

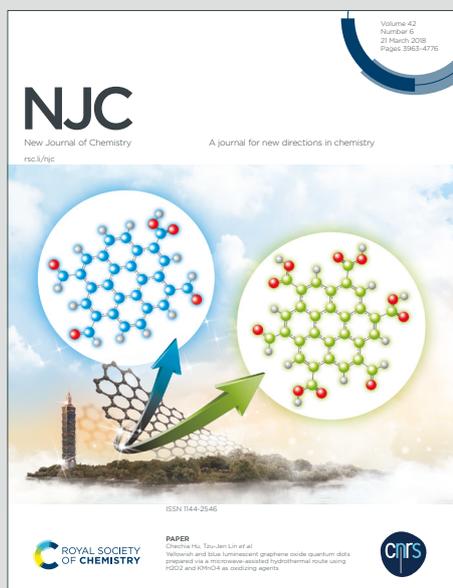
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Synthesis of Dibutyl-trimethylsilanylmethyl-amine and Its Application Towards SO₂ Absorption with Phase Change Behaviors

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ABSTRACT: The enforcement of environmental law worldwide has attracted considerable attention in recent years towards capturing sulfur dioxide (SO₂). The phase change absorption has turned out to be an effective way due to its industrially scalable characteristics. Herein, an aminosilane absorbent namely dibutyl-trimethylsilanylmethyl-amine (DTSMA) was facilely synthesized by a substitution reaction of chloromethyltrimethylsilane and di-n-butylamine. The phase-change absorption performance of SO₂ was systematically studied by using the dimethyl silicone oil (DSO) as solvent. The viscosity of pure DTSMA was only 1.29 mPa·s, which is much lower than the absorbents like ionic liquids and deep eutectic solvents reported elsewhere, and the absorption product is found to be a charge transfer complex DTSMA·SO₂. The absorption capacity of DTSMA can reach to 1.90 and 0.57 mol SO₂/mol DTSMA under 1 and 0.02 atm at 30 °C, respectively. Especially, the DTSMA/DSO solution not only can be almost regenerated within just 60 minutes at 100 °C, but also exhibited selective absorption towards SO₂. All the results indicated that the synthesized DTSMA absorbent processes enormous potential applications in capturing SO₂ with benign circular desorption performance.

KEYWORDS: Dibutyl-trimethylsilanylmethyl-amine, SO₂ capture, Phase change,

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Circular desorption

1. INTRODUCTION

SO₂ is one of the main pollutants released as a result of the burning of fossil fuels. As a colorless gas with a strong pungent odor, SO₂ diffused in the air will causing serious harm to human health, plants and the ecological environment^[1-2]. The treatment of SO₂ has attracted increasing concerns in recent years. By far, wet desulfurization (FGD) technology using calcium-based absorbents is the most effective way for controlling SO₂ emissions^[3-5]. However, the disadvantages of this technology can not be ignored, such as generating a large amount of waste water and by-products (*i.e.*, CaSO₃ and CaSO₄). Thus, one potential approach by using amine as absorbent has been implemented towards SO₂ capture. Yet, this method still has many shortcomings, such as toxicity, equipment corrosion, solvent loss and usually requiring a lot of energy to regenerate solvents^[6-8].

Over the past decades, ionic liquids (ILs) has achieved great progress in the field of SO₂ absorption due to its tunable molecular structure and excellent absorption properties, such as non-volatility and thermal stability^[9-13]. Han et al., firstly reported SO₂ capture by [TMG]L (1,1,3,3-tetramethylguanidinium lactate), which was synthesized by direct neutralization of TMG and lactic acid (L)^[14]. Latter, a series of functional ILs have been developed to meet the demand for effective SO₂ absorption, such as increasing the absorption capacity of SO₂ and reducing desorption enthalpy,

