Mechanistic Study on the Removal of NO₂ from Flue Gas Using Novel Ethylene Glycol-tetrabutylammonium Bromide Deep Eutectic Solvents

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ABSTRACT: The removal of NO₂ (approximately 90% of which is NO) from flue gas is a crucial process for clean power generation from coal combustion. Oxidation of NO to NO₂ followed by NO₂ absorption using sorbents is considered to be a promising technology alternative to selective catalytic reduction (SCR). This study investigated the absorption of NO₂ in flue gas by ethylene glycol (EG)-tetrabutylammonium bromide (TBAB) deep eutectic solvents (DESs) under a range of experimental conditions. The effects of experimental conditions including molar ratio of EG to TBAB, operating temperature, residence time, and the O₂ and steam partial pressure in the flue gas on the denitration performance of EG-TBAB DESs were systematically analyzed. The concentrations of NO₂ in the inlet and outlet were evaluated using a flue gas analyzer. The chemical structure changes of DESs after denitration were characterized using Fourier transform infrared (FT-IR) spectroscopy. The obtained analysis signified that maximum denitration efficiency and capacity were achieved at a EG/TBAB molar ratio of 5:1, 50 °C, and 6 s residence time. EG-TBAB DESs were able to maintain a stable denitration performance after five absorption-desorption cycles. The results of quantum chemical calculation and 1H NMR spectra of EG-TBAB DES show that bromide anions in the EG-TBAB DES maintained strong interactions with NO₂ via hydrogen bonding, leading to increased NO₂ adsorption. The presence of O₂ and steam in the flue gas improved the absorption of NO₂ in EG-TBAB DESs due to chemical reactions and formation of nitrate.

INTRODUCTION

Elimination of nitrogen oxides (NO₅) that are present in the flue gas is critical as NO₅ emissions raise significant environmental concerns such as acid rain, ozone depletion, and photochemical smog.¹⁻⁻³ NO is the primary component of atmospheric NO₅ (~90%); it is inert and has extremely low solubility in common solvents. Current industrial technologies for NO₅ reduction include selective catalytic reduction and selective noncatalytic reduction (SCR⁴ and SNCR⁵, respectively). However, these technologies require a sizable initial investment, high operating costs, and generate secondary pollution, which restrict their commercial utilization.⁶⁻⁻¹⁰ Therefore, developing environmentally friendly, high-performing, and low-cost NO₅ sorbents for simple NO₅ removal systems is of paramount importance.

Deep eutectic solvents (DESs) are mixtures of different compounds that have lower melting points compared to the individual components of mixture.⁸⁻⁻¹⁰ Recently, DESs have been considered as promising alternatives to traditional gas sorbents due to their excellent properties such as “tailormade” characteristics, better structural integrity, ideal solubility, and extraordinary thermal and chemical stabilities.¹¹⁻⁻¹³ Furthermore, DESs are produced from cheap and nontoxic natural sources. Hence, they exhibit great potential in large-scale gas sequestration and sustainable applications.¹⁴⁻⁻¹⁷

Current studies on gas absorption using DESs focus on gases such as CO₂, SO₂, and H₂S.¹⁴,¹⁶⁻⁻¹⁸ However, there are limited studies on using DESs as sorbents for NO₅.¹⁹⁻²¹ Duan et al. found solubility differences in DESs with differing component ratios and operating temperatures by investigating the solubility of pure nitrogen oxide and nitrogen dioxide in various caprolactam-based DESs.²² To the best of our knowledge, a few reports involving the selective removal of NO from flue gas using DESs have been published;²² these reports indicated a 100% NO removal efficiency within 40 min. However, the denitration capacity was significantly lower compared to active acidic gases such as NO₂. Over the past 20 years, many denitration methods have incorporated an oxidation step to oxidize NO to higher-valence NO₅ (e.g., NO₅.

Received: September 19, 2020
Accepted: November 10, 2020
Published: November 25, 2020
and N₂O₃) to improve denitrification efficiency in an absorption tower.⁴⁻²⁶ These oxidation methods included using a strong oxidant, catalytic oxidation, plasma, and others.²⁷,²⁸ Thus, it is feasible to reduce NOₓ emissions via catalytic oxidation of NO followed by NO₂ removal.

