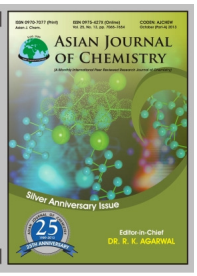
Asian Journal of Chemistry; Vol. 25, No. 18 (2013), 10421-10424

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.15603



Fixation of Ethylenediamine Using Magnesium Tetraphenylporphyrin for CO_2 Capture

FEI GAO[1], JIANBIN ZHANG[1,*], HUIJUAN HUANG[1], YI WEN[2] and TIANRUI HUO[1,*]

[1]College of Chemical Engineering, Inner Mongolia University of Technology, Huhhot 010051, P.R. China
[2]Chinese Academy for Environmental Planning, Beijing 100012, P.R. China

*Corresponding authors: Tel/Fax: +86 471 6575722; E-mail: tadzhang@pku.edu.cn; tianruihuo@163.com

(*Received*: 8 April 2013; *Accepted*: 20 November 2013) AJC-14417

Supramolecular recognition of magnesium tetraphenylporphyrin (MgTPP) with ethylenediamine for CO_2 capture was investigated in CH_2Cl_2 by steady-state fluorescence and UV-visible absorption spectroscopic techniques. The UV-visible spectra showed that interaction of MgTPP with ethylenediamine resulted in red shift of 2 nm for MgTPP Soret band. Once introduced, CO_2 competes with MgTPP for ethylenediamine, which eventually leads to the release of MgTPP. The fluorescence spectra suggested that MgTPP interacted with ethylenediamine to form 1: 1 molecular adducts. The binding of MgTPP with ethylenediamine with the association constants (K_{assoc}) of (3.901 to 4.122) is not only endothermic but entropy-driven with $\Delta H = 4.402$ kJ mol^{-1}, $\Delta S = 25.980$ J mol^{-1} K^{-1} and $\Delta G = -3.374$ kJ mol^{-1} at T = 298.15 K.

Key Words: Magnesium tetraphenyl porphyrin, Ethylenediamine, Spectroscopy, Thermodynamic.

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 this technology, CO_2 reacts with an amine absorption liquid *via* an exothermic, reversible reaction in a gas/liquid contactor. Next step, the CO_2 was removed from the solvent in a regenerator at low pressure and/or high temperature resulting in significant vaporization and solvent loss, which leads to a significant decrease in plant performance and a concurrent increase in operating costs. Recently, attention has focused on replacing amine absorption liquid and controlling the lean amine temperature to reduce amine loss, but the price is loss of the acid gas loading capacity and the solvent regenerability[13,14].

This work mainly focused on providing a new supramolecular approach for potential reducing amine solvent loss. At first, ethylenediamine forms the coordination complexes with magnesium tetraphenyl porphyrin (MgTPP) before the absorption step. Once introduced, CO_2 competes with MgTPP for ethylenediamine, which eventually leads to the release of MgTPP (Figs. 1 and 2). After the desorption step, the released amines form adducts again with the regenerated MgTPP, which could reduce solvent loss and processing costs. The MgTPP amine-fixed agent could be recycled in the amine scrubbing and the approach is simple and reliable.

EXPERIMENTAL

Fluorescence spectra were acquired using an F-4500 fluorescence spectrophotometer. UV-visible spectra were recorded on a Varian CARY 1E UV-visible spectrometer. All solid reagents were weighed using a Sartorius BS224S electric balance. According to previous work[15-17], 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.

In order to discuss the interaction of MgTPP with ethylenediamine, the concentration of MgTPP was fixed at 19.51 μmol/L and the concentrations of ethylenediamine were designed at different concentration gradient. All the experiments were carried at 298.15, 303.15, 308.15 and 313.15 K for 20 min using a constant temperature water SPY-III bath apparatus (accuracy: ± 0.01 K).

