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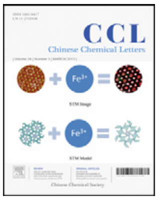

Original article

Supramolecular binding of amines with functional magnesium tetraphenylporphyrin for CO_2 capture

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ABSTRACT

In this work, magnesium tetraphenylporphyrin (MgTPP) was used as a new supramolecular amine-fixing agent. Once introduced, CO_2 easily competes with MgTPP for amines, leading to the release of MgTPP. The processes can be explained by the fact that the association constant (K_{assoc}) values of MgTPP with amines were in the range of 0.6 (ethanolamine) to 3.9 (ethylenediamine), which are lower than the K_{assoc} values of CO_2 with these amines. MgTPP interacted with aniline, ethanolamine, pyrrolidine, or ethylenediamine to form 1:1 adducts. Ethylenediamine presents a stronger K_{assoc} value for MgTPP, so it was considered an optimal agent for CO_2 capture.

1. Introduction

The concentrations of CO_2 in the atmosphere have increased because of human activities, such as the burning of fuels (oil, coal, petroleum and gas), deforestation, and hydrogen production from hydrocarbons (steam conversion and partial oxidation) [1–3]. Research has focused on ways to slow or stop this trend [4–6]. Selective removal of CO_2 from various gases is desirable for operational, economical, and environmental reasons. Chemical absorption of CO_2 using amine-based solvents, such as monoethanolamine, diethanolamine, and methyldiethanolamine [7–10], is a commercially mature technology and the preferred option for CO_2 removal [11,12]. In amine scrubbing, CO_2 reacts with an amine solvent *via* an exothermic and reversible reaction in a gas/liquid reactor. However, the subsequent mechanical breakdown, entrainment, foaming, and chemical degradation processes could lead to amine losses in the gas treatment plant. In the final step, CO_2 is removed from the solvent in a regenerator at low pressure and/or high temperature resulting in considerable vaporization and amine losses, which reduce plant performance and increase operating costs. Recently, attention has been focused on alternative amine solvents and controlling the lean amine temperature to reduce amine losses, but these changes have decreased the CO_2 loading capacity and solvent regeneration [13–15].

In this work, we present data for the use of magnesium tetraphenylporphyrin (MgTPP) as an amine-fixing agent for CO_2 capture. The amines initially form adducts with MgTPP. When CO_2 is introduced, it competes with MgTPP for the amines, which eventually leads to the release of MgTPP (Figs. 1 and 2). The amines can form adducts with the regenerated MgTPP when separated from CO_2, which may reduce amine losses. The results showed that several amines formed adducts with MgTPP and MgTPP were replaced by CO_2 during CO_2 capture (see supporting information (Fig. S1)). In the present work, only the liposoluble porphyrin complex was used. We have attempted to develop new aqueous porphyrin complexes as amine-fixing agents for CO_2 capture in our recent work.

2. Experimental

Fluorescence spectra were acquired using an F-4500 fluorescence spectrophotometer. UV–vis spectra were recorded on a Varian CARY 1E UV–vis spectrometer. All solid reagents were weighed using a Sartorius BS224S electric balance.

MgTPP was prepared using *meso*-tetraphenylporphyrin (H_2TPP, >98%) purchased from Acros Organics (New Jersey, USA). All other reagents and solvents were reagent grade and used as received.

A solution of 1.5 mL MgTPP in CH_2Cl_2 (65 μmol/L) and a series of amine solutions were kept at four temperatures for 20 min by a

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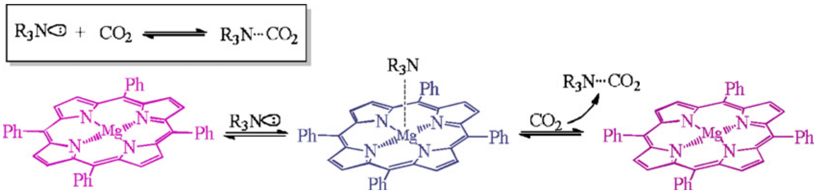

Fig. 1. An amine-fixing agent for CO_2 capture. MgTPP is initially coordinated to amines and then displaced by CO_2.

constant temperature water SPY-III bath apparatus (accuracy: ±0.01 K).