Limited literature data show that DESs significantly absorb pure NO₂.²³ However, the absorption mechanism is still unclear. Meanwhile, little research has been carried out on the absorption of NO₂ by DES at low partial pressures of NO₂. In this study, we addressed the unexploited research by studying the selective absorption of NO₂ from simulated flue gas as a function of DES composition, operation temperature, residence time, and flue gas composition. Current literature supports the understanding of interaction mechanisms between DES components and NO₂ molecules, which facilitate the advancement of high-performing and low-priced NOₓ sorbents.

## RESULTS AND DISCUSSION

### Influence of Operation Temperature

The effect of operating temperature on the removal of NO₂ was analyzed using an ethylene glycol (EG)-tetrabutylammonium bromide (TBAB) molar ratio of 5:1 and 6 s residence time. As shown in Figure 1a, the fresh EG-TBAB DES was colorless. However, as it absorbed NO₂, it turned brown after absorbing NO₂ at 30 °C, dark brown at 50 °C, and light brown at 70 °C. Since pure NO₂ is a red-orange colored gas, the color change before and after NO₂ absorption suggested that NO₂ was successfully absorbed in the EG-TBAB DES solution. The darkest color at 50 °C indicated the highest NO₂ absorption concentration.

NO₂ removal efficiency at different operation temperatures was computed using eq 1, and the calculated results were plotted against the absorption time, as illustrated in Figure 1b. Initially, the NO₂ removal efficiency consistently surpassed 95% at all three operation temperatures. However, the breakthrough time (when removal efficiency drops below 90%) changed significantly with operating temperature. The breakthrough time initially increased from ~600 to ~800 min as the temperature increased from 30 to 50 °C, and then dropped to ~110 min at 70 °C. As shown in Figure 1c, the denitrification capacity (calculated using eq 2) peaked at 50 °C, which was consistent with the longest breakthrough time and dark-brown appearance.

NO₂ removal efficiency and denitrification capacity as a function of temperature were similar to those of NO, as previously reported.²² The longest breakthrough time and the maximum denitrification capacity were detected at 50 °C for both gases in EG-TBAB DESs. The physical absorption was more favorable at low temperatures, whereas elevated temperatures favored chemical absorption. The optimal operating temperature at 50 °C implied that EG-TBAB DESs adsorbed NO₂ both physically and chemically, similar to NO. However, the breakthrough period and the denitrification capability of NO₂ were more than an order of magnitude higher than those of NO. EG-TBAB showed a higher adsorption efficiency for NO₂. Therefore, removal of NO₂ via NO oxidation is a promising alternative for removing NOₓ in flue gases.

Figure S1 displays the Fourier transform infrared (FT-IR) spectra of fresh and used EG-TBAB DES before and after NO₂ absorption at different residence times (operating temperature, 50 °C; EG-to-TBAB molar ratio, 5:1; and 0.15% NO₂).
TBAB. However, differences such as the C=C stretching vibration of the aromatic ring were observed in the intensity and fine structure of absorption wavelengths between fresh and used EG-TBAB DESs; these could be due to weak chemical absorptions between NO2 and EG-TBAB.

Effect of Residence Time. EG-TBAB DESs NO2 removal efficiency and denitrification capacity with respect to residence time are shown in Figure 2a,b, respectively. For a 6 s residence time, the NO2 removal efficiency remained at 100% for the first 550 min and subsequently dropped to the breakthrough point at which the removal efficiency decreased to 90% after ~800 min. When the residence time was reduced to 4.5 s, NO2 removal efficiency remained at 100% for the first 400 min, and then dropped sharply to 90% for 455 min. When the residence time was lowered to 3 s, the NO2 removal efficiency remained at 88% for the first 200 min and then decreased rapidly. The denitrification capacity decreased with shorter residence times, similar to the removal efficiency. These results indicated that the solubility of NO2 in DESs did not reach saturation when the residence time was between 3 and 4.5 s. Increasing the residence time of NO2 gas in the EG-TBAB DESs promoted the interactions and retention of NO2.

