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Supramolecular Fixation of Three Amines using Cobalt Tetraphenylporphyrin for SO_2 Removal

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(Dated: Received on May 14, 2014; Accepted on July 28, 2014)

In this work, supramolecular fixation of three amines, including aniline, ethylenediamine, and diethylamine, using cobalt tetraphenylporphyrin (CoTPP) for SO_2 removal was studied using UV-Vis and fluorescence measurements. The UV-Vis spectra showed that increasing amines concentrations resulted in bathochromic shift for CoTPP Soret absorption band (B band). Once SO_2 was introduced, it competed with CoTPP for aniline, ethylenediamine, and diethylamine, which eventually led to the release of CoTPP and the change of solution colour/absorption band. After that, the CoTPP was regenerated and got back to the first state. The fluorescence spectra offered that CoTPP interacted with aniline, ethylenediamine, and diethylamine to form 1:1 molecular adducts. The interactions of CoTPP with aniline, ethylenediamine, and diethylamine were entropy-driven. The interaction of CoTPP with aniline and diethylamine was endothermic, and that with ethylenediamine was exothermic. Ethylenediamine presented a stronger binding constant value for CoTPP, so it was considered as a potential agent for SO_2 removal.

Key words: Amine, SO_2, Supramolecular fixation, Cobalt tetraphenylporphyrin

I. INTRODUCTION

Sulfur dioxide (SO_2) is a significant atmospheric pollutant, and therefore it is severe in environmental protection. Its main source is flue gas from the burning of fuels with high sulfur content [1]. Removal of SO_2 from flue gas is an increasingly important environmental challenge because of the lowering of the admissible emission limit and numerous desulfurization processes, such as limestone scrubbing that produces a large volume of solid waste [2]. Among many procedures employed to desulfurize exhaust gases, the chemical absorption called amine scrubbing using amine-based solvents has been identified as an option to remove (selectively) SO_2 from gas streams for operational, economical or environmental reasons. In this technology, amine scrubbing is presently both the preferred option and probably the only commercially mature technology [3−5]. SO_2 reacts with an amine absorbent via an exothermic and reversible reaction in a gas/liquid contactor. Meanwhile, SO_2 is removed from the solvent in a regenerator at 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 been focused on replacing amine absorption liquid and controlling the lean amine temperature to reduce amine loss, but the loss of the acid gas loading capacity and the solvent regenerability occurred [6, 7]. To solve the problem, some metal porphyrin compounds have been developed for the gases' removal, for example, Leontiev and coworkers reported Zn-tetraphenylporphyrin was used as the indicator for the SO_2 determination through the revisiting noncovalent SO_2-amine approach [8]. Zhang *et al.* reported Mg-tetraphenylporphyrin was used to fix five amines for the CO_2 capture and SO_2 removal [9]. However, Zn-tetraphenylporphyrin and Mg-tetraphenylporphyrin are photosensitive.

In this work, we use cobalt tetraphenylporphyrin (CoTPP) as an amine-fixing agent for SO_2 removal. Three amines, including aniline, ethylenediamine, and diethylamine, are fixed using CoTPP to form the coordination complexes. Once introduced, SO_2 competes with CoTPP for three amines, which eventually leads to the release of CoTPP (Fig.1). After the desorption step, the released amines form adducts again with the regenerated CoTPP, which could reduce solvent loss and processing costs. The CoTPP amine-fixed agent could be recycled in the amine scrubbing, and the approach is simple and reliable.

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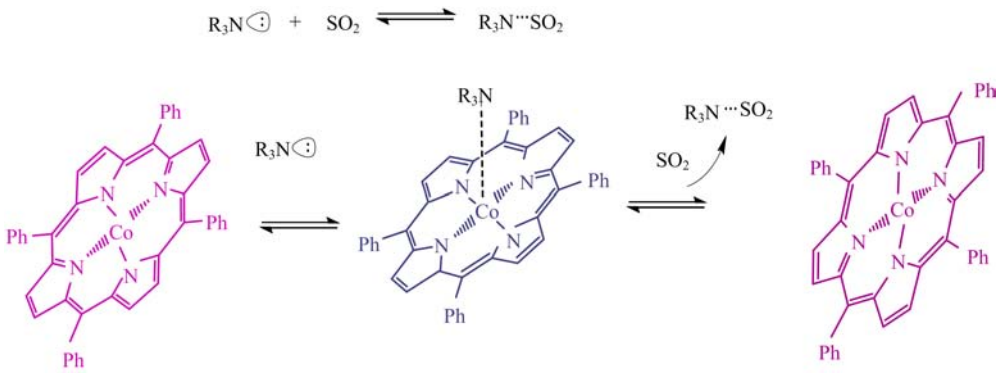

FIG. 1 An amine-fixing agent for SO_2 removal, CoTPP is initially coordinated to amines and then displaced by SO_2.