designing greener ILs and improving its selectivity [15]. The non-volatility property of ILs significantly reduced the energy consumption and environmental pollution during SO₂ capture, nevertheless, the high viscosity characteristic of ILs limited its practical applications [16-17]. Therefore, some researchers used small molecular solvents such as water and methanol to reduce the viscosity of ILs [18-19]. However, the addition of these solvents inevitably reduced the mass absorption capacity of SO₂ and increased the desorption energy consumption. To address the above issue, a possible strategy called phase change absorption has been proposed recently in the field of SO₂ capture. The phase change absorption system consists of two parts, one is the absorbent that can react with SO₂, and the other is the solvent that can adjust the viscosity, mass transfer and reduce volatility of the system. By simply bubbling SO₂ into the system, the homogeneous solution becomes two phases: a SO₂-lean phase and a SO₂-rich phase. In this way, only the SO₂-rich phase needs to be heated for regeneration while the lean SO₂ phase can be used directly without further treatment, this leading to the energy required for regeneration significantly reduced [20]. Some researchers found that ethylenediamine and cyclic diamine can react with SO₂ and water to form sulfites and precipitate from organic solvents [21]. Tertiary diamine like tetramethylethylenediamine (TMEDA), tetramethylpentanediamine (TMPDA) can react with SO₂ to form an electron transfer product, which further absorbs water from air to become pyrosulfite [22]. However, the liquid-solid phase change solvent has problems in its practical applications. The captured SO₂ mainly existed in the solid phase and easily blocked the pipeline, which have resulted in mass transfer problem during the SO₂ absorption

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process. A number of liquid-liquid phase change SO₂ absorption systems have been developed to tackle this problem. For example, N,N-dimethylcyclohexylamine/liquid paraffin [23], N,N-dimethylaniline/liquid paraffin[24], N,N-dimethylethanolamine/hexadecane [25], *etc.* Although these solvent systems could solved the problem of mass transfer ability, some disadvantages occur, such as the absorbent and solvent are volatile and flammable. Therefore, it is urgently required to develop a low flammability, low volatility and low viscosity phase change absorption system that can capture SO₂ efficiently, reversibly and economically.

It should be noticed that organosilicon compound is a kind of low flammability solvent with high resistance to thermal oxidation. It produces silica carbon with high thermal stability in fire and will further forms a silicon oxide protective layer to prevents further combustion of the substance [26]. Moreover, its surface tension is low, which can effectively avoid emulsification and foaming during the absorption process [27]. Therefore, we believe that the organosilicon compound not only can be served as SO₂ absorbent, but also as solvent owing to its low-flammability and low viscosity properties.

In this work, a low viscosity absorbent referred as DTSMA was synthesized, and the non-flammability DSO was used as solvent. The phase change absorption behavior of SO₂ in the mixture of DTSMA/DSO was studied. ¹H, ¹³C NMR and FTIR characterizations were used to determine the phase change absorption products. The absorption capacity under various absorption conditions and distribution of SO₂ both in upper and lower phases were studied comprehensively. Besides, the selective

absorption behavior and cyclic desorption performance of the DTSMA/DSO system were also carried out.

2. EXPERIMENTAL SECTION

2.1 Materials

Chloromethyltrimethylsilane (98%), Di-n-butylamine (99%), Diethylamine (99%), Dipropylamine (99%), Dimethyl silicone oil PMX-200 (viscosity about 20mPa·s) and Deuterated chloroform (99.8%) were purchased from Aladdin Chemical Reagent Ltd. All reagents is used as recieved. SO₂ (99.99 mol%), CO₂ (99.9 mol%), and N₂ (99.999 mol%) were supplied by Chengdu Hongjin Chemical Company.

