Supramolecular Fixation of Magnesium Tetraphenylporphyrin with Ethanolamine for SO₂ Removal

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In this work, supramolecular fixation of magnesium tetraphenylporphyrin (MgTPP) with ethanolamine for removal of SO₂ was investigated in CH₂Cl₂ by steady-state fluorescence and UV-visible spectroscopic techniques. The UV-visible spectra showed that the interaction of MgTPP with ethanolamine resulted in red shift of 2 nm for MgTPP Soret absorption band. Once introduced, SO₂ competes with MgTPP for ethanolamine, which eventually leads to the release of MgTPP. The fluorescence spectra suggested that MgTPP interacted with ethanolamine to form 1: 1 molecular adducts and showed that the binding of MgTPP with ethanolamine with the association constants (K_{assoc}) of (0.584-0.784) is not only endothermic but enthalpy-driven with ΔH = 14.852 kJ mol⁻¹, ΔS =45.290 J mol⁻¹ K⁻¹ and ΔG = 1.333 kJ mol⁻¹ at T = 298.15 K.

Key Words: Magnesium tetraphenyl porphyrin, Ethanolamine, Spectroscopy, Thermodynamic, SO₂.

INTRODUCTION

The emission of sulphur dioxide (SO₂) in flue gases from the burning of fossil fuels has drawn worldwide attention because it is a significant source of atmospheric pollution that threatens the environment and human health[1,2]. They have to be removed (selectively) from these gas streams for operational, economical or environmental reasons and the chemical absorption called amine scrubbing using amine-based solvents is presently both the preferred option and probably the only commercially mature technology[3-5]. In this technology, SO₂ react with an amine absorption liquid *via* an exothermic, reversible reaction in a gas/liquid contactor. Next step, the SO₂ 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[6,7].

This work mainly focused on providing a new supramolecular approach for potential reducing amine solvent loss. At first, ethanolamine forms the coordination complexes with magnesium tetraphenyl porphyrin (MgTPP) before the absorption step. Once introduced, SO₂ competes with MgTPP for ethanolamine, 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. MgTPP amine-fixed
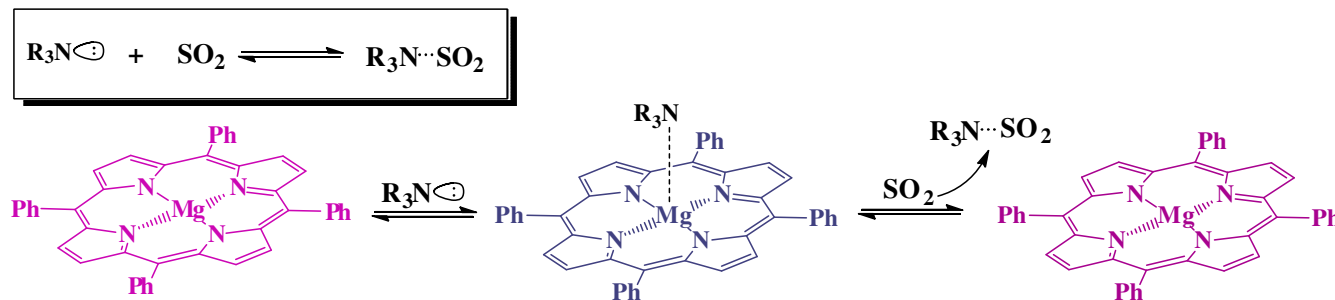

Fig. 1. An amine-fixed agent for SO₂ Capture. MgTPP is initially coordinated to amines and then displaced by SO₂

Fig. 2. Photograph of MgTPP (left), MgTPP + ethanolamine (middle) and MgTPP +ethanolamine + SO₂ (right)

agent was recycled in the amine scrubbing and the approach is simple and reliable. UV-visible spectra showed that the interaction of MgTPP with ethanolamine occurred more efficiently in CH_2Cl_2 to form 1:1 molecular adducts at T = (298.15-313.15) K.

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[8-10], 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 ethanolamine, the concentration of MgTPP was fixed at 19.51 µmol/L and the concentrations of ethanolamine 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 by a constant temperature water SPY-III bath apparatus (accuracy: ± 0.01 K).

RESULTS AND DISCUSSION

When ethanolamine was added to the solution of MgTPP in CH_2Cl_2, the colour change of MgTPP solution from purple to blue (Fig. 2) could be due to the interaction of MgTPP with ethanolamine. When SO₂ gas was bubbled through the solution, the colour changed from blue to purple because that the SO₂ gas may competes with MgTPP for ethanolamine and causes the release of MgTPP. To confirm the above reactions, UV-visible and fluorescence spectral technologies were used.