RESULTS AND DISCUSSION

When ethylenediamine was added to the solution of MgTPP in CH_2Cl_2, the colour change of MgTPP solution from

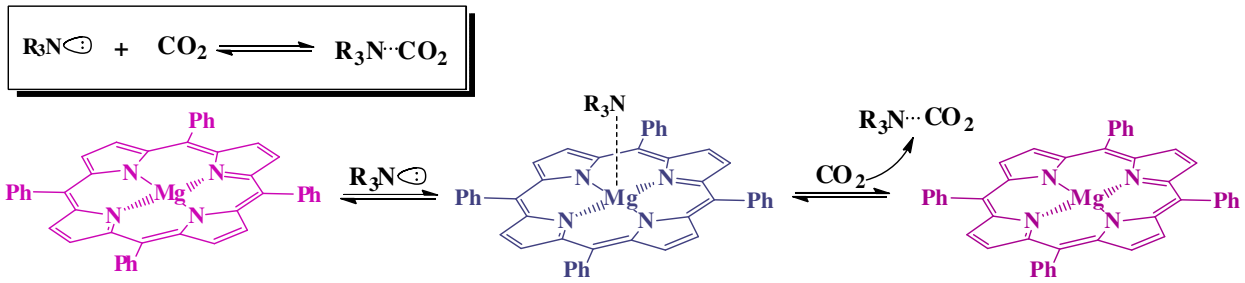


Fig 1. An amine-fixed agent for CO_2 capture. MgTPP is initially coordinated to amines and then displaced by CO_2

purple to blue (Fig. 2) could be due to the interaction of MgTPP with ethylenediamine. When CO_2 gas was bubbled through the solution, the colour changed from blue to purple because that the CO_2 gas may competes with MgTPP for ethylenediamine and causes the release of MgTPP. To confirm the the above reactions, UV-visible and fluorescence spectral technologies were used.

Fig. 2. Photograph of MgTPP (left), MgTPP + ethylenediamine (middle) and MgTPP + ethylenediamine + CO_2 (right)

In a typical experiment, ethylenediamine was added to the MgTPP solution and the absorbance changes were recorded (Fig. 3). The absorption spectra showed a typical Soret band at 424 nm, which was assigned to the Soret band of MgTPP arising from the $a_{1u}(\pi)$-$e_g^*(\pi)$ transition[18]. Similar Soret absorption peaks (B-bands) are observed for most porphyrinic compounds[19,20]. As expected, the solution changed from purple to blue and a bathochromic shift of 2 nm was observed for the Soret band and Q band, suggesting the interaction of MgTPP with ethylenediamine to form the corresponding MgTPP-ethylenediamine adducts. When CO_2 gas was bubbled through the solution, the colour changed from blue to purple and the absorbance spectra returned to its position for free MgTPP (Fig. 3), confirming that the CO_2 gas competes with MgTPP for ethylenediamine, which eventually leads to MgTPP-ethylenediamine adducts dissociated and the adducts of the CO_2 with ethylenediamine formed. The regenerated MgTPP could forms adducts again with the released ethylenediamine when CO_2 was removed. Magnesium tetraphenyl porphyrin thus served as a recycled amine-fixed agent in amine scrubbing for CO_2 capture to reducing amine solvent losses.

Upon excitation at 550 nm, stable state fluorescence spectra with selective excitation of MgTPP were recorded and the maximum emission positions of Q* at 610 nm and 663 nm were observed.

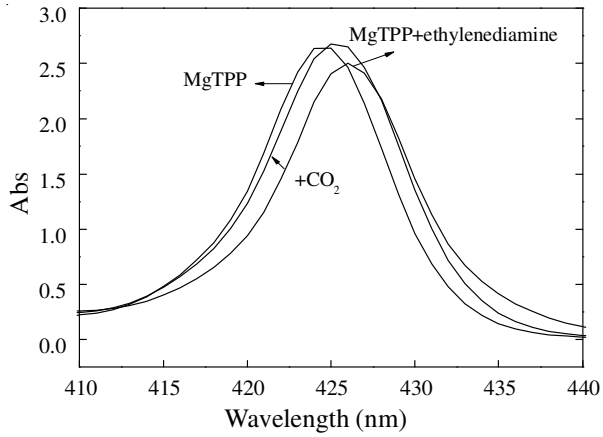


Fig. 3. Absorbance spectral changes ([MgTPP]: 1.95×10^{-5} mol/L, [ethylenediamine]: 0.31 mol/L)

