Absorption of NO in Aqueous Solution of Co(II)-en: Determination of the Equilibrium Constant

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In a wet scrubbing process, the addition of ethylenediamine cobalt(II) (Co(II)-en) to enhance the solubility of NO in aqueous solution may provide a good environmental control technology (coordination catalysis reactions absorption) for removal of NO, after the use of a SO_2 scavenging process, that requires little capital when combined with a highly developed industrial wet desulfurization processes. Under anoxic conditions according to amount of time-dependent absorbed NO under different NO partial pressure, the mole ratio of reacted NO and Co(II)-en in the coordination reaction $n\mathrm{NO} + [\mathrm{Co(en)_3}]^{2+} \leftrightarrow [\mathrm{Co(en)_3(NO)}_n]^{2+}$ was determined to be 1:1, that is $n = 1$. From this, the formula of the formed nitrosyl metal complex is derived to be $[\mathrm{Co(en)_3(NO)}]^{2+}$. For the development of this scrubbing technological process, knowledge of thermodynamic equilibrium data of the reaction $\mathrm{NO} + [\mathrm{Co(en)_3}]^{2+} \leftrightarrow [\mathrm{Co(en)_3(NO)}]^{2+}$ over a range of temperatures is of prime importance. In the temperature range from (30 to 90) °C, the equilibrium constant has been determined, and the experimental data fit the following equation well: $K_p = (3.3153 \pm 0.1160) \times 10^{-4} \exp(4428.5 \pm 96.2/T)/\mathrm{bar}^{-1}$ where the reaction enthalpy is $\Delta H^0 = -(36.821 \pm 0.800)\ \mathrm{kJ \cdot mol^{-1}}$.

Introduction

It is generally accepted that nitric oxides, in addition to sulfur dioxide, are the main cause of environmental pollution such as acid rain, acid smog, and a reduction in the ozone layer. Therefore, many limitations are placed on emissions from tail gases of power plants. For example, the Chinese emission standard of air pollutants from thermal power plants (B13223-2003) regulates that from January 1, 2005, the maximum content of nitric oxides in flue gases from large-scale power stations using coal is (1100 to 1500) $\mathrm{mg \cdot m^{-3}}$.[1] Europe also has new regulations[2] concerning gaseous wastes, with combustion gases needing to be treated before being ejected into the atmosphere. In order to fulfill the requirements of these limitations, there are not only many improvements to the combustion processes that have been implemented (so-called primary measures) but also many new processes developed for the removal of nitric oxides, that is denoxing processes, to get below the regulated concentration in the tail gas. The denitrification method developed in this study is of this kind.

A good denitrification process is selective catalytic reduction (SCR). It can catalytically reduce NO_x to N_2 and H_2O by reacting it with NH_3. The reaction takes place at a temperature of (350 to 400) °C. This process has a leading position on the current denoxing market. Its only drawback is its relatively high capital cost.

Many alternatives to the SCR process that are based on wet scrubbing have been studied in Japan and Germany. Flue gas contains several hundred ppm of NO_x and up to several thousand ppm of SO_2. Most of the NO_x is in the form of relatively insoluble NO. Several simultaneous denitrification and desulfurization processes are proposed by adding metal chelate complexes to solutions to bind NO-forming nitrosyl metal complexes. These complexes can in turn react with absorbed SO_2 to produce reduced nitrogen species such as N_2O, N_2, and sulfate while the metal chelate is regenerated. Fe(II)EDTA, for example, has been used for this purpose. Some other metal complexes can also coordinate NO and be regenerated by other methods.

Available data concerning equilibrium constants for the formation of Fe and other metal nitrosyl complexes are listed in the literature.[12−14] A big drawback of the process using Fe(II) as an absorbent is that it is very easily oxidized in aqueous solutions, hence the whole solution will lose the ability of coordinate NO. More reducing agent must be added to reduce Fe(III) back to Fe(II).