3. Results and discussion

Before the CO_2 capturing processes, we first determined the effects of CH_2Cl_2 on the binding of amines with MgTPP and CO_2. The results showed that CH_2Cl_2 can be considered an optimal solvent and does not affect the binding of MgTPP with CO_2 or the amines.

Several amines were tested in this work and the process can be monitored by the color changes of the reaction mixtures. For example, when aniline was added to the CH_2Cl_2 solution of MgTPP, the color of the MgTPP solution changed from purple to blue (Fig. 2A). This could be attributed to the interaction of MgTPP with aniline. When CO_2 gas was bubbled through the solution, the color changed from blue to violet because CO_2 competes with MgTPP for aniline and MgTPP is released. The ultraviolet–visible (UV–vis) and fluorescence spectra were collected to confirm these interpretations.

In a typical experiment, aniline was added to the MgTPP solution, and the absorbance changes were recorded on an UV–vis spectrometer (Fig. 2B). The absorption spectra showed a typical Soret band at 424 nm, which can be attributed to the $a_{1u}(\pi)$–$e_g^*(\pi)$ transition of MgTPP [16]. Similar Soret absorption peaks (B-bands) can be observed for most porphyrinic compounds [17,18]. The color of the MgTPP solution changed from purple to blue, and a bathochromic shift of 3 nm was observed for the Soret band. This suggests that MgTPP interacted with aniline to form the corresponding MgTPP–aniline adduct. When CO_2 gas was bubbled through the solution, the color changed from blue to violet, and the Soret band returned to its position for free MgTPP (Fig. 2B). This result confirmed that CO_2 competed with MgTPP for aniline, which eventually led to the dissociation of MgTPP–aniline complex and the formation of the CO_2–aniline adduct. The regenerated MgTPP was able to form amine adducts again when CO_2 was removed. MgTPP acted as a recyclable amine-fixing agent in amine scrubbing for CO_2 capture, and reduced amine losses. Under the same conditions, similar observations were made for ethanolamine, pyrrolidine, and ethylenediamine.

The reaction mechanism of MgTPP with several amines (see supporting information (Figs. S2–S4)), including aniline, ethanolamine, pyrrolidine, ethylenediamine, diethylamine, diphenylamine, and triethylamine, was investigated by a fluorescence titration experiment at four temperatures. The spectral changes were monitored by fluorescence spectroscopy ($\lambda_{ex} = 550$ nm) (Fig. 3).

When aniline (0.000–0.691 mol/L) was added to a CH_2Cl_2 solution of MgTPP (19.51 μmol/L), the emission peak of MgTPP was quenched with the sequential additions of aniline at temperatures of 298.15, 303.15, 308.15, and 313.15 K, respectively. This could be attributed to the electron transfer in the complexes between MgTPP and the electron donating amine molecules, because the amine nitrogen with lone pair electrons is coordinated to the metal center of MgTPP [19].

The binding constants of MgTPP with various amines were calculated from the fluorescence spectral data. The binding constant (K) and the binding number (n) are calculated by the following equation,

$$\mathrm{M} + n\mathrm{Q} \rightarrow \mathrm{MQ}_n \tag{1}$$

where Q denotes the quencher (the various amines), M denotes MgTPP, and MQ_n denotes their bound complex, and

$$K = \frac{[\mathrm{MQ}_n]}{[\mathrm{M}][\mathrm{Q}]^n} \tag{2}$$

where K is the intrinsic binding constant, and n is the binding number of amines to MgTPP. [M] is the concentration of free MgTPP, and $[\mathrm{MQ}_n]$ is the concentration of bound complex. If $[\mathrm{M}]_0$ is the total concentration of MgTPP,

$$[\mathrm{M}]_0 = [\mathrm{M}] + [\mathrm{MQ}_n] \tag{3}$$

and hence Eq. (2) can be replaced by

$$\frac{[\mathrm{M}]_0 - [\mathrm{M}]}{[\mathrm{M}]} = \frac{[\mathrm{MQ}_n]}{[\mathrm{M}]} = K[\mathrm{Q}]^n \tag{4}$$

