]

where \( E_{\text{cap,Q}} \) represents electrical energy equivalent to thermal energy of reboiler steam at a capture process. \( E_{\text{cap}} \) and \( E_{\text{comp}} \) are the electrical energy consumptions for CO₂ capture and compression. They were estimated by the following equations in this study.

\[
E_{\text{cap,Q}} = \eta_T M \eta_T Q_{\text{cap}} \tag{11}
\]
\[
E_{\text{cap}} = (P_{\text{blow}} + P_{\text{pump}}) \cdot w_{\text{CO2}} \tag{12}
\]
\[
E_{\text{comp}} = P_{\text{comp}} \cdot w_{\text{CO2}} \tag{13}
\]

where \( \eta_T \) is a thermodynamic efficiency and \( \eta_M \) is the efficiency relevant to the other system losses. The latter includes turbine efficiency and generator efficiency and was 0.76 in this study. The Carnot efficiency is used for \( \eta_T \), expressed in Eq. (14).

\[
\eta_T = \frac{(T_{\text{reg}} + \Delta T) - T_{\text{sink}}}{(T_{\text{reg}} + \Delta T)} \tag{14}
\]

Eq. (14) includes temperature of regeneration steam and implies that the lower temperature makes the energy consumption lower. Fig. 3 shows the effect of the regeneration steam temperature on the conversion coefficient of thermal energy to electrical energy (\( \eta_{\text{el}} \cdot \eta_T \)). The conversion coefficient used in this study is in the similar range to the previous literatures 4, 5, 10.

The net power generation efficiency, \( \eta_{\text{net}} \), can be calculated by dividing the net power output to the lower heating value (LHV) of coal. The efficiency penalty of a power plant with CCS is a decrease in comparison with power output efficiency between a power plant without CCS and with CCS. Table 4 is a summary of the parameters to conduct the energy analysis of a coal-fired power plant with CO₂ capture and compression.

### 3. Results and Discussions

#### 3.1 Prediction of CO₂ solubility

Conventional amines were simulated on CO₂ solubility by the VLE model of amine-based solvents in Fig. 4. The primary alkanolamine, MEA, absorbs CO₂ into the solvent.
mainly as a carbamate anion. As shown in Table 5, \( n = 0.19 \) was applied for MEA based on the result of NMR (Nuclear Magnetic Resonance) analysis \(^{11}\). Tertiary amine, MDEA, absorbs CO\(_2\) only as bicarbonate anion. There was a difference between prediction and measurement results in the low temperature and high CO\(_2\) partial pressure condition because the fraction of bicarbonate, \( n \), was fixed in the all CO\(_2\) loading range. However, the model could acceptably estimate the conditions of absorption and desorption for a conventional chemical absorption process. The estimated VLEs of the three representative amines sufficiently coincided with the measurement results.

Furthermore, in order to confirm the validity of the VLE model, CO\(_2\) cyclic capacity for 10 amines were examined as shown in Fig. 5. CO\(_2\) cyclic capacity was defined as the difference of CO\(_2\) loadings between at 40°C/12 kPa\(_{\text{CO}_2}\) and at 120°C/20-22 kPa\(_{\text{CO}_2}\). Calculated results show a good accordance with measurement data. Fig. 5 also shows that the cyclic capacity relatively increases with \( n \), the ratio of bicarbonate anion. In the calculation of the simulated solvents (\( n = 1; A1 \sim A4 \) in Table 5), the maximum CO\(_2\) cyclic capacity could reach 0.83 mol-CO\(_2\)/mol-amine in CO\(_2\) loading.

### 3.2 Thermal energy requirement of CO\(_2\) capture

Thermal energy requirement was investigated for post-combustion CO\(_2\) capture at a coal-fired power plant. The VLE mode was executed in the range of 11-45 in A and 40-100 in B. In addition, the absorption heat studied was fixed at 60, 70 and 80 kJ/mol for possible amine-based solvents. Other analytical conditions were shown in Table 2. The parameter B is often discussed in connection with the activation energy of a reaction \(^{7,8}\), but the parameter B and desorption heat were treated, respectively, in this study because of the mixed reaction of CO\(_2\) absorption reaction treated with a single overall in the VLE model.

