CHEMICAL ENGINEERING TRANSACTIONS

VOL. 70, 2018

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Timothy G. Walmsley, Petar S. Varbanov, Rongxin Su, Jiří J. Klemeš

ISBN 978-88-95608-67-9; **ISSN** 2283-9216

DOI: 10.3303/CET1870010

Experimental Study of CO_2 Chemical Absorption Kinetics by a Thermomorphic Lipophilic Biphasic Solvent

Daniele P. Tristano[a,b], Rodrigo Rivera-Tinoco[a], Chakib Bouallou[a,*]

[a]MINES ParisTech, PSL Research University, Centre for Energy Efficiency of Systems; 60 bd Saint Michel, Paris, France
[b]Politecnico di Milano, Dipartimento di Energia, Via Lambruschini, 4, 20156 Milano MI, Italy
chakib.bouallou@mines-paristech.fr

Chemical absorption is a frequently used post-combustion process that separates CO_2 from gaseous compounds of the flue gases with the use of specific solvents for which the main drawback is their cost of regeneration. In order to overcome this problem, the new Thermomorphic Lipophilic Biphasic solvents are here studied. The limited solubility of the Lipophilic amines in water offers a new degree of freedom while optimizing the global process: it is in fact possible to carry out the absorption with an initial biphasic solvent (organic, aqueous) that evolves towards a mono-phase solvent after a certain amount of CO_2 is absorbed. This work aims at assessing experimentally the CO_2 absorption kinetic into a Lipophilic amine based solvent, namely 3 M 1:3 DPA (dipropylamine) + DMCA (dimetylcyclohexylamine) + water using a Lewis Cell type reactor. Activation energy values obtained by the Arrhenius law show similar values for those of benchmark amines and the selected solvent seems to require less energy to start the chemical reaction.

1. Introduction

Carbon dioxide capture and storage (CCS) is considered a crucial strategy to meet the CO_2 emission reduction targets. The Intergovernmental Panel on Climate Change (IPCC) 5th Assessment Report (AR5) issued in 2013–14 indicates that it is necessary to keep the temperature rise lower than 2°C relative to preindustrial levels in order to avoid the worst effects of climate change. This means that CO_2 emissions should accordingly be reduced globally by 41-72 % with respect to 2010 levels (IPCC, 2013). Among the different approaches CCS may lead to a reduction in CO_2 emissions of about 85 – 90 %, CCS is suitable if coupled with large emissions sources such as power production utilities and energy intensive emitters, e.g. cement kiln plants (Leung et al., 2014). In this case the Carbon Dioxide is captured from the flue gases, separated from the solvent, transported and finally either stored permanently, reutilized industrially or sold. Around the 70-80 % of the total cost of a full CCS system including capture, transport and storage arises from the capture technologies (Blomen et al., 2011). Frequently is considered the use of post combustion processes to capture such carbon emissions in an existing plant without important modification. A liquid sorbent is used to separate the CO_2 from the flue gases. The sorbent can be regenerated through a stripping or regenerative process by heating and/or depressurization (Bhown and Freeman, 2011). Typical sorbents are monoethanolamine (MEA), diethanolamine (DEA) and potassium carbonate. The most mature method for CO_2 capture for CCS is absorption using MEA (Aaron and Tsouris, 2005), but other solvents may lead to important improvements. Other solvents such as piperazine (PZ) and anion-functionalized ionic liquids are interesting. The piperazine reacts much faster than MEA but its application is more expensive due to its higher volatility (Gurkan et al., 2010). Amine degradation, equipment corrosion and generation of volatile degradation compounds (Da Silva et al., 2013) must be monitored: amine emissions can lead to nitrosamines and nitramines, very toxic for the humans.

Clearly the benchmark solvent aqueous MEA 30 wt% is located in the single organic solvent family. The regeneration duty is one of the limits that do not allow a wide-scale adoption of CO_2 capture by gas-liquid absorption. The high energy requirement while performing CO_2 capture decreases the electrical efficiency of power plants by about 9 % for conventional solvents (Budzianowski, 2016). The flag value for the regeneration duty, valid for 30 % aqueous MEA solvents, is 4,000 kJ/kg CO_2. Overcoming the barrier of high energy requirement of gas–liquid absorption is essential for wide-scale adoption of this carbon capture technology.

