Functionalized Tertiary Amines as SO_2 Absorbents

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Abstract - Nitrile-functionalized amines, including 3-(*N*,*N*-diethylamino)propionitrile, 3-(*N*,*N*-dibutylamino)propionitrile, and *N*-methyl-*N,N*-dipropionitrile amine were synthesized, and their interaction behaviours with SO_2 were compared with those of hydroxyl-functionalized amines by experimental, spectroscopic, and computational methods.

Keywords: SO_2; Absorbent; Amine; Nitrile; Recycle

1. Introduction

The absorption of SO_2 in a liquid absorbent is mostly governed by the interaction between acidic SO_2 and the basic absorbent [1, 2]. In this context, high SO_2 absorption capacity can be easily achieved simply by employing a basic primary or secondary amine as an absorbent [3, 4]. However, the primary and secondary amines with a N-H bond or bonds tend to strongly interact with SO_2, forming sulfamite and/or bisulfite species, which are hard to desorb SO_2 even at elevated temperatures. Moreover, the desorption of SO_2 at elevated temperatures often results in the irreversible decomposition of amines. For this reason, the aqueous solutions of tertiary amines without possessing a N-H bond have been employed as SO_2 absorbents. The most commonly used tertiary amines for this purpose are the tertiary alkanolamines with two or three N-bound hydroxyethyl groups such as *N*-methyl-*N,N*-diethanolamine (MDEA) and *N,N,N*-triethanolamine (TEA). In spite of their high thermal stability toward the degradation, tertiary alkanolamines, however, are also found to exhibit poor recyclability (cyclic capacity) similar to those of primary and secondary amines at temperature around 100 °C. Computational calculation with *N*,*N*-dibutyl-*N*-ethanolamine (DBEA), conducted in this study, suggests that the poor cyclic capacity of tertiary alkanolamines can be ascribed to the interaction of SO_2 with the hydroxyl groups, resulting in the formation of thermally stable zwitterionic species with a tethered sulfite anion (-OSO_2^-) (*vide infra*).

As a means of improving the regenerability of tertiary alkanolamines, a hydroxyl group or groups of alkanolamines have been replaced by an electron-withdrawing nitrile group or groups. With this approach, it is expected that the higher cyclic capacity could be achieved because the additional interaction between SO_2 and the hydroxyl group is not available.

Herein, we report the synthesis of several nitrile-functionalized tertiary amines, including 3-(*N*,*N*-diethylamino)propionitrile (DEAPN), 3-(*N*,*N*-dibutylamino)propionitrile (DBAPN), and *N*-methyl-*N,N*-dipropionitrile amine (MADPN) as well as their performances as SO_2 absorbents. The different absorption behaviors of nitrile-functionalzed tertiary amines from those of tertiary alkanolamines are also discussed on the basis of experimental and computational calculation results.

2. Results and Discussion

The nitrile-functionalized tertiary amines (DEAPN, DBAPN, and MADPN) were synthesized as shown in Scheme 1, and their gravimetric and molar SO_2 absorption capacities were compared with those of hydroxy-functionalized tertiary amines (*t*-alkanolamines). As can be seen in Fig. 1, *t*-alkanolamines exhibit higher gravimetric SO_2 absorption capacities (g SO_2 /g amine) than the nitrile-functionalized tertiary amines at 30 °C. The gravimetric SO_2 absorption at saturation were measured at 0.897 (1.77), 0.730 (2.08), 0.655 (1.39), 1.517 (2.78), 1.084 (2.94), and 1.183 (2.20) for DEAPN, DBAPN, MADPN, DEEA, DBEA, and MDEA, respectively.
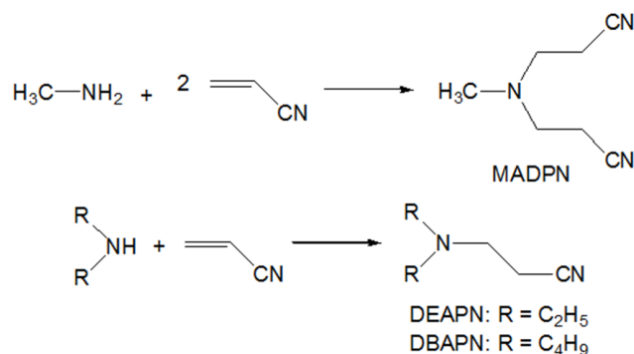
Scheme 1. Synthetic route for the nitrile-functionalized amines.