2.2 Characterizations

¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE III HD 600 spectrometer using CDCl₃ as a solvent. FTIR data was obtained *via* a Bruker TENSOR 27 FTIR spectrometer at room temperature. Thermogravimetric analysis (TGA) was measured on a NETZSCH STA-449 F3 under a flow of nitrogen at the heating rate of 10 °C/min from room temperature to 800 °C. The UV-visible spectrum was recorded by using a UV-visible spectrophotometer from 400 to 800 nm. DTSMA/DSO vapor pressure is performed on a vapor pressure measuring device. The temperature was controlled by a constant temperature oil bath, and the pressure was measured by a pressure sensor (JYB-KO-MAA1 type, Beijing Kunlun Coast Sensor Technology Co., Ltd., China) with an uncertainty of 0.1 kPa. The content of each components in the absorption system was determined by using the gas chromatography (GC-2010, Chengdu Shimadzu Instrument Equipment Co., Ltd., China). An apparatus for

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4 measurement on vapor pressures of DTSMA/DSO solution were constructed according
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6 to the principle of quasi static method. After the pressure in the four-neck flask is 0 kPa,
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8 a sample of solution was placed in the four-necked flask. The equilibrium pressures
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10 were recorded after equilibrium was reached. The temperature was measured by
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12 mercury thermometer (± 0.5 °C). The pressure was measured by a pressure transducer
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14 (Model JYB-KO-MAA1, Beijing Kunlun Coast Sensor Technology Co., Ltd., China)
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16 with an uncertainty of 0.1 kPa.
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21 **2.3 Synthesis of DTSMA absorbent**

22 Under nitrogen protection, chloromethyltrimethylsilane and di-n-butylamine with
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24 a molar ratio of 1:2 were added to a 250 ml three-necked flask, and the mixture was
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26 condensed and refluxed at a constant temperature of 100 °C for 24 h in an oil bath. Then
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28 the mixture was extracted with a 5 wt% sodium carbonate solution, the upper phase
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30 solution was washed three times with deionized water, dried over anhydrous sodium
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32 sulfate, and distilled under reduced pressure to obtain DTMSA.
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41 **2.4 SO₂ absorption and desorption experiments**

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43 The equipment of the SO₂ absorption and desorption experiment was showed in
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45 Figure S1. DTSMA/DSO solution with different DTSMA mass fractions were added
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47 to the Gas-Wash Bottle with a magnet, then, the Bottle was placed in a thermostatic
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49 water bath. Upon absorption of SO₂ gas, the sample was weighed every 5 minutes *via*
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51 an electronic balance with accuracy of ± 0.0001 g, and the added mass was considered
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53 to be the mass of SO₂ absorbed by the solution. During the test, the concentrations of
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55 SO₂ were adjusted by controlling the flow rates of N₂ and SO₂ The absorption
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4 experiment was carried out until the equilibrium was reached. The absorption
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6 performance of CO₂ was also carried out by using the same method as a comparison.
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8 The desorption experiment was performed under a constant temperature in the same
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10 device, prior to the desorption test, the upper phase was separated by dumping. Pure
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12 N₂, at a flow rate of 30 mL/min, was bubbled through the lower phase to desorb SO₂ at
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14 100 °C under atmospheric pressure. After desorption, the upper phase was mixed with
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16 the desorption component for the next absorption experiment.
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21 **2.5 Determination of the component distributions**