Please cite this article as: Tristano D.P., Tinoco R.R., Bouallou C., 2018, Experimental study of co2 chemical absorption kinetics by a thermomorphic lipophilic biphasic solvent , Chemical Engineering Transactions, 70, 55-60 DOI:10.3303/CET1870010

Developers of novel solvents, however, need to keep in mind that while chemical reactions are involved, the rate of the reaction becomes very important (Zhang et al., 2015). The reaction rate is directly linked to the size of the equipments. Thus a higher reaction rate leads to a lower plant size and as a direct consequence, lower associated CAPEX.

Lipophilic amine aqueous solvents are located in "Two immiscible liquid phases" family. Generally during the absorption the solvent shows a unique phase; during regeneration, a liquid-liquid phase split occurs. The formed phases are a CO_2-lean organic phase (on top) and a CO_2-rich aqueous phase (bottom). The main advantage is the possibility to regenerate only the aqueous phase, hence reducing the volumetric mass flow rate sent to the regeneration column. Lipophilic amine solvents refer to a particular type of amine that presents a limited solubility in water. They are less polar than alkanolamines with lower dielectric constant, due to the lack of group OH. This is why they have weaker interaction with water. Referring to last ten years of research, five main research contributions can be recognized concerning phase separation advanced solvents (Zhuang et al., 2016). They studied an important number of different amines: chain amines, cycloalkylamines, aromatic amines, cyclic amines together with others such as piperazine, monoethanolamine, etc. After the screening of an important number of candidates, one of the best proposed options is a Dipropylamine (DPA)-N,N-Dimethylcyclohexylamine (DMCA) aqueous solution. To validate this conclusion, a comparison between the cited mix and the conventional MEA-MDEA one has been performed. The optimal proposed compositions is 3 M with the ratio 1:3 DPA-DMCA. In comparison with the more conventional blend MEA+MDEA and the novel blend AMP+MDEA (sterically hindered amine + tertiary amine), for a fixed time, the DPA+DMCA mix shows a higher loading and higher percentage of CO_2 desorbed. Since both absorption and desorption performances are better, the net capacity is roughly 1.7 times the one of the MEA-MDEA solvent. At the base of the liquid-liquid phase separation, there is a lack of miscibility caused by the chemical structure of the Lipophilic amine. Another contribution comes from IFP energies nouvelles, France: the DMXTM technology. In this case, it is used an aqueous solution of a single tertiary alkanolamine with high dielectric constant. There are no phase composition data available. The developed biphasic absorbent has LCST (the lower critical solution temperature) higher than the absorption temperature.

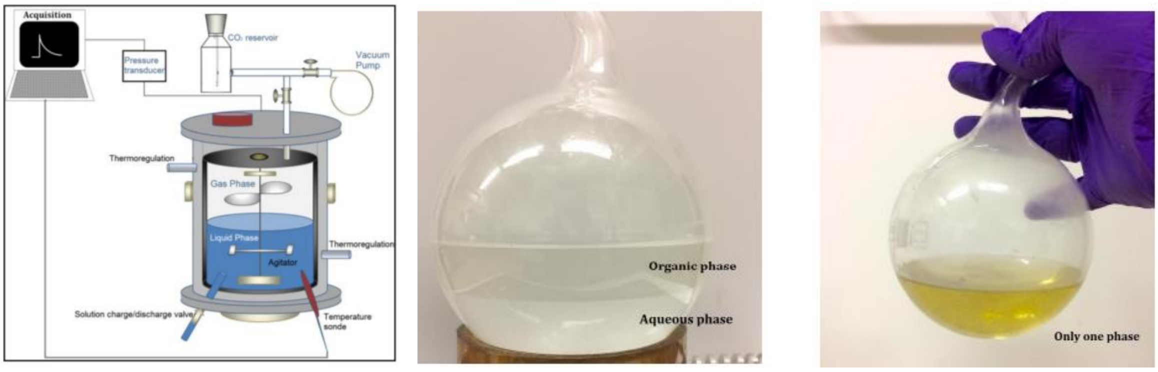
This work aims at assessing experimentally the CO_2 absorption kinetic into a Lipophilic amine based solvent, namely 3 M 1:3 DPA (dipropylamine) + DMCA (dimetylcyclohexylamine) + water using a Lewis Cell type reactor.