In a typical experiment, ethanolamine 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[11]. Similar Soret absorption peaks (B-bands) are observed for most porphyrinic compounds[12,13]. 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 ethanolamine to form the corresponding MgTPP-ethanolamine adducts. When SO₂ gas was bubbled through the solution, the colour changed from blue to purple and the absorbance spectra returned to its position for free MgTPP
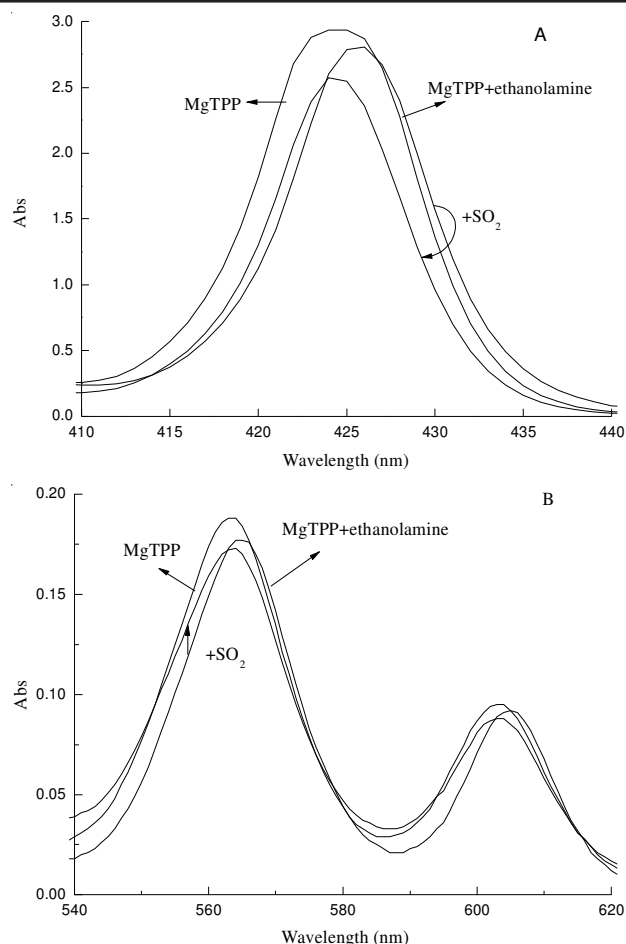

Fig. 3. Absorbance spectral changes ([MgTPP]: 1.95×10^{-5} mol/L, [ethanolamine]: 0.94 mol/L, [SO₂]: 5000 ppm), A: absorbance spectral change of Soret band; B: absorbance spectral change of Q band

(Fig. 3), confirming that the SO₂ gas competes with MgTPP for ethanolamine, which eventually leads to MgTPP-ethanolamine adducts dissociated and the adducts of the SO₂ with ethanolamine formed. The regenerated MgTPP could forms adducts again with the released ethanolamine when SO₂ was removed. MgTPP thus served as a recycled amine-fixed agent in amine scrubbing for SO₂ 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 and 663 nm were observed.

MgTPP is a potential amine-fixed agent, so the reaction mechanism of MgTPP with ethanolamine was investigated by 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 ethanolamine were designed in the range of (0.000 to 0.938) mol/L for emission spectral measurements. The emission spectra of MgTPP significantly quenched with stepwise addition of ethanolamine at the four temperatures (Fig. 4), which was due to electron transfer taking place from the interaction of MgTPP with acceptor ethanolamine molecules because the ethanolamine nitrogen is coordinated to the metal center of MgTPP[14].
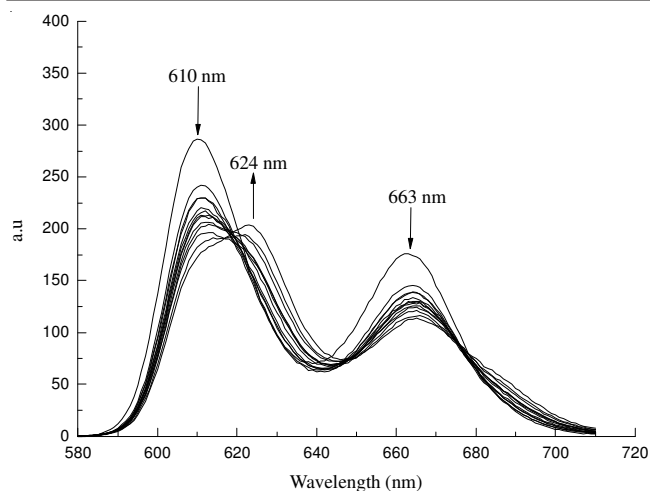
Fig. 4. Fluorescence emission spectral changes of MgTPP with increasing ethanolamine concentrations at T = 298.15 K

The fluorescence intensities of MgTPP decrease with increasing concentration of ethanolamine, which suggests that the binding of MgTPP with ethanolamine is nonfluorescent. This phenomenon also proves that fluorescence quenching is static.