The result in Fig. 6 shows that the lowest value in the thermal energy requirement was 21 GJ/t-CO\(_2\), and that large cyclic capacity and low absorption heat made the

| No. | Amine\(^*1\) | \( n \) | A | B | \( \Delta \alpha_{\text{CO}_2}(\text{calc}) \)\(^*2\) | \( \Delta \alpha_{\text{CO}_2}(\text{meas}) \)\(^*2\) | \( \Delta H_{\text{abs}} \)\(^*3\) |
|-----|--------------|------|---|---|-----------------|-----------------|------------------|
| 1   | MEA          | 0.19 \(^{11}\) | 301| 82 | 0.28            | 0.28 \(^{11}\)   | 88 \(^{15}\)       |
| 2   | AMP          | 0.96 \(^{11}\) | 30.2| 77 | 0.60            | 0.61 \(^n\)     | 79 \(^{23}\)       |
| 3   | EAE          | 0.67 \(^{11}\) | 27.2| 70 | 0.47            | 0.48 \(^{13}\)   | 78 \(^{23}\)       |
| 4   | PAE          | 0.73 \(^{11}\) | 27.4| 70 | 0.50            | 0.51 \(^{12}\)   | 68 \(^{20}\)       |
| 5   | IPAE         | 0.91 \(^{11}\) | 30.5| 78 | 0.61            | 0.60 \(^{12}\)   | 68 \(^{20}\)       |
| 6   | DEA          | 0.40 \(^{11}\) | 31.5| 78 | 0.40            | 0.40 \(^{n}\)   | 60 \(^{23}\)       |
| 7   | DMAE         | 1             | 29.9| 75 | 0.55            | 0.54 \(^{n}\)   | 62 \(^{23}\)       |
| 8   | DEAE         | 1             | 31.0| 80 | 0.67            | 0.67 \(^{10}\)   | 59 \(^{20}\)       |
| 9   | MDEA         | 1             | 28.0| 66 | 0.32            | 0.34 \(^{10}\)   | 60 \(^{20}\)       |
| 10  | TEA          | 1             | 27.5| 60 | 0.15            | 0.16 \(^{n}\)   | 50 \(^{23}\)       |
| 11  | A1(calc)     | 1             | 15.0| 40 | 0.41            | -               | -                |
| 12  | A2(calc)     | 1             | 22.0| 60 | 0.60            | -               | -                |
| 13  | A3(calc)     | 1             | 29.0| 80 | 0.74            | -               | -                |
| 14  | A4(calc)     | 1             | 36.0| 100| 0.83            | -               | -                |

\(^*1\) MEA: monoethanolamine, AMP: 2- amino-2-methyl-1-propanol, EAE: 2-(ethylamino)ethanol, PAE: 2-(propylamino)ethanol, IPA: 2-(isopropylamino)ethanol, DEA: diethanolamine, DMAE: 2-(dimethylamino)ethanol, DEAE: 2-(diethylamino)ethanol, MDEA: N-methyl(diethanolamine, TEA: triethanolamine, A1 ~ A4: Hypothetical amines, whose VLEs were estimated by parameters in Table 5

\(^*2\) \( \Delta \alpha_{\text{CO}_2} \) is a difference between CO\(_2\) loadings at 40°C/12 kPa\(_{\text{CO}_2}\) and at 120°C/20-22 kPa\(_{\text{CO}_2}\)

\(^*3\) \( \Delta H_{\text{abs}} \) is assumed equal to \( \Delta H_{\text{des}} \)

\(^*4\) Data was measured in the same method of the references \(^{12} \sim {14}\)

\(^*5\) Data was measured in the same method of the reference \(^{15}\)
thermal energy requirement small. Considering about the current solvent performance of about 3 GJ/t-CO₂ in thermal energy requirement, amine-based solvents have the high capability to reduce it. As shown in Table 5 and Fig. 5, one of key research concepts to develop advanced solvents should be to investigate amines classified into hindered or tertiary amines which mainly form a bicarbonate anion.

Low-temperature regeneration, which was attractive because of the capability to use low-grade waste heat, was evaluated for CO₂ capture with the amine-based solvents. Fig. 7 shows the effect of the regeneration temperature on the thermal energy requirement for simulated amine-based solvents. In the range from 90 °C to 130 °C, the thermal energy requirement of each solvent was slightly increased with lowering regeneration temperature. At 130 °C in temperature, the thermal energy requirement was 2.0 GJ/t-CO₂. Obviously, the temperature change had an effect on regeneration pressure.

Although the effect of regeneration temperature on the thermal energy requirement was small in this study, this analysis based on vapor-liquid equilibrium did not consider decreases in reaction kinetics and mass transport phenomena. That is, their effects increase the difference from equilibrium and may increase thermal energy requirement.

3.3 Decrease in power generation efficiency

Energy analysis of a coal-fired power plant with CO₂ capture and compression was carried out to evaluate the potential of amine-based solvents. Fig. 8 shows the effects of the thermal energy requirement of the amine-based solvent on the efficiency penalty of power generation. A decrease in power output is caused by gross power reduction by extraction of regeneration steam, electrical energy consumption of CO₂ capture, and electrical energy consumption of CO₂ compression. The gross power reduction was directly related to the performance of the amine-based solvent. As shown in Fig. 8, lowering the thermal energy requirement of the amine-based solvent contributes to the reduction in efficiency penalty. In the case of 2.0 GJ/t-CO₂ in thermal energy requirement, the efficiency penalty was estimated at 7.2 %pt. In order to recover 1%pt. in the efficiency penalty, it is necessary to decrease 0.6 GJ/t-CO₂.