Effect of EG/TBAB Molar Ratio. Figure 3 shows the EG-TBAB DES denitrification capacity and the removal efficiency of NO2 as a function of EG-to-TBAB ratio at 50 °C for 6 s residence time. The breakthrough time increased as the molar ratio increased from 3:1 to 5:1, but decreased with a further increase of the molar ratio from 5:1 to 50:1 (cf. Figure 3a). With an EG-TBAB of 50:1 and pure EG, the NO2 removal efficiency was very low and did not reach the breakthrough point at any stage throughout the process. The denitrification capacity followed the same trend of the removal efficiency, i.e., initially increasing as the EG content reached 5:1 but subsequently decreasing significantly (cf. Figure 4b). NO2 interacted strongly with EG-TBAB DESs via H-bonding, which is detailed in the following section. DESs contain a large number of asymmetric ions, which in turn leads to a lower lattice energy. The delocalization of charges in hydrogen bonds between halogen ions and HBD is the primary reason for the reduction of the melting point of DES. In addition to the expected BrHN hydrogen bonds, EG also forms hydrogen bonds with the bromine cation (e.g., OHNBr), resulting in both Ch-EG and Br-EG clusters. At the optimal molar ratio of 5:1, the original crystal structures may have been destroyed, and extensive H-bond networks were formed. This observation was in agreement with our previous study,22 which speculated that there was no melting point and the lowest glass-transition temperature was detected at the 5:1 molar ratio. These results differed from previous work on NO removal by EG-TBAB DESs,22 where the optimum molar ratio was 50:1. This result can be attributed to the weak H-bonding between NO and EG-TBAB.

Regeneration Capability of EG-TBAB DESs. To investigate the regeneration performance and desorption of NO2, N2 was bubbled through the NO2-EG-TBAB DESs at 90 °C for 3 h under a similar experimental setup. NO2 removal efficiency and denitrification capacities of the regenerated EG-TBAB DES samples were analyzed at 6 s flue gas residence time at 50 °C, as shown in Figure 4. No observed drop in removal efficiency and denitrification capacity was detected after five cycles of absorption–desorption runs, e.g., the absorption capacities (g NO2/100 g DES) of DES are 48.94, 48.15, 47.31, 47.29, and 47.19, which indicated an excellent regeneration ability of EG-TBAB DESs. The reversibility and
stability of NO₂ absorption—desorption for EG-TBAB DESs further proved that the NO₂ molecules were absorbed by EG-
TBAB DESs.

Quantum Chemical Calculation on the Interaction of EG-TBAB DESs with NO₂. The structures of EG-TBAB DESs with NO₂ were optimized and calculated using DFT-DMol.

Each preliminary configuration was considered, and the lowest-energy complex was considered with optimized structure (Figure 5). The structure variables for the optimized geometries are listed in Table 1. The organization of gaseous molecules around the anion is correlated to the absorption. Figure 5a shows that the Br anion interacted strongly with the N atom in NO₂ at 5.36 Å. The positively charged H in EG interacted strongly with an O atom from NO₂ at 2.24 Å. Due to these strong interactions, the average O–N–O angle bends from 179.98 to 134.01° and the N–O bond length elongates by 7% to 1.19 Å. These angle and bond length changes were more pronounced for NO₂ in an EG-TBAB-NO₂ complex than for isolated NO₂. Figure 5c shows that the Br anion in EG-
TBAB DES was the primary active site for NO₂ absorption. Hydrogen bonding played a critical role in NO₂ absorption. The interaction energy and absorption enthalpy are essential to affect the gas absorption capacity. The binding energy and absorption enthalpy for the EG-TBAB-NO₂ complex (−36.97 kJ/mol) were larger than those for EG-TBAB DES (−34.91 kJ/mol) and NO₂ (−2.05 kJ/mol), indicating that NO₂ absorption preferably occurs in EG-TBAB DES. In addition, absorption resulted in a change in charge distribution. The net charge (−0.65e) transferred from DES to NO₂ on the EG-
TBAB DES–NO₂ complexes, which allowed the Br anions to maintain strong interactions with NO₂ that facilitate NO₂ adsorption.

A comparison between the ¹H NMR spectra of EG-TBAB DES before and after NO₂ absorption is shown in Figure 6. It can be observed that the standard peaks of H atom in TBAB at 1.3 and 3.35 ppm, which are assigned to the chemical shift of the H atom connected to C(2) and C(4,5), respectively, shifted down to 1.40 and 3.40 ppm. The peak of −OH in EG shifted up from 3.85 to 3.95 ppm. These results demonstrate that the EG and Br⁻ can form a hydrogen bond and an intermolecular force with NO₂, which in turn may enhance the NO₂ absorption. Also, it can be seen that the intensity of the peaks experienced a slight change in intensity. This phenomenon could be caused by the reaction of NO₂ and OH···Br⁻, which further indicates that the positive charge is not evenly distributed over the TBAB. This finding was also consistent with the density functional theory (DFT) results of the EG-TBAB DES NO₂ absorption.