In static quenching,

$$\frac{[\mathrm{M}]_0}{[\mathrm{M}]} = \frac{F_0}{F} \tag{5}$$

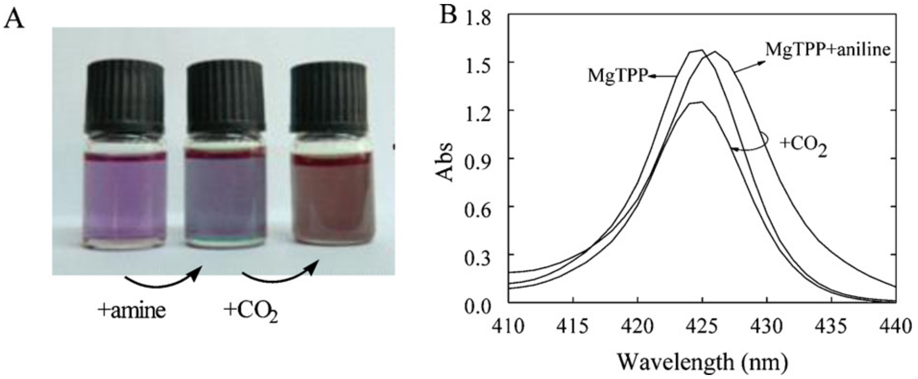

Fig. 2. (A) Photograph of MgTPP (left), MgTPP + aniline (middle), and MgTPP + aniline + CO_2 (right). (B) Changes in the absorbance spectra of MgTPP and MgTPP–aniline in CH_2Cl_2 at room temperature ([MgTPP]: 1.95×10^{-5} mol/L, [aniline]: 0.69 mol/L).

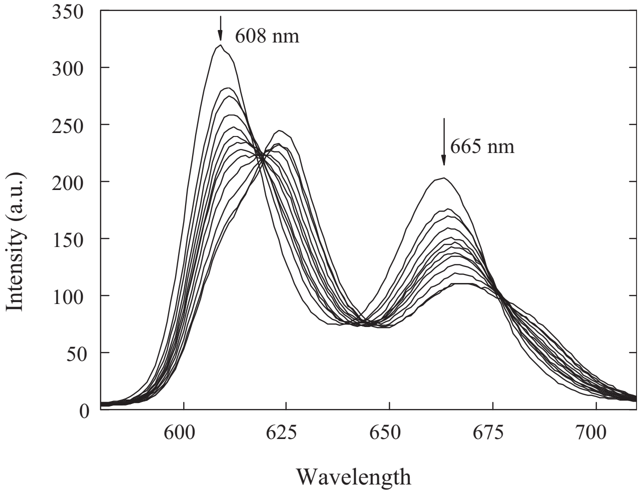

Fig. 3. Fluorescence spectral changes of MgTPP–aniline with addition of aniline in CH_2Cl_2 at 298.15 K.

where $[M]_0$ denotes the total concentration of MgTPP, [M] denotes the concentration of free MgTPP, and F_0 and F are the fluorescence intensities in the absence and presence of the amines, respectively.

The fluorescence measurements of MgTPP–amine binding were performed at four temperatures. The resulting data were analyzed using Origin software to estimate the binding affinity (K) and the enthalpy of the binding process (ΔH). Thermodynamic parameters were estimated by an analysis of the plots of $\ln K$ *vs.* $1/T$ (van't Hoff plot) obtained using the experimental data at the above temperatures [20,21]. The gradient of the straight line of a plot of $\ln K$ *vs.* $1/T$ is equal to $-\Delta H/R$, which indicates the value of ΔH and the corresponding free energy (ΔG) were calculated from Eq. (6),

$$\Delta G = -RT \ln K \tag{6}$$

The binding free energy coupled with the binding enthalpy derived from the fluorescence data allowed the calculation of the entropic contribution to the binding ($T\Delta S$), where ΔS is the calculated binding entropy using the standard relationship,

$$\Delta G = \Delta H - T\Delta S \tag{7}$$

The fluorescence titration results suggested that MgTPP interacted with aniline (Figs. 4 and 5), pyrrolidine, ethylenediamine, or ethanolamine to form 1:1 adducts.

According to previous methods [20,21], we calculated the association constants (K_{assoc}) and molar Gibbs energy of reaction (ΔG) (Table 1). Using a van't Hoff plot, the molar enthalpy (ΔH) and entropy (ΔS) of the reactions between MgTPP and amines were calculated (Table 2).