Fig. 8 also indicates that lowering the thermal energy requirement makes the ratio of that to overall efficiency penalty small. That means, in the next stage, CO₂ compression and the steam cycle of a power plant should be examined in detail.

If steam quality, such as temperature and pressure, required by the CO₂ capture process is controlled in the
low level, efficiency penalty could be reduced as shown in Fig. 3. Fig. 9 shows the effect of regeneration temperature on the efficiency penalty. By the decrease in regeneration temperature, the efficiency penalty caused by steam extraction was reduced, but the efficiency penalty by CO2 compression was increased. As a result, the efficiency penalty stayed almost constant independent of the regeneration temperature.

4. Conclusions

The potential of amine-based solvents was examined by a simple thermodynamic analysis for low-energy CO2 capture from the flue gas from a thermal power plant. CO2 solubility of the amine-based solvents was modeled on the basis of CO2-amine reactions and they were covered for developed and developing ones. The power output of the coal-fired power plant with CCS was estimated combining the energy consumptions of both CO2 capture and compression.

The results showed that the solvent characteristics of high CO2 cyclic capacity and low absorption heat had a critical effect on reducing the thermal energy requirement for CO2 capture. In the case of CO2 capture from 12% CO2-containing flue gas, the lowest thermal energy requirement was shown as approximately 2 GJ/t-CO2, and the efficiency penalty of power generation was reduced to 7.2%. Concerning the impact of CO2 capture and compression on the power generation system, 1%pt. of power generation efficiency could be recovered by lowering 0.6 GJ/t-CO2 of the thermal energy requirement of CO2 capture. The low energy requirement of CO2 capture means that the ratio of energy consumption of CO2 compression to the total energy penalty is high; therefore, CO2 compression and the steam cycle should be analyzed in detail in the next stage. Additionally, regeneration temperature in the range of 90 °C to 130 °C did not have a significant effect on energy consumption.

The results mean that amine-based solvents are still attractive in post-combustion CO2 capture. This comprehensive analysis for a CO2 capture and compression integrated with a thermal power plant was for process evaluation and will be extended to apply to other amine-based CO2 capture technologies and other CO2 emission sources.

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Nomenclature

\( A, B \) parameters in Eq. (2) [\( \text{kJ/mol} \)]

\( a_0 \) amine concentration [mol/L]

\( C_s \) specific heat of solvent [\( \text{kJ/(kg K)} \)]

\( E_{\text{aux}} \) auxiliary power consumption in a power plant [kW]

\( E_{\text{cap}} \) electrical energy consumption for CO2 capture process [kW]

\( E_{\text{cap,Q}} \) decrease in gross power output by steam extraction for CO2 capture process [kW]

\( E_{\text{comp}} \) electrical energy consumption for CO2 compression process [kW]

\( E_{\text{gross}} \) gross power output [kW]

\( E_{\text{net}} \) net power output [kW]

\( \Delta \) acceleration of gravity [m/s²]

\( H \) Henry’s constant [kPa L/mol]

\( \Delta H_{\text{abs}} \) enthalpy change of CO2 absorption into solvent or heat of absorption [kJ/mol]

\( \Delta H_{\text{des}} \) enthalpy change of CO2 desorption into solvent or heat of desorption [kJ/mol]

\( \Delta H_{\text{vap}} \) enthalpy change of vaporization [kJ/mol]

\( h \) pump head [m]

\( K \) overall equilibrium constant, \( K = H/K' \) [kPa]

\( K' \) equilibrium constant [L/mol]

\( M_{\text{CO2}} \) molecular weight of CO2 [g/mol]

\( M_{\text{H2O}} \) molecular weight of H2O [g/mol]

\( N \) compression stage number [-]

\( n \) ratio of bicarbonate anion to absorbed CO2 [-]

\( n_a \) amount of substance for a tonne of flue gas [kmol/t]

\( P_{\text{blow}} \) electrical energy consumption of flue gas blower [kWh/t]

\( P_{\text{pump}} \) electrical energy consumption of solvent circulation pump [kWh/t]

\( P_{\text{comp}} \) electrical energy consumption of CO2 compression
The ratio of CO₂ absorbed to amine molecule [mol-CO₂/μ]