Effects of Steam on NO₂ Absorption. Figure 7 shows the EG-TBAB DESs NO₂ removal efficiency and denitrification capacity for steam compositions of 0 and 5% at 50 °C. In the absence of steam, the NO₂ removal efficiency of EG-TBAB DESs remained at 100% for the first 500 min but dropped significantly thereafter. However, with 5% steam, the NO₂ removal efficiency remained at 100% for the duration of the experiment (1000 min), with a concentration of 50 ppm NO after 200 min (Figure 7a). The denitrification capability of the EG-TBAB DESs increased by 30% in the presence of steam (cf. Figure 7b). These results signified that the existence of steam in the flue gas enhanced the removal of NO₂ by EG-
TBAB DESs and may be due to interactions between polar H₂O and NO₂ molecules. NO₂ could react with H₂O to form HNO₃ at low temperatures, i.e., 3NO₂ + H₂O = 2HNO₃ + HNO₄.

Table 1. Structural Parameters of EG-TBAB DESs before and after NO₂ Absorption

| structural parameters | DES | NO₂ | DES-NO₂ | Δ |
|-----------------------|-----|-----|---------|---|
| C−O−H (deg)           | 108.19 | 108.01 | 0.18    |   |
| O−H (Å)               | 0.97  | 0.97 | 0       |   |
| O−N (Å)               | 1.11  | 1.19 | 0.08    |   |
| O−N−O (deg)           | 179.98 | 134.01 | 45.97   |   |

Figure 5. Optimized structure of complexes (a) EG-TBAB DES, (b) NO₂, and (c) EG-TBAB DESs with NO₂.

Figure 6. ¹H NMR spectra of EG-TBAB DES before and after NO₂ absorption.
NO. EG-TBAB had a high adsorption capacity for HNO₃ and NO.Only the generated NO (50 ppm) was detected. Figure S2 displays the FT-IR spectra of EG-TBAB DESs before and after NO₂ removal in the presence and absence of steam. Peaks ascribed to aromatic carbon (∼1610 cm⁻¹), stretched aromatic rings (1560–1490 cm⁻¹), and out-of-plane aromatic C–H vibrations (700–900 cm⁻¹) were observed for all samples. The peak at 1650 cm⁻¹ corresponds to −N−O vibration bands from NO₃⁻. When 5% steam was added to the flue gas, NO₃⁻ was formed after absorption of NO₂, suggesting that steam improved NO₂ absorption. This result further confirmed the aforementioned mechanism of NO₂ absorption by EG-TBAB DESs.

**Influence of Steam and Oxygen on NO₂ Removal.** Oxygen plays a critical role in NO₂ removal by EG-TBAB DES because it oxidizes NO to NO₂ at low temperatures and thus enhances NO₂ removal efficiency. Figure 8a shows the changes of NO₂ removal efficiency and NO concentration in the outlet flow as a function of flue gas O₂ concentration with 5% steam. The NO₂ removal efficiency was 100% for all three conditions investigated. However, the outlet concentration of NO decreased as the O₂ partial pressure increased and dropped below the detection limit with 10% O₂ in the flue gas. The denitrification capacity also increased with O₂ partial pressure (cf. Figure 8b).

These results indicated that the NO₂ removal efficiency and denitrification ability of the EG-TBAB DESs can be promoted by the coexistence of oxygen and steam. One possible reason for this synergic effect of O₂ and steam is that absorbed O₂ in EG-TBAB could dissociate and convert to active lattice oxygen and thus catalytically oxidize NO₂ to HNO₃. As shown in Figure S3, peaks corresponding to vibration bands of −N−O from NO₃⁻ (1650 cm⁻¹) were noted in both the presence and absence of O₂, but higher peak intensities were observed at higher O₂ partial pressures; this indicated an increased concentration of NO₃⁻ and greater removal of NO₂. NO₂ removal efficiency and denitrification capacity were higher than those for NO in EG-TBAB DESs, further indicating the feasibility of oxidizing NO into NO₂ in flue gases, with subsequent removal using EG-TBAB DES in the presence of steam and oxygen without the formation of secondary products. The outcome provides a potential route for designing future industrial denitrification technologies.