$[\mathrm{Co(en)_3}]^{2+}$ solutions could potentially rapidly absorb NO and O_2 simultaneously from gas, forming two separate nitrosyl metal complexes, which subsequently react with each other, leading to the regeneration of the $[\mathrm{Co(en)_3}]^{2+}$ solution. This is a coordination catalysis reaction. Such a process could result in a high removal efficiency of NO for a very long time.[15] The $[\mathrm{Co(en)_3}]^{2+}$ works as an intermediate to enhance the solubility of NO and O_2 in the aqueous solution by forming nitrosyl complexes achieving oxidation of NO by O_2 through the reaction $2\mathrm{NO} + \mathrm{O_2} + 2\mathrm{OH^-} \rightarrow \mathrm{NO_2^-} + \mathrm{NO_3^-} + \mathrm{H_2O}$. The low concentration and long time of activity of the solution in this process require little running capital. This process could accompany the current existing wet scrubbing process using ammonia for SO_2 removal to gain additional cleaning of the tail gas. Weisweiler et al. have investigated such a system, NO reacting with Co(II)-Trien and Co(II)-Tetren.[16] Not much kinetic and thermodynamic data are available in the literature in relation to this process, although several cobalt chelates have been tested as additives at the bench scale.

The reaction between NO and $[\mathrm{Co(en)_3}]^{2+}$ is likely to be

$$n\mathrm{NO} + [\mathrm{Co(en)_3}]^{2+} \leftrightarrow [\mathrm{Co(en)_3(NO)}_n]^{2+} \tag{1}$$

where n in the reaction is unknown. For the development of the complete denoxing technical process, consisting of the

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absorption and subsequent regeneration of the solution, detailed knowledge about the thermodynamic data of the above reaction is necessary.

Theory

Nitric oxide is nonreactive in water (in the absence of oxygen), and the solubility of NO in water is 0.00517 g/100 g at 30 °C and 0.00316 g/100 g at 50 °C.[11] The solubility decreases with an increase in temperature; the solubility of NO in aqueous solution was found to be independent of pH over the range (pH 2 to 13).[12] The derivation of equilibrium constant functions for reaction 1 is given as follows.[13]

The thermodynamic equilibrium constant is defined by the following equation:

$$K(T) = \Pi a_i^{\mathrm{vi}} \tag{2}$$

For the reaction of NO with $[\mathrm{Co(en)_3}]^{2+}$, $K(T)$ can be rewritten as:

$$K(T) = \frac{[\mathrm{Co(en)_3(NO)}_n]^{2+}}{[\mathrm{NO}]^n[\mathrm{Co(en)_3}]^{2+}} \frac{\gamma^{\mathrm{r}}_{[\mathrm{Co(en)3(NO)n]2+}}}{\gamma^{\mathrm{r}}_{\mathrm{NO}}{}^{n}\, \gamma^{\mathrm{r}}_{[\mathrm{Co](en)_3 2+}}} \tag{3}$$

For diluted, ideal solutions the rational activity coefficient can be neglected, i.e.

$$\gamma_i^{\mathrm{r}} = \frac{a_i}{c_i} = 1 \tag{4}$$

Application of Henry's law, i.e.

$$p_{\mathrm{NO}} = H_{\mathrm{pc}}[\mathrm{NO}] \tag{5}$$

where H is the Henry coefficient, and p_{NO} is the partial pressure of NO, leads to

$$[\mathrm{NO}]^n = p_{\mathrm{NO}}{}^n / H_{\mathrm{pc}}{}^n \tag{6}$$

and by substituting eq 6 into eq 3, the equation for the equilibrium constant has the following form:

$$K(T) = \frac{[\mathrm{Co(en)_3(NO)}_n]^{2+}}{\dfrac{p_{\mathrm{NO}}{}^n}{H_{\mathrm{pc}}{}^n}[\mathrm{Co(en)_3}]^{2+}} = \frac{[\mathrm{Co(en)_3(NO)}_n]^{2+}}{\dfrac{p_{\mathrm{NO}}{}^n}{H_{\mathrm{pc}}{}^n}\{[\mathrm{Co(en)_3}]_0^{2+} - [\mathrm{Co(en)_3(NO)}_n]^{2+}\}} \tag{7}$$