The thermodynamic data showed that interactions of MgTPP with aniline or ethylenediamine were spontaneous and entropy-driven coordination reactions. The interactions of MgTPP with ethanolamine and pyrrolidine were enthalpy-driven coordination reactions, and the latter interactions may spontaneously occur at low temperature. The ΔH values indicated that these coordination reactions are endothermic processes except for the reaction with pyrrolidine. However, the UV–vis and fluorescence spectra showed that the interactions between MgTPP and diethylamine were weak, and MgTPP hardly interacted with diphenylamine or triethylamine (see supporting information (Figs. S5–S7)). Steric hindrance could have contributed to these results [22].

Rudkevich reported that the K_{assoc} values for Zn-tetraphenylporphyrin (ZnTPP) with amines were between 7.0×10^2 (diethylamine) and 7.0×10^4 (quinuclidine) [23]. However, the binding constants between CO_2 and amines are about 10 [24,25]. In the present study, the K_{assoc} values of MgTPP with amines were between 0.6 (ethanolamine) and 3.9 (ethylenediamine). The binding constants between MgTPP and amines are smaller than or comparable to those between CO_2 and amines, and it is easier for CO_2 gas to compete with MgTPP for amines than with ZnTPP.

Thermodynamic data for the binding of MgTPP with amines were calculated. The results suggested that central magnesium ion of MgTPP interacted with aniline, pyrrolidine, ethanolamine, and ethylenediamine to form 1:1 adducts. The aniline, pyrrolidine, and ethanolamine only present an *N* atom, so one MgTPP molecule only binds one amine molecule. On the other hand, the ethylenediamine

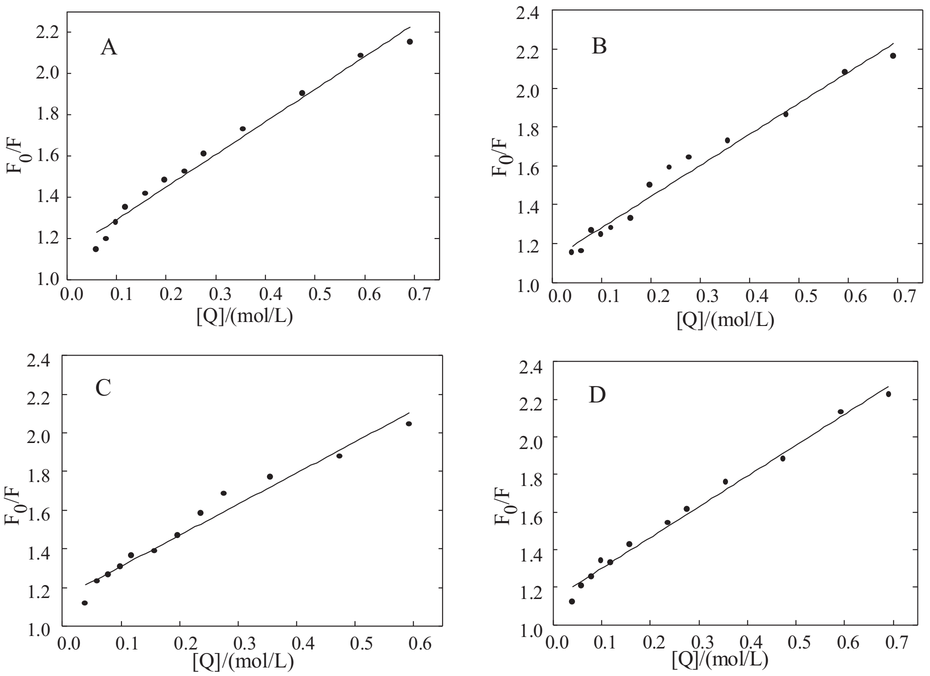

Fig. 4. Plots of F_0/F *vs.* [Q] for MgTPP with aniline at 298.15 K (A, $R^2 = 0.981$, $K_{assoc} = 1.585 \pm 0.069$), 303.15 K (B, $R^2 = 0.976$, $K_{assoc} = 1.600 \pm 0.075$), 308.15 K (C, $R^2 = 0.969$, $K_{assoc} = 1.613 \pm 0.055$), and 313.15 K (D, $R^2 = 0.989$).

Table 1
The association constants (K_{assoc}) and ΔG of binding of MgTPP with amines (a: ethanolamine; b: aniline; c: ethylenediamine; and d: pyrrolidine).