II. EXPERIMENTS

Cobalt tetraphenylporphyrin (CoTPP, 99%) was purchased from Hunan Jineng New Materials Technology Limited Company (Hunan province, China). All other reagents and solvents were reagent grade and used as received. A solution of 1.0 mL CoTPP in CH_2Cl_2 with concentration of 0.0549 mmol/L and a series of aniline, ethylenediamine, and diethylamine solutions were kept at temperature of 298.15, 303.15, 308.15, and 313.15 K for 30 min by a constant temperature water SPY-III bath apparatus (accuracy: ±0.01 K).

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

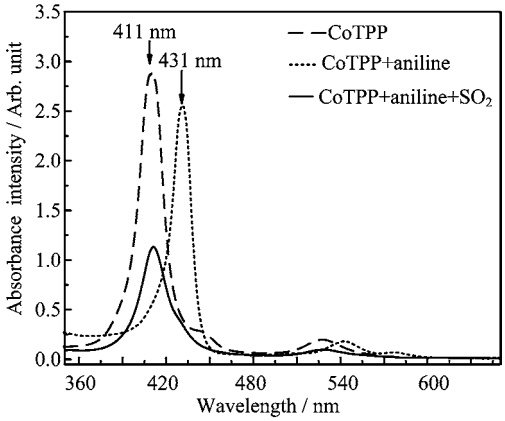

FIG. 2 Absorbance spectral changes of the reaction of CoTPP with anilline and that after the introduction of SO_2. [CoTPP]: 0.0549 mol/L, [aniline]: 0.691 mol/L, [SO_2]: 5000 ppmv.

III. RESULTS AND DISCUSSION

In a typical experiment, aniline was added into the CoTPP solution, and the absorbance bands changes of aniline were recorded (Fig.2). The absorption spectra showed a typical Soret band (B-band) at 411 nm, which was assigned to the Soret band of CoTPP arising from the $a_{1u}(\pi)$-$e_g^*(\pi)$ transition [10]. Similar Soret bands were observed for most porphyrinic compounds [11, 12]. As expected, the solution color changed from purple into light yellow; a bathochromic shift of 20 nm was observed for the Soret band, indicating the interaction of CoTPP with aniline to form CoTPP-aniline adduct. When SO_2 was briefly bubbled into the solution, the solution color changed from light yellow into violet, and the Soret band returned to the position of free CoTPP. CoTPP-aniline adduct dissociated, and the SO_2-aniline adducts were formed. Thus, CoTPP-aniline adduct served as an indirect dealing with SO_2. To calculate thermodynamic parameters, the binding constants of CoTPP with aniline, ethylenediamine, and diethylamine were determined at T=298.15, 303.15, 308.15, and 313.15 K using fluorescence measurements. The fluorescence intensity at λ=652 nm with different concentration of CoTPP was measured to find the calibration curve.

Meanwhile, the concentration of aniline, ethylenediamine, and diethylamine was designed in the range of 0.0593 mmol/L to 0.0692 mmol/L for emission spectral measurements. The emission spectra of CoTPP were significantly quenched with the increasing concentration of amines. The quenching processes were attributed to electron transfer taking place from the interaction of CoTPP with these amines molecules acceptor (Fig.3).

Rudkevich *et al.* reported that the K_{assoc} values for Zn-tetraphenylporphyrin (ZnTPP) with amines were 700 for diethylamine and 7.0×10^4 for quinuclidine [8]. However, the binding constants between SO_2 and amines are in the range of 1.1×10^4 to 7.0×10^4 [8]. In this work, the binding constants of CoTPP with aniline, ethylenediamine, and diethylamine were calculated from the fluorescence spectral data. The binding constants K and the binding number of CoTPP with aniline, ethylenediamine, and diethylamine (n) are calculated by the following equation [13, 14].

DOI:10.1063/1674-0068/27/05/616-620

TABLE I Thermodynamic parameters for the reaction of CoTPP with three amines obtained from fluorescence measurements.