Magnesium tetraphenyl porphyrin (MgTPP) is a potential amine-fixed agent, so the reaction mechanism of MgTPP with ethylenediamine was investigated by the fluorescence titrimetric method at the four temperatures of (298.15, 303.15, 308.15 and 313.15) K. Meanwhile, the concentration of MgTPP was fixed at 19.51 μmol/L and the concentrations of ethylenediamine were designed in the range of (0.000 to 0.314) mol/L for emission spectral measurements. The emission spectra of MgTPP significantly quenched with stepwise addition of ethylenediamine at the four temperatures (Fig. 4 and supporting information), which was due to electron transfer taking place from the interaction of MgTPP with acceptor ethylenediamine molecules because the ethylenediamine nitrogen is coordinated to the metal center of MgTPP[21].

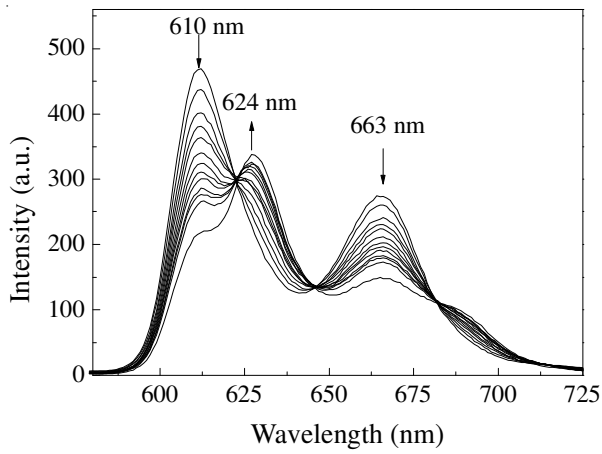


Fig. 4. Fluorescence emission spectral changes of MgTPP with increasing ethylenediamine concentrations at T = 298.15 K