T (K)	K_{assoc}				ΔG (kJ/mol)			
	a	b	c	d	a	b	c	d
298.15	0.584 ± 0.024	1.585 ± 0.069	3.901 ± 0.040	1.190 ± 0.044	1.333	−1.141	−3.374	−421.075
303.15	0.646 ± 0.048	1.600 ± 0.075	4.002 ± 0.167	1.091 ± 0.017	1.101	−1.186	−3.495	−214.444
308.15	0.686 ± 0.029	1.613 ± 0.055	4.113 ± 0.124	0.993 ± 0.021	0.966	−1.225	−3.622	17.588
313.15	0.784 ± 0.030	1.638 ± 0.055	3.965 ± 0.071	0.860 ± 0.031	0.644	−1.285	−3.586	383.894

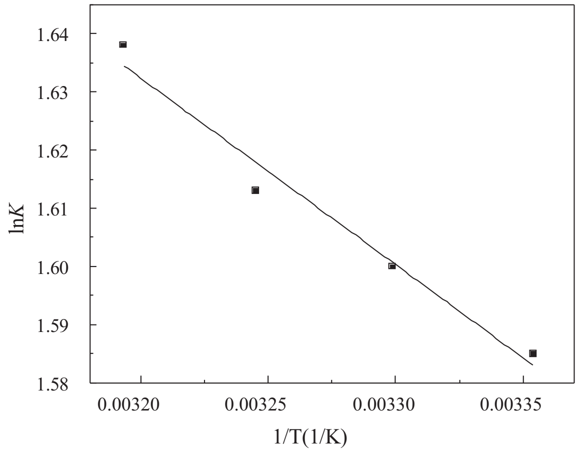

Fig. 5. van't Hoff plot of ln K vs. $1/T$ for MgTPP with aniline (E: $Y = 1.125 - 198.449X$, $R^2 = 0.975$).

Table 2
Thermodynamic parameters (ΔH and ΔS) of MgTPP with amines.

Amines	ΔH (kJ/mol)	ΔS (J/(mol K))
Ethanolamine	14.852 ± 1.129	45.290 ± 3.698
Aniline	1.650 ± 0.187	9.353 ± 0.613
Ethylenediamine	4.402 ± 0.076	25.980 ± 0.250
Pyrrolidine	−15.805 ± 0.734	−52.727 ± 5.261

can present two N atoms, the 1:1 adducts should be due to the formation of a polymeric complex (as ...Mg...NRN...Mg... NRN...Mg..., which Mg denotes the Mg atom in MgTPP molecule and NRN denotes ethylenediamine molecule).

4. Conclusion

MgTPP could be used as a renewable amine-fixing agent to reduce amine losses in CO_2 capture. Initially, the MgTPP–amine adducts are formed. Once CO_2 is introduced, it competes with MgTPP for amines, which eventually leads to the release of MgTPP. The amines then form adducts again with the regenerated MgTPP after CO_2 is released. The interactions between MgTPP and diethylamine are weak, and MgTPP hardly interacts with diphenylamine, or triethylamine because of steric hindrance. Based on the present investigation, ethylenediamine is an excellent agent for CO_2 capture because it has two amino sites and stronger K_{assoc} values for MgTPP. This method could be used to modify the system for CO_2 capture in aqueous solutions and we are investigating this with water soluble metalloporphyrins.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cclet.2013.01.043.