η  

η  

η  

η  

η  

η  

η  

η  

ρ  

ρ  

ρ  

ρ  

ρ  

ρ  

ρ  

ρ  

References

1) Liang, Z.; Rongwong, W.; Liu, H. et al., Int. J. Greenh. Gas Control, 40, 26-54 (2015)
2) Metz, B.; Davidson, O.; de Coninck H.; Loos, M.; Meyer, L., Carbon Dioxide Capture and Storage. IPCC, Cambridge University Press, (2005)
3) Oexmann, J.; Hensel, C.; Kather, A., Int. J. Greenh. Gas Control, 2, 539-552 (2008)
4) Lucquiaud, M.; Gibbins, J., Chem Eng Res. Des., 89, 1553-1571 (2011)
5) Hagi, H.; Neveux, T.; Le Moullac, Y., Energy, 91, 306-323 (2015)
6) Goto, K.; Yogo, K.; Higashii, T., Applied Energy, 111, 710-720 (2013)
7) Kim, I.; Hoff, K. A.; Hessen, E. T.; Haug-Wrberg, T.; Svendsen, H. F., Chem. Eng. Sci., 64, 2027-2038 (2009)
8) Mathias, P. M.; O’Connell, J. P., Ind. Eng. Chem. Res., 51, 5090-5097 (2012)
9) Okabe, K.; Mano, H.; Fujioka, Y., Int. J. Greenh. Gas Control, 2, 485-491 (2008)
10) Freeman, S. A.; Dugas, R.; Van Wagener, D.; Nguyen, T.; Rochelle, G. T., Energy Procedia, 1, 1489-1496 (2009)
11) Yamada, H.; Shimizu, S.; Okabe, H.; Matsuizaki, Y.; Chowdhury, F. A.; Fujioka, Y., Ind. Eng. Chem. Res., 49, 2449-2455 (2010)
12) Yamada, H.; Chowdhury, F. A.; Goto, K.; Higashii, T., Int. J. Greenh. Gas Control, 17, 99-105 (2013)
13) Yoma, H.; Higashii, T.; Chowdhury, F. A.; Goto, K.; Kazama, S., WIT Trans. Ecol. Environ., 157, 515-523 (2012)
14) Chowdhury, F. A.; Okabe, H.; Shimizu, S.; Fujioka, Y., Energy Procedia, 1, 1241-1248 (2009)
15) Goto, K.; Okabe, H.; Chowdhury, F. A.; Shimizu, S.; Onoda, M., Int. J. Greenh. Gas Control, 5, 1214-1219 (2011)
16) Chowdhury, F. A.; Yamada, H.; Higashii, T.; Matsuzaki, Y.; Kazama, S., Energy Procedia, 37, 265-272 (2013)

Appendix A

“VLE model of CO₂ absorption into amine-based solvent”

CO₂ absorption into an amine-based solvent is generally expressed in the two reactions (I) and (II) shown in Section 2.1. In this study, the following reaction (Ia) is modelled by combining the two reactions in order to calculate CO₂ solubility of amine-based solvents.

\[
(2 - n)\text{R}_1\text{R}_2\text{NH}_2 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow (1 - n)\text{R}_1\text{R}_2\text{NCOO}^- + n\text{HCO}_3^- \quad \text{(Ia)}
\]

where each ionic species can be given with \( n, a_0 \) and \( a_\). They are the ratio of bicarbonate in CO₂ absorption, initial amine concentration and CO₂ loading, respectively.

\[
[\text{R}_1\text{R}_2\text{NCOO}^-] = (1 - n)a_0 \quad \text{(2a)}
\]

\[
[\text{HCO}_3^-] = n a_0 \quad \text{(3a)}
\]

In addition, physical gas transfer from gas to liquid can be assumed with Henry’s law:

\[
[H][\text{CO}_2] \quad \text{(5a)}
\]

Using the equations above, CO₂ solubility can be expressed as follows:
For the CO₂ absorption by only carbamate anion, (6a) can be modified:

\[
p_{\text{CO}_2} = K \frac{(1-n)^{1-\alpha} n \alpha a_O^2}{[1 - (2-n)\alpha a_o]^\alpha} \tag{6a}
\]

(0 < n < 1)

For the CO₂ absorption by only bicarbonate, (6a) can be modified:

\[
p_{\text{CO}_2} = K \left( \frac{\alpha}{1-2\alpha} \right)^2 \tag{7a}
\]

(n = 0)

Also, (8a) is for CO₂ absorption by only bicarbonate.

\[
p_{\text{CO}_2} = K \frac{\alpha a_o}{1 - \alpha} \tag{8a}
\]

(n = 1)

Fig. A-1 explains the sensitivity of the parameters on the VLE curves of the amine-based solvents. When the parameter A becomes larger or the parameter B becomes smaller, the VLE curves shift to higher region of CO₂ partial pressure. B has another influence to widen the difference of the VLE curves between temperatures. The ratio of bicarbonate anion to sum of carbamate and bicarbonate anions, n, has a direct influence on maximum CO₂ loading. Therefore, the proposed model could simulate various VLE curves by setting the parameters.