2. Assessment of absorption kinetics

The aim is to evaluate experimentally the kinetics of the CO2 absorption into a 3 M 1:3 DPA+DMCA aqueous solvent for three different operating temperatures. The evaluation of the kinetic parameters is a key element to foresee the size of a future pilot plant. In order to perform the experiments, a Lewis Cell based apparatus is employed. Basically by the analysis of the pressure decrease curve due to the absorption and introducing proper hypothesis on the gas-liquid mass transfer model, it will be possible to determine an "Apparent Kinetic constant", i.e. the kinetic constant which provides global information on the phenomena without entering the details of the reaction mechanism. Finally, the identification of the observed and apparent kinetic constant are carried out.

2.1 Experimental apparatus

The Lewis Cell is a closed reactor surrounded by a jacket which allows the circulation of water in order to thermo-regulate the system (Figure 1). Its internal diameter is 63 x 10^{-3} m. The effective volume is 359 x 10^{-6} m^3. For the gaseous phase the agitation is ensured by a helical 4 blades agitator; for the liquid phase the agitator is a Rushton six blades turbine, and its diameter is 42.5 x 10^{-3} m. In both cases the agitator is put in rotation via magnetic interaction. Moreover, four small Teflon made deflectors are placed inside the cell to avoid the vortex formation and a central ring stabilizes the interfacial area, allowing evaluating it. The interfacial area value is 0.001534 m^2. The pressure is captured by a DRUCK pressure captor, which is kept at 120 °C to avoid condensation problems, located at the top of the cell. The incertitude related to the pressure values is 8 % of the value itself. The main branches are the CO_2 injection one and the solvent charging/discharging one. These are located respectively on the top and at the bottom of the cell. Furthermore, it is possible to branch a vacuum pump to the cell. Concerning the hydrodynamics of the cell, a mass transfer correlation is known and established by Amararene and Bouallou (2004).



(a) (b) (c)

Figure 1: Experimental apparatus (a), visual properties of the amine prior to CO_2 capture (b), visual properties of the amine after CO_2 capture (c)

2.2 Amine properties

Thermo-physical properties of the solvent mixture are hardly predicted because the properties are barely known for single DPA and DMCA. In literature most of the known data are related to the CO_2 interaction with classic solvents such as MEA and MDEA. Properties, such as CO_2 diffusion coefficient in the solvent, Henry's constant, the density and viscosity of the solvent are considered as presented here-after.
The density and viscosity of the solvent have been evaluated using Aspen Properties. In the databank, the DPA and DMCA properties are available for pure components. The Electrolyte-NRTL model has been selected to properly consider the properties of the system. The values of the solvent density (1) and viscosity (2) for a temperature range 20 °C – 40 °C have been correlated in the following expressions. Both density and viscosity values are compared to experimental data obtained in the laboratory. A difference of 1 % was observed between calculated and experimental values.

$$\rho(\mathrm{T}) = -0.0027\times T^2 - 0.4047\times T + 925.4 \tag{1}$$

Where T is considered in °C.

$$\mu(\mathrm{T}) = 4\times 10^{-7}\times T^2 - 6\times 10^{-5}\times T + 0.0045 \tag{2}$$

Where viscosity values are expressed in Pa-s and T is considered in °C.
The values of Henry's law have been estimated using the work of Wang et al. (1991). Since correlations that estimate the Henry's coefficient are not present in the state-of-the-art for the considered solvent, in this work the following assumptions have been considered: it has been replaced the molar fraction of MDEA with the one of DMCA, and for the mix, since the DPA is present in a minor way, a fictitious DMCA* concentration has been considered, and it is equal to the sum of both DPA and DMCA molar fractions. The values have been correlated in between 20 °C and 40 °C:

$$\mathrm{H}_{\mathrm{CO_2}}(\mathrm{T}) = 0.2372\times T^2 - 25.011\times T + 4788.8 \tag{3}$$

Where Henry's constant for CO_2 in the solvent mixture is expressed in Pa m^3 mol^{-1} and T is considered in °C.