**CONCLUSIONS**

EG-TBAB DESs have demonstrated excellent performance in the removal of NO₂ from flue gas. The peak denitrification efficiency and capacity were attained at a 5:1 EG-to-TBAB molar ratio, 50 °C, and 6 s residence time. The presence of steam and oxygen in the flue gas promoted NO₂ absorption by EG-TBAB DESs due to the formation of nitrate via reactions with O₂ and H₂O. Hydrogen bonding played a significant role during NO₂ absorption. Br anions maintained a strong interaction with NO₂, resulting in high denitrification capacity. EG-TBAB DESs displayed an excellent denitrification consistency after five cycles of absorption and desorption, suggesting that the desorption of NO₂ was relatively easy and required low energy input for regeneration. Therefore, DESs have potential as high-performing denitrification sorbents with applications in industrial denitrification technologies.

**MATERIALS AND METHODS**

Ethylene Glycol-tetrabutylammonium Bromide DES Preparation. Pure analytical ethylene glycol (EG) and tetrabutylammonium bromide (TBAB) reagents utilized in
this study were from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. To understand the effect of molar ratio of EG and TBAB, different ratios (4:2, 6:2, 8:2, 10:2, 20:2, and 100:2) of these compounds were prepared and stored based on the previously reported methods. The Karl Fischer coulometric titration method was used to analyze the H2O content of the desiccated DES solutions, which was found to be less than 0.5 wt %.

Classification of Ethylene Glycol-tetrabutylammonium Bromide DESs. The characterization methods for the EG-TBAB DESs are described in detail from our previous study. In brief, a Thermo Fisher Nicolet PerkinElmer device (Figure S1) was used to detect the change in the ATR-FT-IR spectra. The difference in the 1H NMR spectra of EG-TBAB DES samples before and after the absorption of NO2 was recorded using a 400 MHz spectrometer (Bruker Avance III, Switzerland) with heavy water (D2O) as a solvent and tetramethylsilane (TMS) as the internal standard.

DFT Analysis of DES Structure. Density functional theory (DFT) was used to determine quantum chemical interactions between DESs and NO2. Detailed specifications of the DFT analysis method/procedure are found elsewhere. The Brillouin-zone integrations were achieved by means of a 4 × 2 × 1 Monkhorst Pack grid. All of the computations were calculated by the DMol3 program.

NO2 Absorption Experiments. NO2 absorption experiments were conducted in a bubble column reactor and were illustrated and described in detail in our previous study. The experiments were carried out in a glass container immersed in a H2O bath, which had a temperature accuracy of ±0.10 °C. The gas distributor consisted of a 2 cm disk base, and the magnitude of the bubbles formed was about 2 mm. The effects of DES residence time, operational temperature, and molar ratio on the removal efficiency of NO2 were examined using a simulation of the flue gas that contained 0.15 vol % NO2 and then stabilized with the addition of nitrogen gas. In addition, 0–5 vol % steam and 0–10 vol % oxygen were injected to the simulated flue gas to investigate the effects of oxygen and steam on the removal of NO2 with EG-TBAB DESs. The concentration of NO2 in the outlet gas was continuously monitored by a German-made MRU MGAS online flue gas analyzer. The online flue gas analyzer had a detection accuracy of ±2 ppm, and the experimental runs were repeated for at least three times for result accuracy. Residence time ranging from 3 to 6 s was used in this study.

The NO2 removal efficiency (η) was computed by eq 1

\[ \eta = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \]  

(1)

where \( C_{in} \) and \( C_{out} \) are the concentrations of NO2 (ppmv) in the inlet and outlet of the flue gas, respectively.

The quantity of the absorbed NO2 (denitrification capacity) was calculated by eq 2

\[ m_{\text{NO2}}(\text{gNO2}/100 \text{ gDES}) \]

\[ = \frac{M_{\text{DES}} \times \rho_{\text{NO2}} \times \int_{t_1}^{t_2} (C_0 - C_{\text{NO2}}(t)) \, dt}{m_{\text{DES}} \times M_{\text{NO2}}} \]  

(2)

where \( m_{\text{NO2}} \) is the mass absorption capability of NO2 in EG-TBAB DES, \( t_1 \) and \( t_2 \) are the initial and saturation times during absorption, respectively, \( Q \) (mL/min) is the flow rate of the gas stream, and \( m_{\text{DES}} \) and \( \rho_{\text{NO2}} \) stand for the mass of DES that was used during absorption and the density of NO2, respectively.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04604.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was financially supported by the Education Department Excellent Talents Training Program of Liaoning Province (2020LNQN21) and the Excellent Talents Training Program of University of Science and Technology Liaoning (2019RC12). Funding from the Key R&D Funding Scheme of Liaoning Province (2017308008) is also acknowledged. The

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authors thank A/Prof. Guangyue Li for his suggestion at the Quantum Chemical Calculation.

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