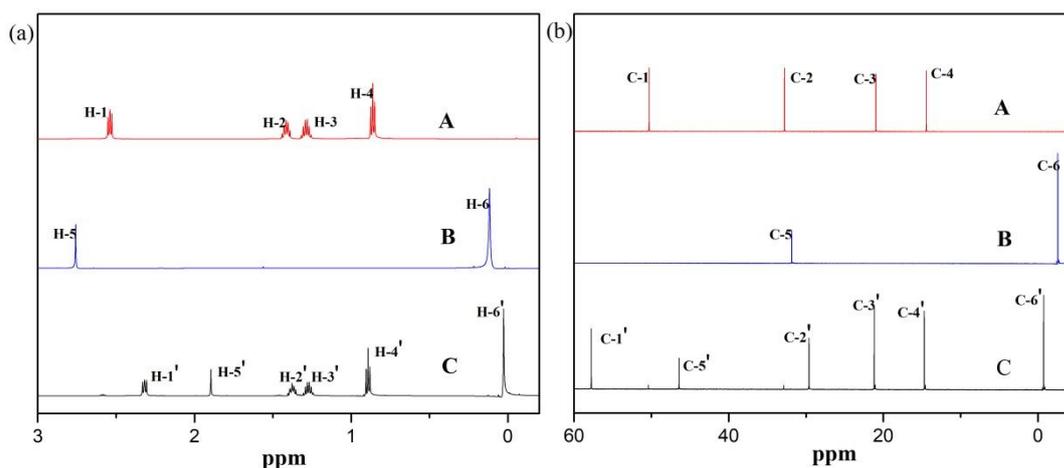
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25 DTSMA/DSO solution with 40 wt% of DTSMA was added to a Gas-Wash Bottle
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27 followed by bubbling SO₂ gas at a rate of 50 ml/min. Then, the DTSMA/DSO solution
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29 with a absorption capacity of 0.8-1.8 mol SO₂/mol DTSMA was obtained. After waiting
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31 for three days, the upper and lower phases were separated. The contents of SO₂ and
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33 DTSMA in the solution were measured by gas chromatography, and the mass of the
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35 DSO was calculated by the subtraction method.
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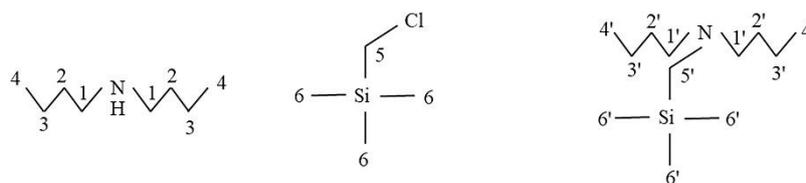
43 **3. RESULTS AND DISCUSSION**

44 **3.1 Synthesis of the DTSMA absorbent**

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48 NMR and FTIR characterizations were performed to determine whether DTSMA
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50 was successfully synthesized. ¹H and ¹³C NMR spectra of the di-n-butylamine,
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52 chloromethyltrimethylsilane and DTSMA product were showed in Figure 1. After the
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54 substitution reaction, the total NMR peaks number of di-n-butylamine and
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56 chloromethyltrimethylsilane was the same as the number of DTSMA product, but there
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are some change in chemical shifts of NMR in DTSMA. The proton H-5 (2.76 ppm) of the methylene group connected to Si moved to H-5' (1.90 ppm), this result suggested that the Cl atom of chloromethyltrimethylsilane was replaced by the N atom of di-n-butylamine. The electron-withdrawing ability of N atom is weaker than Cl, thus have caused the protons on the C5 atom move to higher field due to the rising electron cloud density of C5. Similarly, the H-1 (2.54 ppm) of the methylene group attached to N moved to H-1' (2.32 ppm) after the reaction because the alkyl group belongs to the electron-donating group. This conclusion was also supported by ^{13}C NMR spectra. After Cl on chloromethyltrimethylsilane was substituted by $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{N}$ -group, the C atom on the methylene (C-5) and methyl group (C-6) attached to Si have shifted towards lower field. This was because the $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{N}$ - was very large and exhibited obvious stereo compression effects and strong deshielding effects [28]. The C atom on the methylene group (C-1) attached to N has shifted to lower field could be also attributed to the stereo compression effects.





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Figure 1. (a) ^1H NMR (600 MHz, CDCl_3) and (b) ^{13}C NMR (600 MHz, CDCl_3) spectra for Di-n-butylamine (A), Chloromethyltrimethylsilane (B) and DTSM (C).