The numbers in parentheses are the molar absorption capacities (mole SO_2/mole amine). It is worthwhile to note that the molar absorption capacities of t-alkanolamines are in the range 2.20 – 2.94. If SO_2 is absorbed in t-alkanolamines only through the chemical interaction, the molar SO_2 absorption capacities of t-alkanolamines cannot exceed 1. In this context, it is assumed that physical interaction is also involved in the absorption of SO_2 in t-alkanolamines. As zwitterionic species with a tethered sulfite anion ($-OSO_2^-$) are expected to produce from the interaction of SO_2 with t-alkanolamines [30], it is conceivable that substantial amounts of SO_2 are absorbed in t-alkanolamines through the physical interaction between acidic SO_2 and the bacic sulfite anion. In contrast to the t-alkanolamines, nitrile-functionalized tertiary amines do not possess an additional fuctional group to chemically interact with SO_2. Moreover, their basicities are also too weak to form stable charge transfer complexes with SO_2 due to the presence of an electron-withdrawing nitrile group. Therefore, it is considered that the absorption of SO_2 in nitrile-functionalized tertiary amines is mostly governed by the physical interactions via hydrogen bonding between SO_2 and CH_2 groups (*vide infra*). This is probably one of the reasons why nitrile-functionalized tertiary amines exhibited lower absorption capacities than the corresponding t-alkanolamines. Nonetheless, the absorption capacities of nitrile-functionalized tertiary amines are still sufficiently high enough to remove SO_2 present in small quantities in flue gases.

Interestingly, the nitrile-functionalized tertiary amines exhibited higher absorption rates than the corresponding t-alkanolamines. It is well recognized that the viscosity of a physical sorbent for SO_2 capture decreases with the increase of the SO_2 absorption in the solvent, whereas the viscosity of a chemical sorbent increases rapidly with increasing absorption of SO_2 [5,6]. In this context, the higher rates of absorption for the nitrile-functionalized tertiary amines could be ascribed in part to their lower viscosities, resulting in the faster mass transfer (see *vide infra*).

To examine the reversibility of SO_2 absorption, SO_2 was absorbed in a tertiary amine at 30 °C for 2 h at a rate of 20 mL min^{-1} and desorbed at 80 °C for 2 h by bubbling N_2 at a rate of 20 mL min^{-1} at atmospheric pressure. As can be seen in Fig. 2, the recycle experiments with DEAPN, DBAPN, and MADPN clearly demonstrate that the absorbed SO_2 can be completely desorbed at 80 °C, allowing all the nitrile-functionalized tertiary amines to be recyclable without any loss of initial performances. On the contrary, t-alkanolamines, DEEA, DBEA, and MDEA exhibited extremely poor recyclability.

As can be seen in Fig. 3, after the first absorption-desorption cycles, it was observed that approximately 40-45% of SO_2 absorbed in the t-alkanolamines remained undesorbed. The same amounts of desorbed SO_2 in the first cycle were found to be re-absorbed and easily desorbed in the following cycles. This is a strong indication that the absorption of SO_2 in t-alkanolamines proceeds through both chemical and physical interactions. Considering the amounts of undesorbed SO_2 in the first cycle, it is likely that SO_2 interacts with a t-alkanolamine approximately in a 1:1 molar ratio.