2.3 Mass transfer model

The equation (4) describes the mass transfer in presence of chemical reactions. This is the case of pseudo-first order fast reaction, in which k_L represents the gas-liquid transfer coefficient (Amararene and Bouallou, 2004).

$$\varphi = \mathrm{k_L E}\left(\mathrm{C_{in}} - \frac{\mathrm{C_{bulk}}}{\cosh(\mathrm{Ha})}\right) \tag{4}$$

Where 'in' stands for interface and bulk for liquid bulk phase. This means that the driving force is the difference between the concentration of the considered specie at the interface and the one far from it. The Enhancement factor increase the flux taking into account the presence of chemical reactions. It is worth it to notice that if the Enhancement factor is considered constant, the complex phenomenon is still described with a conventional mass transfer equation. Far from the interface it can be assumed that due to the turbulences the bulk phase is perfectly mixed hence the concentrations are constant. Assuming that the Henry's coefficient is constant and uniform, the previous equations can be rewritten in terms of pressure. The term $\cosh(Ha)$ for a Hatta number greater than 25 is greater than 10^{10}. It is possible to neglect the term $\frac{C_{bulk}}{\cosh(Ha)}$ in Eq(4). The concentration of CO_2 remains almost constant in the liquid bulk phase during a single experience. Due to the very fast chemical reaction the CO_2 absorbed does not reach the bulk phase, except for the physically dissolved one. Hence, the term of concentration of CO_2 in the bulk is manly represented by Henry constant as follows:

$$C_{CO_2\,in} = \frac{p_{CO_2}}{H_{CO_2}} - C_{CO_2,bulk} \tag{5}$$

$$C_{CO_2\,bulk} = \frac{p_{CO_2,eq}}{H_{CO_2}} \tag{6}$$

The previous flux formulation can be rewritten as shown in Eq(7):

$$\varphi = \frac{k_L E}{H_{CO_2}}\left(p_{CO_2} - p_{CO_2,eq}\right) \tag{7}$$

So now two different formulations of the same flux are obtained. Thanks to this equality it is possible to determine the “slope of the absorption”. In details:

$$\frac{V_g}{aRT}\frac{dp}{dt} = \frac{k_L E}{H_{CO_2}}\left(p_{CO_2} - p_{CO_2,eq}\right) \tag{8}$$

$$\ln\left(\frac{p_{CO_2} - p_{CO_2,eq}}{p_{CO_2,t=t_0} - p_{CO_2,eq}}\right) = \frac{k_L a\, E\, R\, T}{V_g\, H_{CO_2}}(t - t_0) = \beta(t - t_0) \tag{9}$$

From the experimental data the CO_2 partial pressure can be easily computed by subtracting from the total pressure recorded by the instrument the inert pressure, which is basically the solvent pressure. Hence it is possible to obtain the curve Pressure vs time and obtain the parameter β.

Absorption temperature:20°C	
Injection	β
a	-0.0016
b	-0.0018
c	-0.0019

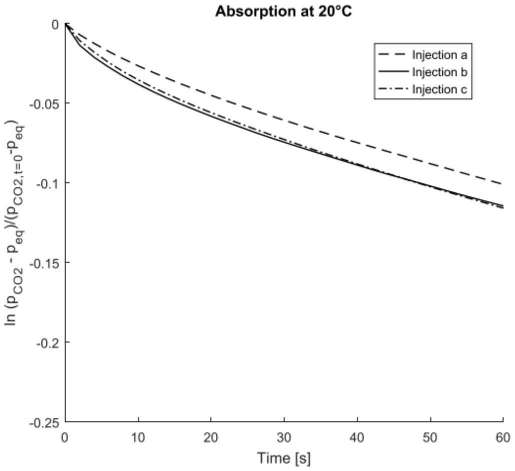


Figure 2: CO_2 absorption into DPA + DMCA 3 M at 20 °C: normalised logarithmic pressure decreases

Knowing the value of the slope, it is possible to compute the correlated Enhancement factor. The value of the observed kinetic constant can be computed. This procedure has been carried out for the three different temperatures, namely 20 °C, 30 °C and 40 °C and in triplicate tests. The apparent kinetic constant describes the chemical reaction without entering the details of the reaction mechanism. For this global apparent study, it is interesting to consider the two amines as a unique reactant in order to estimate the stoichiometric ratio between the CO_2 and the reacting amine. Finally, expressing the logarithm of k in terms of the reciprocal of the temperature, a linear trend can be obtained providing the values of the term as an Arrhenius Law. The error bars in Figure 3 refer to the repeatability test. The errors are computed as the 3.75 % of the logarithm of the average apparent kinetic constant.