Adduct	T/K	K	ΔG/(kJ/mol)	ΔH/(kJ/mol)	ΔS/(J/(mol K))
CoTPP-aniline	298.15	1.796±0.065	−1.452	2.016±0.026	11.633±0.080
	303.15	1.820±0.070	−1.510	2.016±0.026	11.633±0.080
	308.15	1.849±0.089	−1.575	2.016±0.026	11.633±0.080
	313.15	1.868±0.081	−1.626	2.016±0.026	11.633±0.080
CoTPP-ethylenediamine	298.15	2.905±0.152	−2.643	−1.278±0.173	4.589±0.056
	303.15	2.889±0.090	−2.674	−1.278±0.173	4.589±0.056
	308.15	2.856±0.169	−2.689	−1.278±0.173	4.589±0.056
	313.15	2.837±0.099	−2.715	−1.278±0.173	4.589±0.056
CoTPP-diethylamine	298.15	1.268±0.051	−0.590	5.262±0.846	19.607±0.277
	303.15	1.302±0.080	−0.665	5.262±0.846	19.607±0.277
	308.15	1.368±0.058	−0.802	5.262±0.846	19.607±0.277
	313.15	1.396±0.058	−0.869	5.262±0.846	19.607±0.277

$$\mathrm{M} + n\mathrm{Q} \overset{K}{\leftrightarrow} \mathrm{MQ}_n \tag{1}$$

where Q is the quencher known as aniline, ethylenediamine, and diethylamine. M is the CoTPP, and MQ_n is the binding fixation of them.

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

where [M] is the concentration of free CoTPP, and $[\mathrm{MQ}_n]$ is the concentration of binding complexes. If $[\mathrm{M}]_0$ is the total concentration of the CoTPP:

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

And hence Eq.(2) is 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 process,

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

where F_0 and F are the fluorescence intensities at λ=652 nm in the absence and presence of these amines.

According to the above equation, the following formula can be depicted as follows:

$$\frac{F_0}{F} = 1 + K[\mathrm{Q}]^n \tag{6}$$

If one CoTPP molecule binds one molecule amine, plot of F_0/F to [Q] is linear. If one CoTPP molecule binds two molecules of these amines, plot of F_0/F to $[\mathrm{Q}]^2$ is also linear. So n is their binding number, which may also be a fraction. A linear plot of F_0/F to [Q] for CoTPP with aniline is shown in Fig.4, which indicates that one CoTPP molecule binds one molecule of aniline to form 1:1 adducts. The linear plots of F_0/F to [Q] for CoTPP with ethylenediamine and diethylamine are shown in Supplementary material.

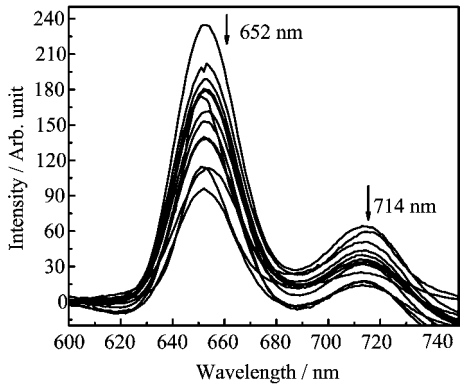

FIG. 3 Fluorescence emission spectral changes of CoTPP with increasing aniline concentrations of 0.0593, 0.0790, 0.0988, 0.119, 0.158, 0.198, 0.237, 0.277, 0.356, 0.474, 0.593, 0.692 mol/L (from bottom to up) at T=303.15 K.

Thermodynamic parameters were calculated by the analysis of $\ln K$ *vs.* $1/T$ plot (van't Hoff plot) obtained by the experimental data. The slope of this straight line of $\ln K$ *vs.* $1/T$ is equal to $-\Delta H/R$, which indicates the values of ΔH, ΔG, and ΔS can be calculated from the following relationships [15]:

$$\Delta G = -RT\ln K \tag{7}$$

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{9}$$

By linear analysis, the van't Hoff plot for the bindings of CoTPP-aniline is shown in Fig.5, and those for CoTPP-ethylenediamine and CoTPP-diethylamine are shown in