To elucidate the role of functional group on the SO_2 absorption in tertiary amines, theoretical investigation was conducted at the B3LYP level of the theory (6-31+G* for C, H, N, O, and S) using the Gaussian 03 program. Fig. 4 is the optimized structure showing the interaction of SO_2 with DBAPN. As can be seen in the optimized structure, there is a weak interaction between the sulfur atom of SO_2 and the amino nitrogen atom. The oxygen atoms of SO_2 are also found to weakly interact with each of the hydrogen atoms of methylene groups bonded to the nitrile and amino groups. The interaction enthalpy (ΔH) was calculated as -8.1 kcal mol^{-1}, suggesting that the SO_2 absorption in DBAPN is a favorable process.
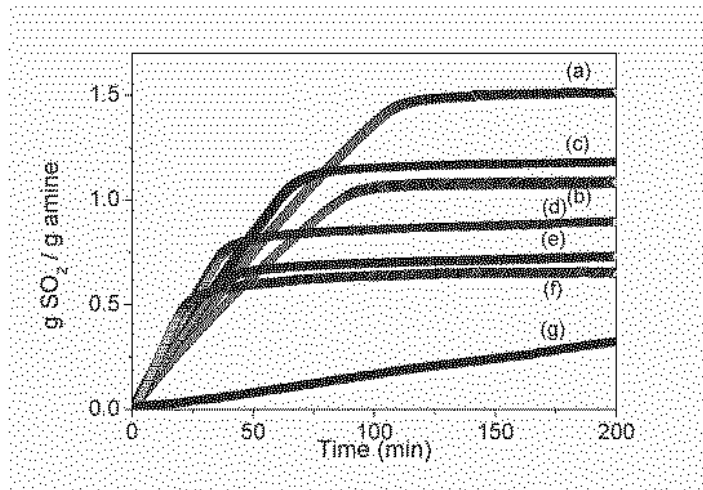
Fig. 1: Gravimetric SO_2 absrption capacity of (a) DEAPN, (b) DBAPN, (c) MADPN, (d) DEEA, (e) DBEA, (f) MDEA, and (g) TBA at 30 °C.
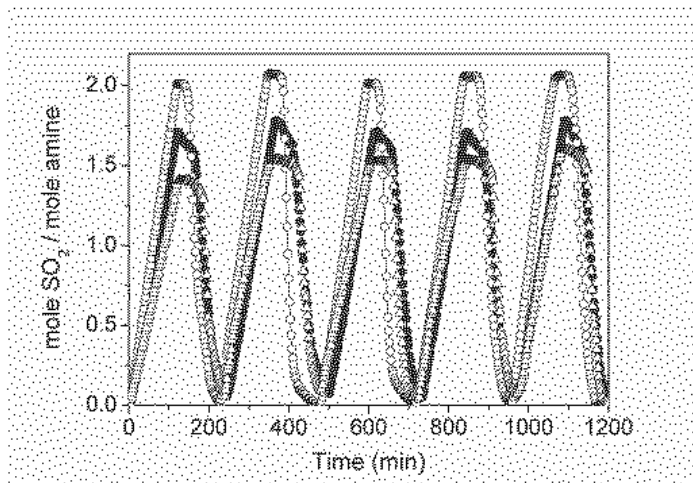

Fig. 2: SO_2 absorption-desorption cycles of DEAPN (-●-), DBAPN (-○-), and MADPN (-Δ-). In each cycle, SO_2 is absorbed at 30 °C and at atmosphere pressure, and desorbed at 80 °C.
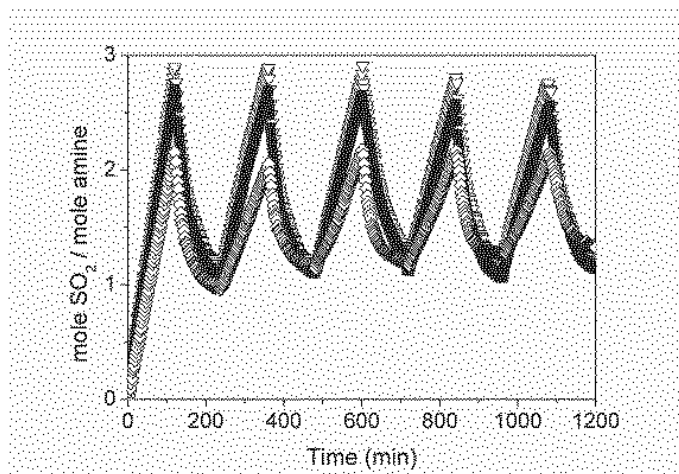

Fig. 3: SO_2 absorption-desorption cycles of DEEA (-■-), DBEA (-∇-), and MDEA (-◊-). In each cycle, SO_2 was absorbed at 30 °C and at atmosphere pressure, and desorbed at 80 °C.
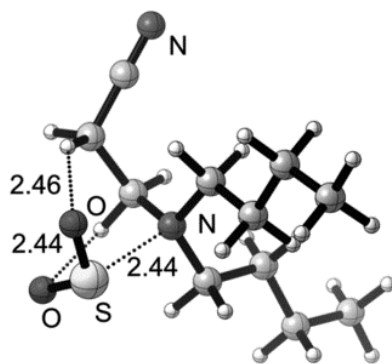
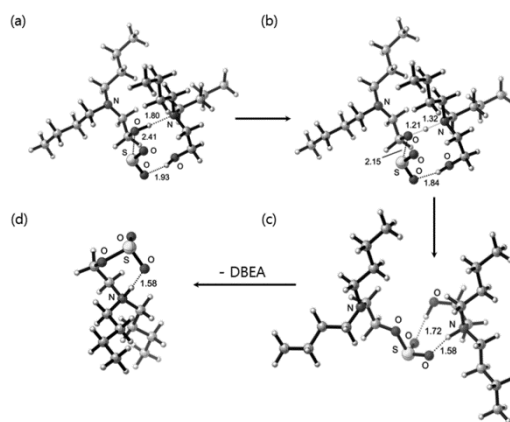Fig. 4: Optimized structure showing the interaction of SO_2 with DBAPN (ΔH = -8.1 kcal mol^{-1}).