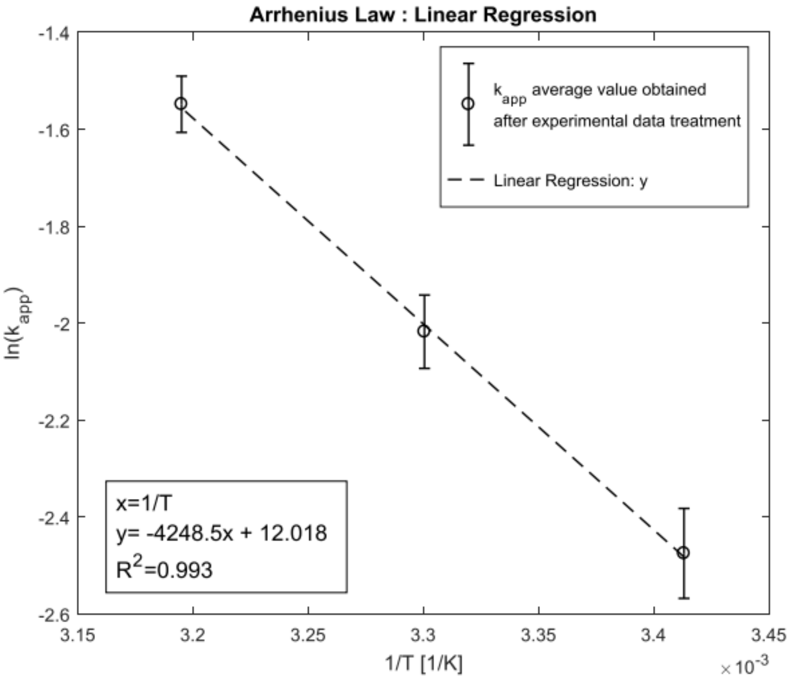


Figure 3: Arrhenius law for the apparent kinetic constant for CO_2 absorption into aqueous solution of DPA + DMCA 3 M

This is a first approximation since the thermo-physical properties of the system DPA-DMCA-Water-CO_2 are basically not known. Only previous work presented by Boulmal et al. (2017) shows apparent kinetic constants as in this work. A comparison with the values obtained by Amann and Bouallou (2009) for the solvent TETA, by Versteeg et al. (1996) for MEA and the ones obtained by Cadours and Bouallou (1998) for MDEA is below presented. It is however suggested to carry out a detailed modelling of the reaction mechanism and defining the values for specific reactions constants in order to properly describe the system (Toro-Molina et al., 2011).

Table 1: Arrhenius law comparison among amine solvents

Solvent	Work	Temperature	Arrhenius law, k [$m^3\ s^{-1}\ mol^{-1}$]
MEA	Versteeg et al. (1996)	<40 °C	$k = 4.4\times10^{8}e^{-\frac{5400}{T}}$
MDEA	Cadours and Bouallou (1998)	23 °C – 70 °C	$k = 2.96\times10^{5}e^{-\frac{5332.8}{T}}$
TETA	Amann and Bouallou (2009)	40 °C – 80°C	$k = 1.98\times10^{9}e^{-\frac{6315.3}{T}}$
DPA + DMCA	This work	20 °C – 40°C	$k = 1.657\times10^{5}e^{-\frac{4248.5}{T}}$

3. Conclusions

Experimental data shed light on several relevant points about solvents used. Amines studied show activation energy values in line with literature while comparing with other solvents. The selected solvent seems to require less energy to start the chemical reaction. No solids precipitation was observed at the end of each absorption test, which enables to envisage a similar concentration of amine in the solvent to be practically used in industrial plants. One observation, however, is the problem of foaming that requires a more accurate study to evaluate its impact on the overall efficiency of carbon capture by this solvent.

The mass transfer model seems to properly describe the total number of moles of CO_2 absorbed within the single absorption test, but it is less precise while assessing the flux from the gaseous phase to the liquid one at the very beginning of the absorption. Arrhenius law for apparent kinetic constants is for the first time available with experimental data. Moreover, this is a first approximation since the thermo-physical properties of the system DPA-DMCA-Water-CO_2 are basically not known. Concerning density and viscosity, both calculated data show a deviation of maximum 1 % from the experimental data. The later confirms that for this specific solvent, the thermodynamic model Electrolyte-NRTL considered is appropriate.