where $[\mathrm{Co(en)_3}]^{2+}{}_0$ is the initial concentration of $[\mathrm{Co(en)_3}]^{2+}$, $[\mathrm{Co^{2+}(en)_3(NO)}_n]$ is the concentration of the NO adduct obtained by graphically integrating the outlet NO in the tail gas, and $[\mathrm{Co(en)_3}]^{2+}$ is the current concentration of $[\mathrm{Co(en)_3}]^{2+}$ in the solution. Thus, eq 8 can be derived:

$$\frac{[\mathrm{Co(en)_3}]_0^{2+}}{[\mathrm{Co(en)_3(NO)}_n]^{2+}} - 1 = \frac{H_{\mathrm{pc}}{}^n}{p_{\mathrm{NO}}{}^n K(T)} \tag{8}$$

This expression contains the Henry coefficient (H_{pc}) for NO in aqueous media. Values quoted in the literature for the temperature dependence of the Henry coefficient vary considerably. For practical purposes, the Henry coefficient may be eliminated by the introduction of the K_{p}, which is based on measured variables, i.e.

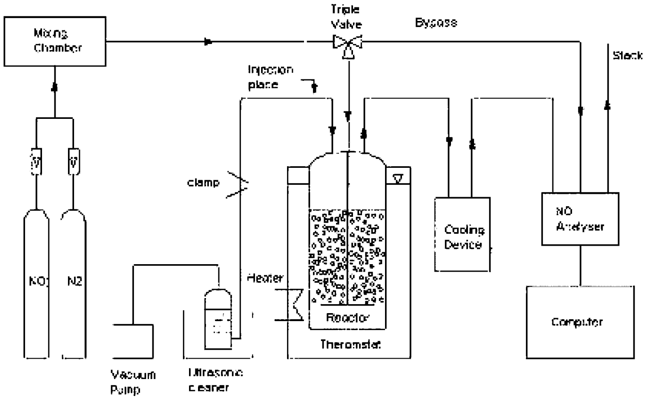

Figure 1. Experimental setup for the determination of the equilibrium constant.

$$K_{\mathrm{p}} = \frac{K(T)}{H_{\mathrm{pc}}{}^n} = \frac{[\mathrm{Co(en)_3(NO)}_n]^{2+}}{p_{\mathrm{NO}}{}^n[\mathrm{Co(en)_3}]^{2+}} = \frac{[\mathrm{Co(en)_3(NO)}_n]^{2+}}{p_{\mathrm{NO}}{}^n\{[\mathrm{Co(en)_3}]^{2+}{}_0 - [\mathrm{Co(en)_3(NO)}_n]^{2+}\}} \tag{9}$$

Given several K_{p} values instead of $K(T)$ for different temperatures, a regression can be performed to obtain a K_{p}/T relationship and to determine if the data are in accord with the Van't Hoff equation. The experiments are performed at several p_{NO} to calculate n according to eq 8 and K_{p} according to eq 9, and also at several temperatures to evaluate the enthalpy of the reaction.

Experimental Section

Materials. The $\mathrm{CoCl_2 \cdot 6H_2O}$ used was produced by the Longhua factory, Guangdong Province, China, with a mass fraction of more 99 %. The anhydrous ethylenediamine (purity of beyond 99%), produced by the Shanghai Lingfeng Co. Ltd., was of analysis quality. The water used to prepare solutions was distilled. NO used is produced by the Shanghai Standard Gas Co. Ltd.