Fig. 5: Optimized structures showing the reaction pathway for the interaction of SO_2 with DBEA:
(a) reactant (G = 0 kcal mol^{-1}), (b) transition state ($\Delta G^{\ddagger}$ = +2.5 kcal mol^{-1}), (c) intermediate species
(ΔG = -0.6 kcal mol^{-1}), and (d) product (ΔG = -4.6 kcal mol^{-1}).

For comparison, the interaction of SO_2 with DBEA was also calculated. In order to better reflect the the absorption behavior of SO_2 in DBEA, two DBEA molecules were included in the calculation. Fig. 5a, 5b, 5c, and 5d are the optimized structures of the reactant, transition state, intermediate species, and the product for the interaction of SO_2 with DBEA, respectively. The numbers in the parentheses are energies relative to that of the reactant. As can be seen in the optimized structure of the transition state (Fig. 5b), there is a strong intermolecular hydrogen bonding interaction between the hydroxyl group of the first DBEA molecule and the nitrogen atom of the second DBEA molecule. Such a hydrogen bonding interaction seems to be a driving force for the interaction of SO_2 with the first DBEA molecule through the sulfur atom. The interaction distances of O···H, N···H, and S···O(H) were calculated as 1.21, 1.32, and 2.15 Å, respectively. The transition state energy was calculated as only +2.5 kcal mol^{-1}, suggesting that there is practically no activation barrier for the interaction of SO_2 with the hydroxyl group. As can be seen in Fig. 5c, strong intermolecular interactions among three molecules result in the formation of an ionic intermediate species consisting of [DBEAH]$^+$ and [Bu$_2$NCH$_2$CH$_2$O-SO$_2$]$^-$ anion with a covalently bound -OSO$_2^-$ group, which interacts with two protic hydrogen atoms of the hydroxyl and N-H groups of [DBEAH]$^+$. Gibbs free energy of formation (ΔG) for the intermediate species was calculated as -0.6 kcal mol^{-1}. The intermediate species seems to transform immediately into the final product, a zwitterionic compound having a structure of Bu$_2$N$^+$(H)CH$_2$CH$_2$O-SO$_2^-$, via a proton transfer from [DBEAH]$^+$ to [Bu$_2$NCH$_2$CH$_2$O-SO$_2$]$^-$. Gibbs free energy of formation (ΔG) for the final product was calculated as -4.6 kcal mol^{-1}. Thus generated DBEA molecule is capable of interacting with SO_2, leading to the formation of Bu$_2$N$^+$(H)CH$_2$CH$_2$O-SO$_2^-$. As a result such consecutive interactions of DBEA with SO_2, 1:1 adduct of DBEA and SO_2 is produced.

To support the computational results on the nature of SO_2 absorption in the functionalized tertiary amines, the interactions of SO_2 with DBAPN and DBEA were investigated by ^{1}H and ^{13}C NMR spectroscopy in DMSO-d_6 using a high