Nomenclature

a	Interfacial Area, m^2	k	Kinetic constant reaction, m^3 s^{-1} mol^{-1}
C_i	Concentration of the i specie, mol m^{-3}	k_L	Mass transfer coefficient, m s^{-1}
E	Enhancement factor	p_i	Pressure, Pa
Ha	Hatta number	T	Temperature, °C
H_i	Henry constant of the I, Pa m^3 mol^{-1}	t	Time, s
R	Ideal gas constant, Pa m^3 mol^{-1} K^{-1}	V_g	Volume of phase i, m^3

Greek alphabet

β	Slope, s^{-1}
μ	Dynamic Viscosity, Pa s
ρ	Density, kg/m^3
φ	Specific flux, mol^3 s^{-1} m^{-2}

References

Aaron D., Tsouris C., 2005, Separation of CO$_2$ from flue gas: a review, Separation Science and Technology, 40, 321-48.

Amann J.M.G., Bouallou C., 2009, A new aqueous solvent based on a blend of N-methyldiethanolamine and triethylene tetramine for CO$_2$ recovery in post-combustion: Kinetics study, Energy Procedia, 1, 901–908.

Amararene F., Bouallou C., 2004, Kinetics of carbonyl sulfide (COS) absorption with aqueous solutions of diethanolamine and methyldiethanolamine, Industrial and Engineering Chemistry Research, 43(19), 6136-6141.

Blomen E., Hendriks C., Neele F., 2009, Capture technologies: improvements and promising developments, Energy Procedia, 1, 1505-1512.

Bhown A.S., Freeman B.C., 2011, Analysis and status of post combustion carbon dioxide capture technologies, Environmental Science & Technologies, 45, 8624-8632.

Boulmal N., Rivera-Tinoco R., Bouallou C., 2017, Lipophilic amine aqueous solutions for CO$_2$ capture: Comparison of absorption rates for HexylAmine (Hxa), DiMethylCyclohexylAmine (DMCA) and Hxa-DMCA mixtures. Chemical Engineering Transactions, 61, 1201-1206.

Budzianowski W.M., 2016, Explorative analysis of advanced solvent process for energy efficient carbon dioxide capture by gas liquid absorption, International Journal of Greenhouse Gas Control, 49, 108–120.

Cadours R., Bouallou C., 1998, Rigorous simulation of gas absorption into aqueous solutions, Industrial and Engineering Chemistry Research, 37(3), 1063-1070.

Da Silva C.F., Dias A.P.B., Santana A.P.R., Pizzo J.S., De Souza F.M., Lazarin A.M., Sernaglia R.L., Andreotti E.I.S., 2013, Intercalation of amines into layered calcium phosphate and their new behaviour for copper retention from ethanolic solution, Open Journal of Synthesis Theory and Applications, 2, 1–7.

Gurkan B.E., De la Fuente F.C., Mindrup E.M., Ficke L.E., Goodrich B.F., Price E.A., Schneider W.F., Brennecke J.F., 2010, Equimolar CO$_2$ absorption by anion-functionalized ionic liquids, Journal American Chemical Society, 132, 2116-7.

Leung D.Y.C., Caramanna, G., Maroto-Valer, M., 2014, An overview of current status of carbon dioxide capture and storage technologies, Renewable and Sustainable Energy Reviews, 39, 426-443.

IPCC, 2013, Fourth assessment report: Climate change 2013.

Toro-Molina, C, Rivera-Tinoco, R, Bouallou, C., 2011, Adaptive Random Search Method + Genetic Algorithms for reaction kinetics modelling: CO$_2$ absorption systems, Chemical Engineering Transactions, 25, 19-24.

Versteeg G.F., Van Dijck L.A.J., Van Swaaij W.P.M., 1996, On the kinetics between CO$_2$ and alkanolamines both in aqueous and non-aqueous solutions, An Overview, Chemical Engineering Communications,144, 1, 113-158.

Wang Y.W., Xu S., Otto F.D., Mather A.E., 1992, Solubility of N$_2$O in alkanolamines and in mixed solvents, The Chemical Engineering Journal, 48, 31-40.

Zhang G., Yang Y., Xu, G., Zhang K., Zhang D., 2015, CO$_2$ capture by chemical absorption in coal-fired power plants: Energy saving mechanism, proposed methods and performance analysis, International Journal of Greenhouse Gas Control, 39, 449-462.

Zhuang Q., Clements B., Dai J., Carrigan L., 2016, Ten years of research on phase separation absorbents for carbon capture: Achievements and next steps, International Journal of Greenhouse Gas Control, 52, 449-460.