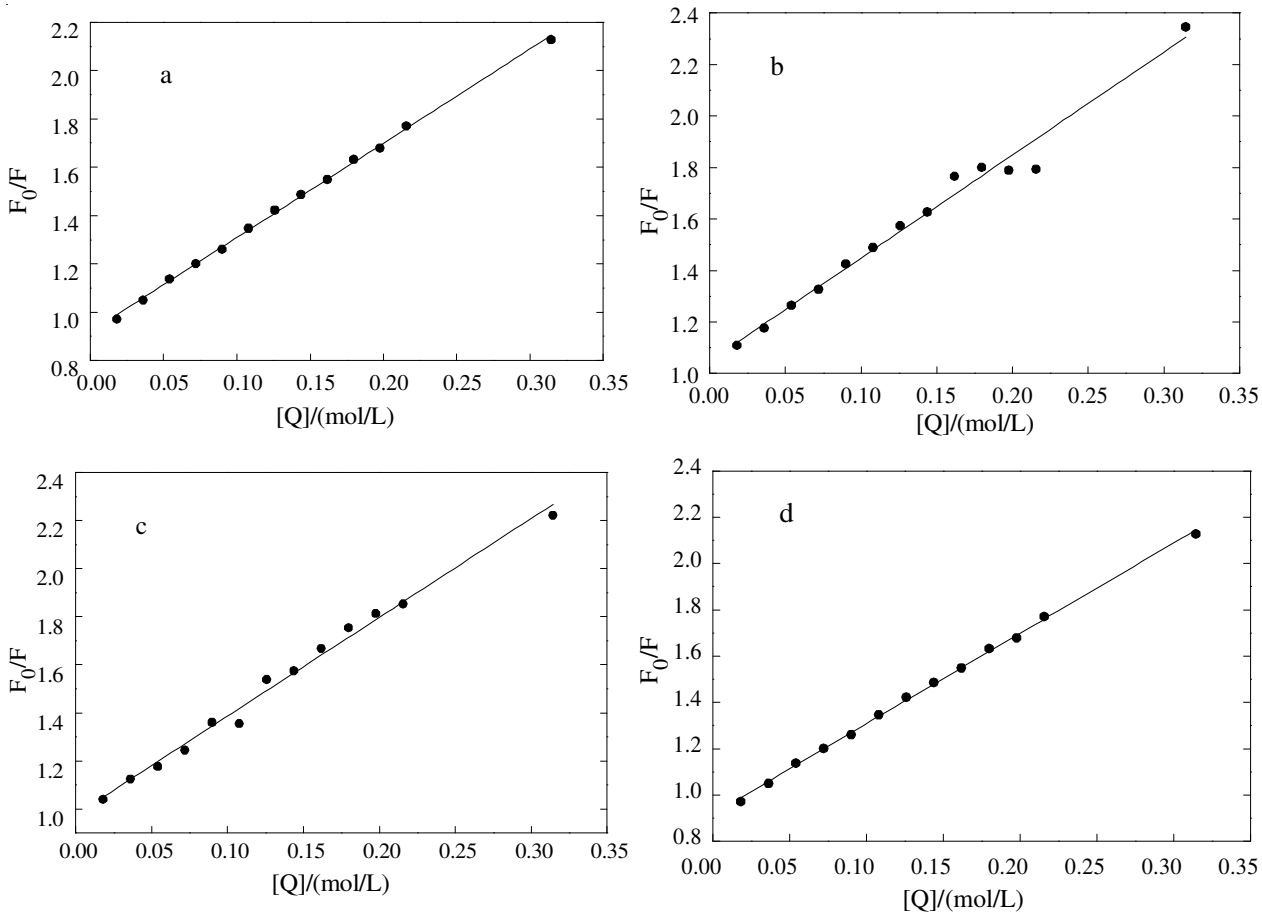


Fig. 5. Linear dependencies of F_0/F on [Q] MgTPP with [Q] at 298.15 K (a: $R^2 = 0.999$, $K_{assoc} = 3.901 \pm 0.040$), 303.15 K (b: $R^2 = 0.981$, $K_{assoc} = 4.002 \pm 0.167$), 308.15 K (c: $R^2 = 0.991$, $K_{assoc} = 4.113 \pm 0.119$), 313.15 K (d: $R^2 = 0.998$, $K_{assoc} = 3.965 \pm 0.071$)

The fluorescence intensities of MgTPP decrease with increasing concentration of ethylenediamine, which suggests that the binding of MgTPP with ethylenediamine is non-fluorescent. This phenomenon also proves that fluorescence quenching is static.

According to previous methods[22,23], the binding constants of MgTPP with ethylenediamine were calculated. In static quenching, the following formula can be obtained:

$$F_0/F = 1 + K\,[Q]^n \quad (1)$$

$$[M]_0/[M] = F_0/F \quad (2)$$

where [Q] denotes the concentration of free quencher of ethylenediamine, $[M_0]$ denotes the total concentration of MgTPP and [M] denotes the concentration of free MgTPP. A linear plot of F_0/F to [Q] indicates that one MgTPP molecule can bind one ethylenediamine molecule (Fig. 5) to form stable 1:1 molecular adducts in CH_2Cl_2.

The fluorescence spectra of MgTPP-ethylenediamine binding are performed at 298.15 to 313.15 K. Thermodynamic parameters were estimated by the analysis of ln K *versus* 1/T plot (van't Hoff plot) obtained by the experimental data at the above temperatures. The gradient of this straight line of ln K *versus* 1/T is equal to -ΔH/R, which indicates the values of ΔH, ΔG and ΔS can be calculated from the following relationships:

$$\Delta G = -RT \ln K = \Delta H - T\Delta S \quad (3)$$

By linear analysis, the van't Hoff plot for the binding of MgTPP to ethylenediamine is depicted in Fig. 6. The values of the thermodynamic parameters are shown in Table-1.