DOI:10.1063/1674-0068/27/05/616-620

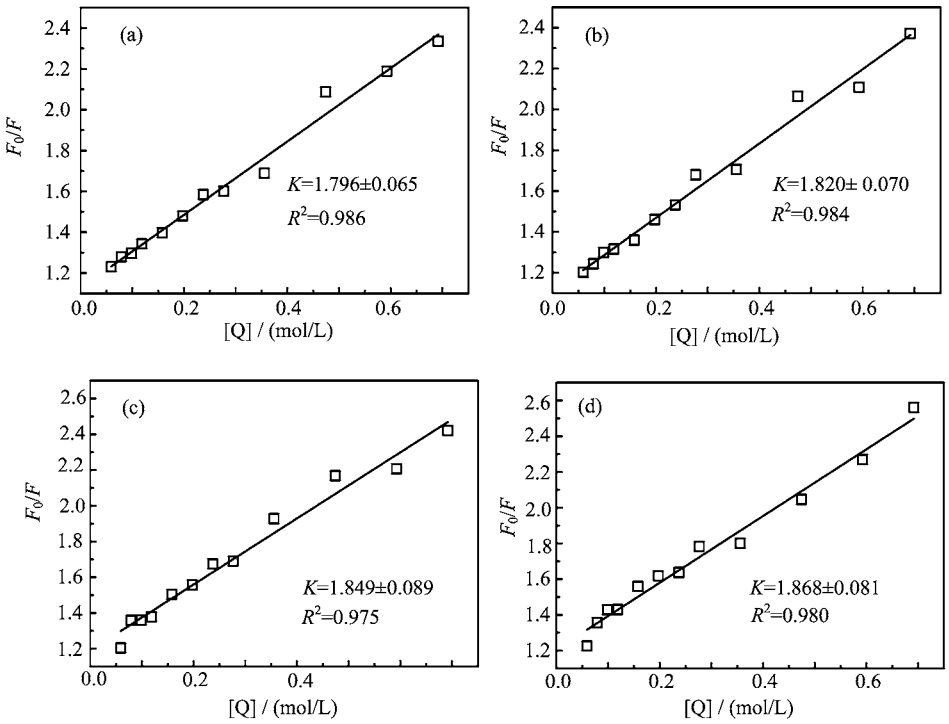

FIG. 4 Plots of F_0/F *vs.* [Q] for CoTPP with aniline at (a) 298.15 K, (b) 303.15 K , (c) 308.15 K, and (d) 313.15 K.

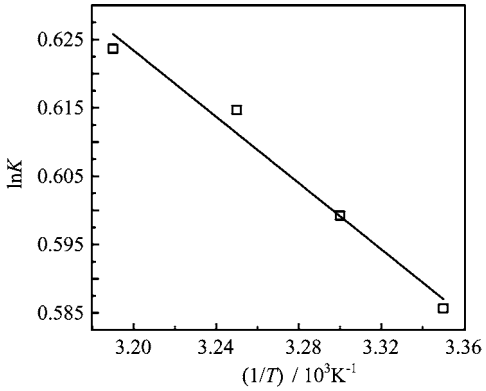

FIG. 5 Van't Hoff plot of ln$K$ *vs.* $1/T$ for CoTPP with aniline (y=1.399−242.448x, R^2=0.967).

Supplementary material. The values of the thermodynamic parameters are listed in Table I.

From Table I, the negative ΔG and positive ΔS demonstrate that the interactions of CoTPP with aniline, ethylenediamine, and diethylamine are entropy-driven. The interaction of CoTPP with aniline and diethylamine is endothermic, and the interaction of CoTPP with ethylenediamine is exothermic.

IV. CONCLUSION

It is now possible to remove SO_2 by utilizing its non-covalent chemistry with aniline, ethylenediamine, and diethylamine. Once introduced, SO_2 competes with CoTPP for aniline, ethylenediamine, and diethylamine. The binding constants of CoTPP with aniline were determined in the range of 1.796 to 1.868, the binding constants of CoTPP with ethylenediamine were determined in the range of 2.905 to 2.837, and the binding constants of CoTPP with ethylenediamine were determined in the range of 1.268 to 1.396. The thermodynamic data for the CoTPP binding to aniline showed that the binding of CoTPP with aniline and diethylamine is not only endothermal but also entropy-driven. The interaction of CoTPP with ethylenediamine is exothermic and entropy-driven. CoTPP can interact with aniline, ethylenediamine, and diethylamine to form 1:1 molecular adducts, and the bind of CoTPP with ethylenediamine was stronger than other amines. Thus CoTPP which formed CoTPP-ethylenediamine with ethylenediamine may serve as a potential desulfurization substance.

V. ACKNOWLEDGMENTS

This work was supported by the Foundation of the Program for New Century Excellent Talents in University (No.NCET-12-1017), the Program for Young Talents of Science and Technology in Universities of Inner Mongolia Autonomous Region (No.NJYT-12-B13), the National Natural Science Foundation of China (No.21166017 and No.21466028), the Program for Graduate Scientific Research Innovation of Inner

DOI:10.1063/1674-0068/27/05/616-620

Mongolia Autonomous Region (No.S20141012816), the Research Fund for the Doctoral Program of Higher Education of China (No.20111514120002), the Program for Grassland Excellent Talents of Inner Mongolia Autonomous Region, the Inner Mengolia Science & Technology Plan, the Inner Mongolia Talented People Development Fund, and the Yongfeng Boyuan Industry Co., Ltd., Jiangxi Province, China.

Supplementary material: The linear plots of F_0/F to [Q] for CoTPP with ethylenediamine and diethylamine, and the van't Hoff plots for the bindings of CoTPP-ethylenediamine and CoTPP-diethylamine are shown.

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DOI:10.1063/1674-0068/27/05/616-620