References

[1] A.J. Morris, G.J. Meyer, E. Fujita, Molecular approaches to the photocatalytic reduction of carbon dioxide for solar fuels, Acc. Chem. Res. 42 (2009) 983–1994.
[2] R. Monastersky, A burden beyond bearing, Nature 458 (2009) 1091–1094.
[3] D.M. D'Alessandro, B. Smit, J.R. Long, Carbon dioxide capture: prospects for new materials, Angew. Chem. Int. Ed. 49 (2010) 6058–6082.
[4] H. Choi, Y.C. Park, Y.H. Kim, Y.S. Lee, Ambient carbon dioxide capture by boron-rich boron nitride nanotube, J. Am. Chem. Soc. 133 (2011) 2084–2087.
[5] E.R. Monazam, L.J. Shadle, R. Siriwardane, Performance and kinetics of a solid amine sorbent for carbon dioxide removal, Ind. Eng. Chem. Res. 50 (2011) 10989–10995.
[6] S. Lee, T.P. Filburn, M. Gray, J.W. Park, H.J. Song, Screening test of solid amine sorbents for CO_2 capture, Ind. Eng. Chem. Res. 47 (2008) 7419–7423.
[7] A. Aroonwilas, A. Veawab, P. Tontiwachwuthikul, Behavior of the mass-transfer coefficient of structured packing in CO_2 absorbers with chemical reactions, Ind. Eng. Chem. Res. 38 (1999) 2044–2050.
[8] C. Lastoskie, Caging carbon dioxide, Science 330 (2010) 595–596.
[9] J. Kemper, G. Ewert, M. Grünewald, Absorption and regeneration performance of novel reactive amine solvents for post-combustion CO_2 capture, Energy Procedia 4 (2011) 232–239.
[10] J.F. Zhang, O. Nwani, Y. Tan, D.W. Agar, Carbon dioxide absorption into biphasic amine solvent with solvent loss reduction, Chem. Eng. Res. Des. 89 (2011) 1190–1196.
[11] K. Veltman, B. Singh, E.G. Hertwich, Human and environmental impact assessment of postcombustion CO_2 capture focusing on emissions from amine-based scrubbing solvents to air, Environ. Sci. Technol. 44 (2010) 1496–1502.
[12] G.T. Rochelle, Amine scrubbing for CO_2 capture, Science 325 (2009) 1652–1654.
[13] X.L. Ma, X.X. Wang, C.S. Song, Molecular basket sorbents for separation of CO_2 and H_2S from various gas streams, J. Am. Chem. Soc. 131 (2009) 5777–5783.
[14] K.E. Gutowski, E.J. Maginn, Amine-functionalized task-specific ionic liquids: a mechanistic explanation for the dramatic increase in viscosity upon complexation with CO_2 from molecular simulation, J. Am. Chem. Soc. 130 (2008) 14690–14704.
[15] J. Stewart, R.A. Lanning, Reduce amine plant solvent losses, Hydrocarb. Process. 73 (1994) 67–81.
[16] W.Q. Zheng, N. Shan, L.X. Yu, X.Q. Wang, UV–visible, fluorescence and EPR properties of porphyrins and metalloporphyrins, Dyes Pigments 77 (2008) 153–157.
[17] J.P. Collman, Y.L. Yan, T. Eberspacher, X.J. Xie, Oxygen binding of water-soluble cobalt porphyrins in aqueous solution, Inorg. Chem. 44 (2005) 9628–9630.
[18] K. Wynne, S.M. Lecours, C. Calli, M.J. Therien, R.M. Hochstrasser, Porphyrin-quinone electron transfer revisited. The role of excited-state eegeneracy in ultrafast charge transfer reactions, J. Am. Chem. Soc. 117 (1995) 3749–3753.
[19] A. Satake, Y. Kobuke, Dynamic supramolecular porphyrin systems, Tetrahedron 61 (2005) 13–41.
[20] J.G. Xu, Z.B. Wang, Fluorometry, 3rd ed., Science Press, Beijing, 2006.
[21] S. Iotti, A. Sabatini, A. Vacca, Chemical and biochemical thermodynamics: from ATP hydrolysis to a general reassessment, J. Phys. Chem. A 114 (2010) 1985–1993.
[22] C.J. Liu, W.C. Lu, Optical amine sensor based on metallophthalocyanine, J. Chin. Inst. Chem. Eng. 38 (2007) 483–488.
[23] A.V. Leontiev, D.M. Rudkevich, Revisiting noncovalent SO_2–amine chemistry: an indicator-displacement assay for colorimetric detection of SO_2, J. Am. Chem. Soc. 127 (2005) 14126–14127.
[24] M. Al-Juaied, G.T. Rochelle, Thermodynamics and equilibrium solubility of carbon dioxide in diglycolamine/morpholine/water, J. Chem. Eng. Data 51 (2006) 708–717.
[25] R.H. Weiland, T. Chakravarty, A.E. Mather, Solubility of carbon dioxide and hydrogen sulfide in aqueous alkanolamines, Ind. Eng. Chem. Res. 32 (1993) 1419–1430.