Procedure. The investigations were carried out in a closed laboratory-scale bubble. A diagram of the experimental setup is given in Figure 1. The bubble column is operated continuously with respect to the gas phase and batchwise for the liquid phase. The 250 mL solution of $\mathrm{CoCl_2 \cdot 6H_2O}$ is first poured into a bottle and is degassed by evacuating the air over the solution with simultaneous sonification using an ultrasonic cleaner (Shanghai, China) for about 20 min until no bubbles are released from the liquid. The solution is then poured into the column while maintaining the solution closed to air. After the degassing, 5 mL of ethylenediamine is injected into the solution to obtain get the desired Co(II)-en concentration in the solution. A known mixture of NO and N_2 is then bubbled continuously through the Co(II)-en solution until equilibrium is reached. The time needed is different in each temperature studied. When the NO partial pressure at the entrance of the bubble column is equal to the NO partial pressure at the exit of the bubble column, equilibrium is reached. The inlet NO concentrations vary between (300 and 800) ppm. The gas flow rate of the experiments is around 700 $\mathrm{mL \cdot min^{-1}}$, and absorption occurs at atmosphere pressure. The temperature at which the reaction took place is adjusted by means of a thermostated water bath. For all experiments, 0.0025 $\mathrm{mL \cdot min^{-1}}$ aqueous Co(II)-en is used.

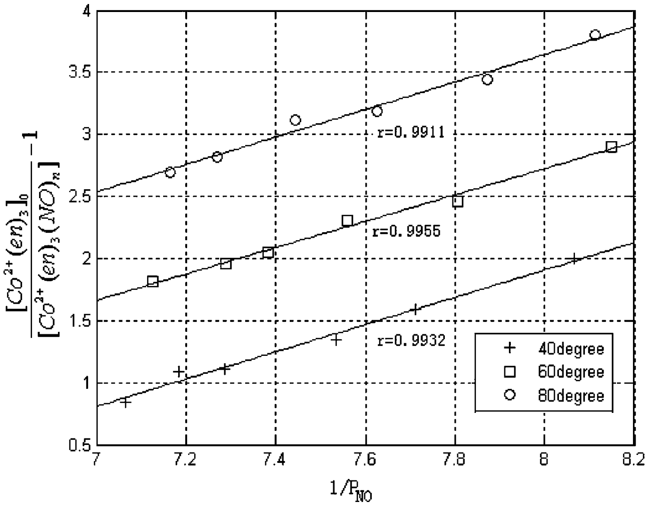

Figure 2. Log−log plot of $[Co(en)_3]_0^{2+}/[Co(en)_3(NO)_n]^{2+} - 1$ vs $1/P_{NO}$ at (40, 60, and 80) °C.

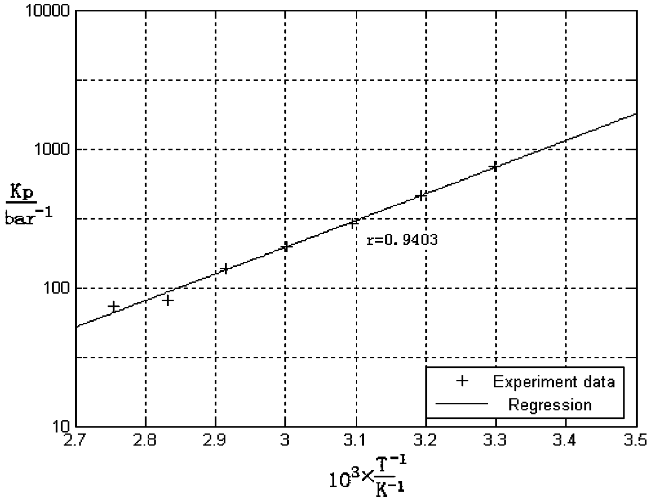

Figure 3. Experimental values for K_p at different temperature and the regression through all points.

Analysis. The NO partial pressure at the outlet of the bubble column is measured continuously by means of a gas analyzer (Testo 335, made in Germany). The inlet concentration was measured via a bypass arrangement. The registered time profile of the outlet partial pressure is integrated and the amount of absorbed NO determined.