pressure NMR tube. As can be seen in Fig. 6a and 6b, the peak corresponding to the OH group of DBEA at 4.22 ppm completely disappeared when the NMR tube containing a solution of DBEA in DMSO-d_6 was pressurized with 2 bar of SO_2. Instead, a new peak appeared at 9.89 ppm, which could be assigned to the hydrogen atom bonded to the nitrogen atom of [DBEAH]$^+$ [30]. In addition, all the peaks associated with the CH_2 groups bonded to the nitrogen and oxygen atoms were found to shift downfield by 0.424-0.644 ppm. Considering the disappearance of the peak for the hydroxyl group of DBEA along with the appearance of the peak at 9.89 ppm and the relatively large peak shifts for the methylene groups, it is evident that SO_2 interacts chemically with DBEA through the hydroxyl group, forming an ionic species with a covalently bound -OSO_2^- [7,8]. The involvement of the hydroxyl group during the chemical absorption of SO_2 in DBEA was further demonstrated by ^{13}C NMR experiments. As can be seen in Fig. 7a and 7b, the chemical shifts of the carbon atoms of the hydroxyethyl group bound to the nitrogen atom were found to move upfield by 5.2 (C-O) and 4.7 ppm (C-N), respectively.
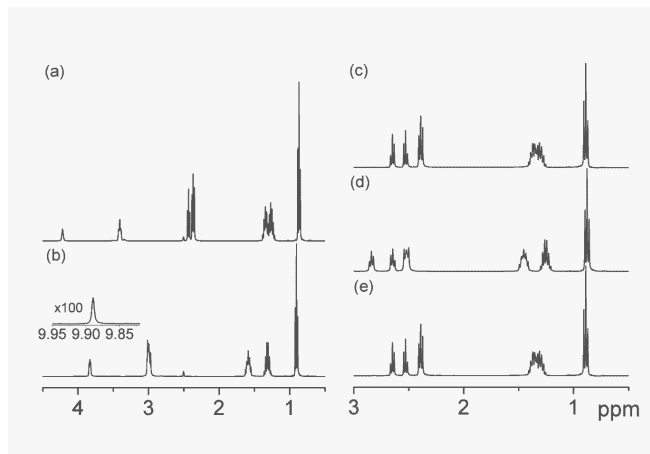

Fig. 6: ^1H NMR spectra showing the interactions of amines with SO_2 in DMSO-d_6: (a) DBEA, (b) DBEA under pressure of 1 bar of SO_2, (c) DBAPN, (d) DBAPN under pressure of 1 bar of SO_2, and (e) N_2 flowed (d) at 80 °C.

In contrast, the peak corresponding to the methylene carbons of the butyl groups adjacent to the nitrogen atom moved upfield by only 1.6 ppm from 53.9 to 52.3 ppm, implying that the change in electronic environment is greater for the hydroxyethyl group than for the butyl groups. In consideration of this, it is likely that SO_2 prefers interacting with the hydroxyl group to the interaction with the nitrogen atom. Similar bonding mode was also suggested for interaction of between SO_2 and diethylaminoundecanol [7].

Fig. 6c and 6d show the ^1H NMR spectra for the interaction of DBAPN with SO_2. Contrary to the interaction of SO_2 with DBEA, the peaks associated with the CH_2 groups shifted downfield, and the degree of peak shift in the range 0.116-0.192 ppm was considerably smaller than that observed for the interaction of SO_2 with DBEA, indicating that physical interaction is predominant. Such downfield shifts were also observed in the ^{13}C NMR spectra. As can be seen in Fig. 7c and 7d, the peaks associated with the CH_2 groups bonded to the nitrogen atom and nitrile group shifted downfield by only 0.192, 0.116, and 0.129 ppm from 2.648, 2.529, and 2.392 to 2.840, 2.645, and 2.521 ppm, respectively. Fig. 7c and 7d are the ^{13}C NMR spectra showing the interaction of SO_2 with TBAPN. Similar to ^1H NMR results, the degree of peak shift for the CH_2 groups of CH_2CH_2CN moiety is much less pronounced than that for the CH_2 groups of CH_2CH_2OH moiety. In consideration of the smaller degree of peak shifts and the computational results, it is reasonable to assume that SO_2 interacts physically with DBAPN.

3. Conclusion

We have demonstrated that the tertiary amines bearing a nitrile functional group are highly efficient for the rapid and reversible absorption of SO_2. The saturation capacity of SO_2 in the nitrile-functionalized tertiary amines are approximately 2 moles per mole of amine. The physically absorbed SO_2 in the nitrile-functionalized tertiary amines can be readily and completely desorbed by heating at 80 °C under N_2 gas flow, thereby allowing the tertiary amines to be reused without any loss in their initial capacities. In contrast to the nitrile-functionalized tertiary amines, the hydroxy-functionalized tertiary amines interact chemically with SO_2, forming irreversible 1:1 zwitterionic species bearing a

covalently bound-OSO_2^- group, which are hard to evolve SO_2 even at the elevated temperature of 120 ℃.

Acknowledgements

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