From Fig. 5, MgTPP can interacts with ethylenediamine to form 1: 1 molecular adducts at T = (298.15 to 313.15) K. From the Table 1, the K_{assoc} value of the interaction is 3.901 at T = 298.15 K. However, the binding constants between CO_2 and amines are about $10^{24,25}$. So CO_2 gas can compete with MgTPP for ethylenediamine easily. The thermodynamic data showed that interaction of MgTPP with ethylenediamine is not only endothermic but entropy-driven coordination reactions.

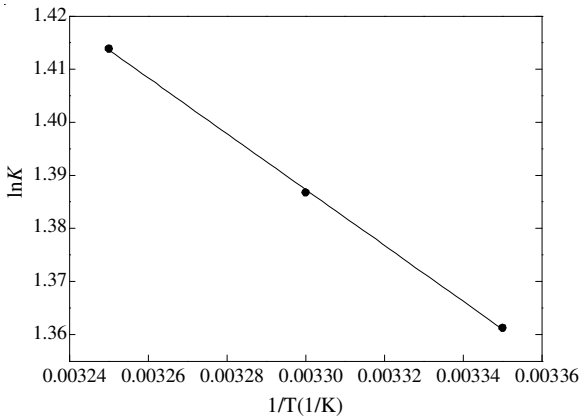


Fig. 6. van't Hoff plot of MgTPP-ethylenediamine (the regression equation: $Y = 3.125 - 526.510X$, $R^2 = 0.999$)

TABLE-1
THERMODYNAMIC PARAMETERS FOR MgTPP-ETHYLENEDIAMINE OBTAINED FROM FLUORESCENCE MEASUREMENTS

Temp. (K)	K_{assoc}	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
298.15	3.901 ± 0.040	-3.374	4.402 ± 0.076	25.980 ± 0.250
303.15	4.002 ± 0.167	-3.495	4.402 ± 0.076	25.980 ± 0.250
308.15	4.122 ± 0.124	-3.622	4.402 ± 0.076	25.980 ± 0.250
313.15	3.965 ± 0.071	-3.586	4.402 ± 0.076	25.980 ± 0.250

Conclusion

The spectral results suggested that MgTPP served as a regenerated amine-fixed agent is now possible in amine scrubbing for CO_2 capture to reduce amine solvent losses utilizing its noncovalent chemistry with ethylenediamine. Firstly, the MgTPP-ethylenediamine adducts were formed. Once introduced, CO_2 competes with MgTPP for ethylenediamine, which eventually leads to the release of MgTPP. After desorption, the released ethylenediamine forms adducts again with the regenerated MgTPP. In addition, we investigated reaction mechanisms and calculated the thermodynamic data for the MgTPP binding to ethylenediamine. The results suggested that MgTPP interacted with ethylenediamine to form 1:1 coordination complexes. The ethylenediamine can present two N atoms, so 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). The K_{assoc} indicated the binding ability between MgTPP and ethylenediamine is smaller than its between CO_2 and ethylenediamine proving that CO_2 can competes with MgTPP for ethylenediamine easily.

ACKNOWLEDGEMENTS

This work was supported by Foundation of the National Natural Science Foundation of China (21166017), Inner Mongolia Autonomous Region's Educational Commission (No. NJZZ11068), the research fund for the Doctoral program of Higher Education of China (20111514120002), the program for New Century Excellent Talents in University (NCET-12-1017), the program for Young Talents of Science and Technology in Universities of Inner Mongolia Autonomous Region (NJYT-12-B13), the Natural Science Foundation of Inner Mongolia Autonomous Region (2011BS0601, China) and the Inner Mongolia Talented People Development Fund.

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