In addition, the chemical structure of DTSM was further confirmed by FTIR spectroscopy (Figure 2). The N-H bond of di-n-butylamine at 3293 cm^{-1} disappeared after the reaction, indicated the disappearing of the N-H bond. Besides, the C-N bond of di-n-butylamine at 1139 cm^{-1} changed from a moderately strong peak to a weak peak of the DTSM, demonstrated that the tertiary amine was successfully synthesized from a secondary amine [29-30]. Furthermore, the C-Cl bond of chloromethyltrimethylsilane at 645 cm^{-1} disappeared after the reaction suggested that the C-Cl bond has disappeared. The Si-C bond of chloromethyltrimethylsilane at 856 cm^{-1} also appeared in spectrum of the product, proved that the Si-C bond was successfully introduced into DTSM [31]. The DTSM synthesis reaction can be seen in Scheme 1.

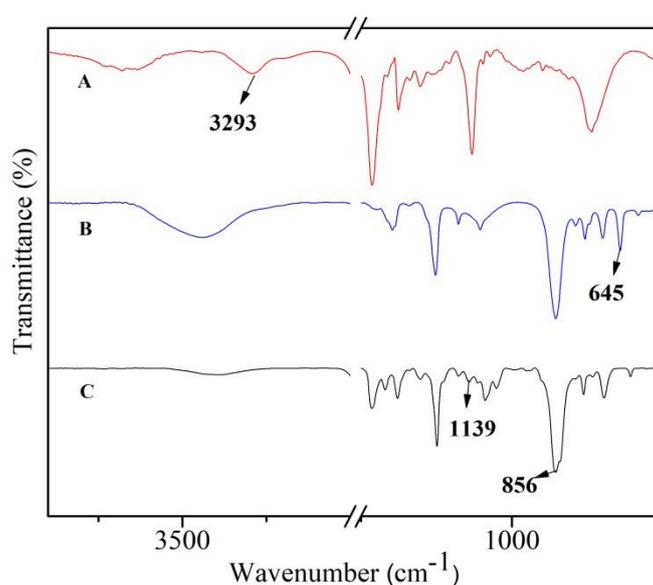
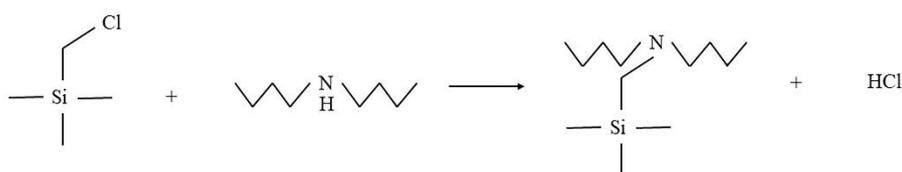


Figure 2. Infrared spectra of di-n-butylamine (A), Chloromethyltrimethylsilane (B)

and DT SMA (C).

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Scheme 1. Synthetic equation for synthesis of DT SMA.

3.2 Comparison of SO₂ absorption capacity of different aminosilanes

As a comparison of the absorption performance of DT SMA, different aminosilanes (Dipropyl-trimethylsilanylmethyl-amine and Diethyl-trimethylsilanylmethyl-amine) were synthesized by using dipropylamine and diethylamine as the raw material with chemical structure analogous to di-n-butylamine. The NMR and FTIR spectra showed in Figure S2-S4 have turned out that the both of dipropyl-trimethylsilanylmethyl-amine and diethyl-trimethylsilanylmethyl-amine were successfully synthesized. The SO₂ absorption capacity of the three aminosilanes were compared using a 20 wt% aminosilanes/DSO solution at 30 °C and 1 atm (Figure 3). The results showed that the absorption capacity of the three types of aminosilanes (DT SMA, dipropyl-trimethylsilanylmethyl-amine and diethyl-trimethylsilanylmethyl-amine) were 2.20, 2.24 and 1.92 mol SO₂, respectively. Among them, diethyl-trimethylsilanylmethyl-amine has the smallest absorption capacity, this could be attributed to its volatile property. Moreover, it should be noted that the absorption capacity of dipropyl-trimethylsilanylmethyl-amine and DT SMA is basically the same due to the similar chemical structure. The SO₂ absorption performances of DT SMA were further studied in the following due to its higher yield in the synthesis process.