According to previous methods[15,16], the binding constants of MgTPP with ethanolamine were calculated. In static quenching, the following formula can be obtained:

$$\frac{F_0}{F} = 1 + K[Q]^n \tag{1}$$

$$\frac{[M]_0}{[M]} = \frac{F_0}{F} \tag{2}$$

where [Q] denotes the concentration of free quencher of ethanolamine, $[M_0]$ 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 ethanolamine molecule (Fig. 5) to form stable 1:1 molecular adducts in CH_2Cl_2.

The fluorescence spectra of MgTPP-ethanolamine binding are performed at T = (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:
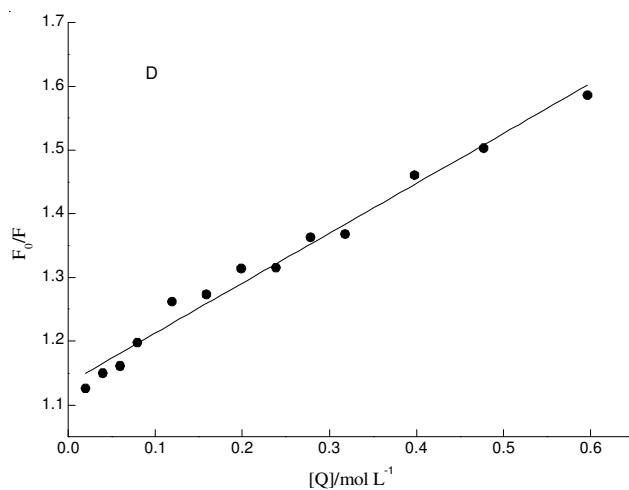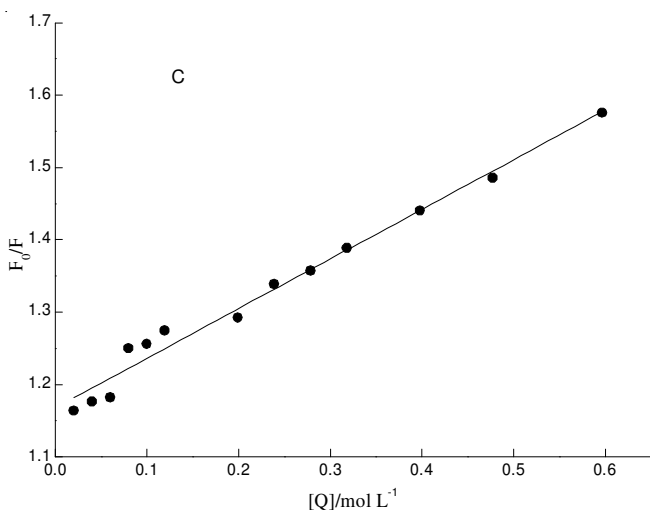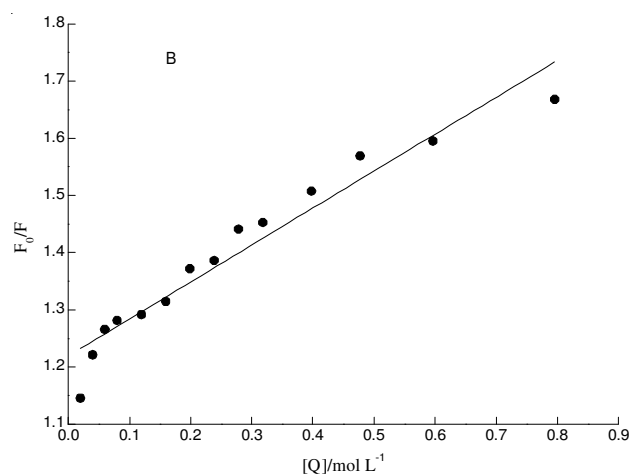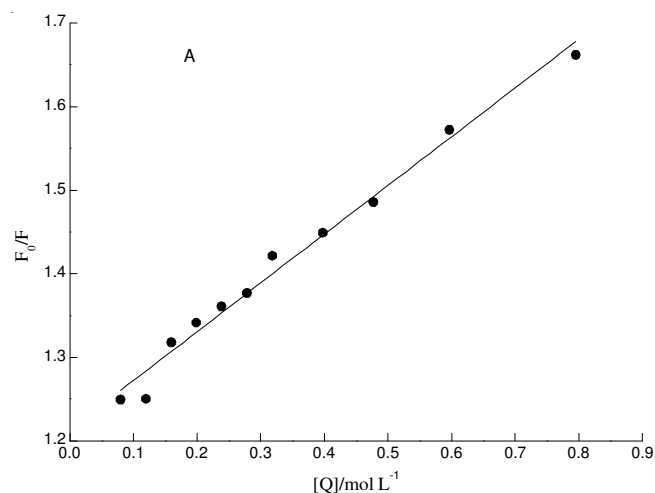