Results and Discussions

The present study is based on 26 experiments that were carried out over the temperature range of (30 to 90) °C. The reciprocal of NO partial pressure versus $[Co(en)_3]_0^{2+}/[Co(en)_3(NO)_n]^{2+} - 1$ (log−log plot) for temperatures of (40, 60, and 80) °C is shown in Figure 2. The slope of the lines of best fit are 1.09 ± 0.1080 (40 °C), 1.06 ± 0.0846(60 °C), and 1.10 ± 0.1208(80 °C), respectively, indicating that the value of n is 1 in $Co^{II}(en)_3(NO)_n$, i.e., the reaction should be

$$NO + [Co(en)_3]^{2+} \Leftrightarrow [Co(en)_3(NO)]^{2+} \tag{10}$$

The value of K_p is calculated for every experimental point according to eq 9. A plot of K_p versus the reciprocal of T is given in Figure 3. Figure 3 depicts the experimental data, in the form of a van't Hoff plot. All experimental data fit the van't Hoff plot well. This indicates that the reaction enthalpy is independent of temperature over the temperature range studied.

Table 1. Calculated K_p Values Determined Using Equation 14

temperature/°C	K_p/bar^{-1}
20	1205.7
25	936
40	459
50	297
80	93

The van't Hoff equation is

$$\left(\frac{\partial \ln K_p}{\partial T}\right)_p = \frac{\Delta H^0}{RT^2} \tag{11}$$

and integration of this equation gives

$$\ln K_p = -\frac{\Delta H}{RT} + C \tag{12}$$

From the regression of the data shown in Figure 3:

$$\ln K_p = 4428.5/T - 8.0118 \tag{13}$$

From this expression, the following equilibrium expression, as a function of temperature,

$$K_p = (3.3153 \pm 0.1160) \times 10^{-4} \exp(4428.5 \pm 96.2/T)/\text{bar}^{-1} \tag{14}$$

is obtained. From eqs 12 and 14, the reaction enthalpy is equal to

$$\Delta H^0 = -(36.821 \pm 0.800)\ \text{kJ}\cdot\text{mol}^{-1} \tag{15}$$

The values of K_p values at different temperatures, calculated from eq 14, are given in Table 1.

The temperature dependence of the equilibrium constant can provide data for a kinetic investigation of the scrubbing denitrification process. Our former investigation[17] indicated that a very high nitric oxide removal efficiency could be achieved by the Co(II)-en complex solution in the presence of oxygen. Combining the mechanism of the absorption of oxygen by Co(II)-en complex, the denitrification kinetics maybe systemically investigated, and data could be provided for industrial scale-up. Sulfur dioxide could be largely absorbed by the complex solution because of the solutions high pH. Little sulfur will be absorbed, and the sulfite produced will lead to complicated reactions in the solution.

Conclusion

The equilibrium constants of the reaction between NO and Co(II)-en in the temperature range of (30 to 90) °C, an Co(II)-en concentration of 0.0025 mol·L^{-1}, and an NO inlet concentration range of (300 to 800) ppm have been determined. The experiments were carried out in a closed laboratory-operated bubble column, in batch with respect to the liquid phase and continuously with respect to the gas phase. The equilibrium constant was determined using the uptake of NO. The results of this study will be valuable input for subsequent experimental and modeling studies to determine the kinetic constants of the relevant reactions in the deNOx process at various process conditions and an optimum deNOx absorber design.

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Glossary

[ ]	aqueous phase concentration, mol·L^{-1}

ΔH^0	reaction enthalpy, kJ·mol^{-1}
vi	symbol representing stoichiometric factor
a	activity, dimensionless
H_{pc}	Henry's coefficient, bar·mol^{-1}·L
K	equilibrium constant, L·mol^{-1}
K_p	modified equilibrium constant, bar^{-1}
P	partial pressure, bar
T	temperature, K
en	ethylenediamine
γ^r	rational activity coefficient, dimensionless
n	stoichiometric factor, dimensionless

Indices

i	*i*th component
0	initial value (of the concentration)

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