Fig. 5. Linear dependencies of F_0/F on [Q] at 298.15K (A: R^2 = 0.985, K_{assoc} = 0.584 ± 0.024), 303.1 K (B: R^2= 0.939, K_{assoc} = 0.646 ± 0.048), 308.15 K (C: R^2 = 0.982, K_{assoc} = 0.686 ± 0.029), 313.15 K (D: R^2 = 0.983, K_{assoc} = 0.784 ± 0.030)

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

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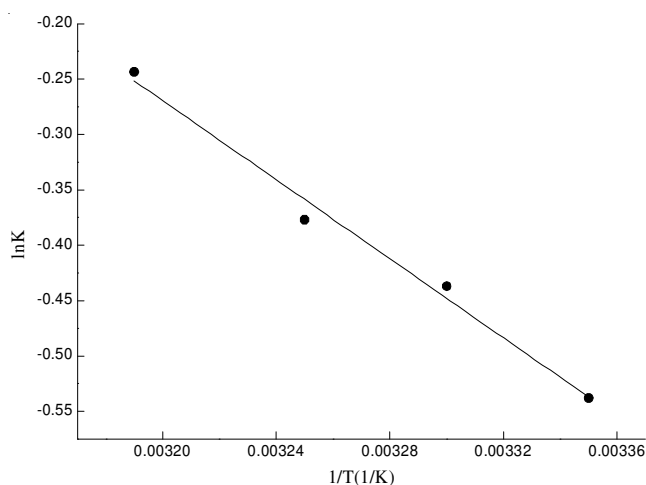

Fig. 6. van't Hoff plot of MgTPP-ethanolamine (the regression equation: $Y = 5.447 - 1786.442X$, $R^2 = 0.989$)

TABLE-1 THERMODYNAMIC PARAMETERS FOR MgTPP-ETHANOLAMINE OBTAINED FROM FLUORESCENCE MEASUREMENTS				
T (K)	K_{assoc}	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
298.15	0.584±0.024	1.333	14.852±1.129	45.290±3.698
303.15	0.646±0.048	1.101	14.852±1.129	45.290±3.698
308.15	0.686±0.029	0.966	14.852±1.129	45.290±3.698
313.15	0.784±0.030	0.644	14.852±1.129	45.290±3.698

From the Fig. 5 and supporting information 2, MgTPP can interact with ethanolamine 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 0.584 at T = 298.15 K and in Rudkevich's work[17], the K_{assoc} value of SO_2 with ethanolamine is about1000. So SO_2 gas can compete with MgTPP for ethanolamine easily. The thermodynamic data showed that interaction of MgTPP with ethanolamine is not only 1.64 and endothermal but enthalpy-driven coordination reactions at temperatures (298.15, 303.15, 308.15 and 313.15) K.

Conclusion

The spectra results suggested MgTPP served as a regenerated amine-fixed agent is now possible in amine scrubbing for SO_2 capture to reduce amine solvent losses utilizing its noncovalent chemistry with ethanolamine. Firstly, the MgTPP-ethanolamine adducts were formed. Once introduced, SO_2 competes with MgTPP for ethanolamine, which eventually leads to the release of MgTPP. After desorption, the released ethanolamine forms adducts again with the regenerated MgTPP. In addition, we investigated reaction mechanisms and calculated the thermodynamic data for the MgTPP binding to ethanolamine. The results suggested that MgTPP interacted with ethanolamine to form 1: 1 coordination complexes. The K_{assoc} indicated the binding ability between MgTPP and ethanolamine is smaller than its between SO_2 and ethanolamine proving that SO_2 can competes with MgTPP for ethanolamine easily.

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