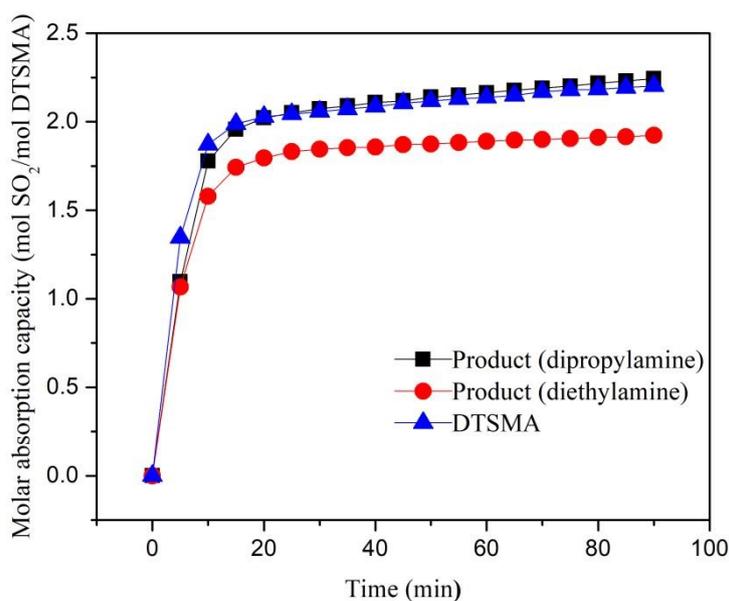


Figure 3. Absorption capacity of different aminosilanes.

3.3 Properties of the DTSMA/DSO solution

In order to study the absorption stability of the DTSMA/DSO solution, pure DTSMA (100 wt%) and DTSMA/DSO solution with 20 wt% of DTSMA were purged with N₂ at a flow rate of 50 mL/min under 30 °C (Figure 4) and 100 °C (Figure S5). After 6 hours of treatment, the weight loss of pure DTSMA was about 0.9 wt% and 2.6 wt%, whereas the weight loss of the solutions with 20 wt% DTSMA solution was only 0.4 wt% and 1.5 wt%, indicated that the introduction of DSO was very beneficial to reduce the volatility of the DTSMA. The relationship between vapor pressure and liquid phase composition was also measured at a constant temperature (Figure S6), it can be seen that the addition of the DSO can reduce the vapor pressure of the DTSMA/DSO system. The saturated vapor pressure of the pure absorbent DTSMA was 1.93 kPa, while the vapor pressure of the DTSMA/DSO solution with 20 wt% of DTSMA was 1.20 kPa. Furthermore, the thermal stability of the prepared solution was studied by

TGA analysis in a pure N₂ environment (Figure S7). The thermal stability of DTSMA/DSO solution increased remarkably with the introduction of DSO. For instance, a 10 wt % weight loss of pure DTSMA occurs at 77 °C, while 137 °C for the latter.

Under experimental condition (45 °C), the viscosity of pure DTSMA and solution with 40 wt% of DTSMA were 1.29 and 2.63 mPa·s, respectively. In comparison with the absorbents reported in the literature, pure DTSMA has the minimum viscosity. These values were much lower than the viscosity of the most previously reported ILs and deep eutectic solvents (Table 1). After SO₂ absorption, the absorption capacity of pure DTSMA solution was 1 mol SO₂/mol DTSMA, and the viscosity was only 29.46 mPa·s. The low viscosity values could be attributed to the low polarity of DTSMA and DSO, this feature might enable DTSMA a better mass transfer rate during the SO₂ capture process compared to the high-viscosity ILs and deep eutectic solvents reported elsewhere.

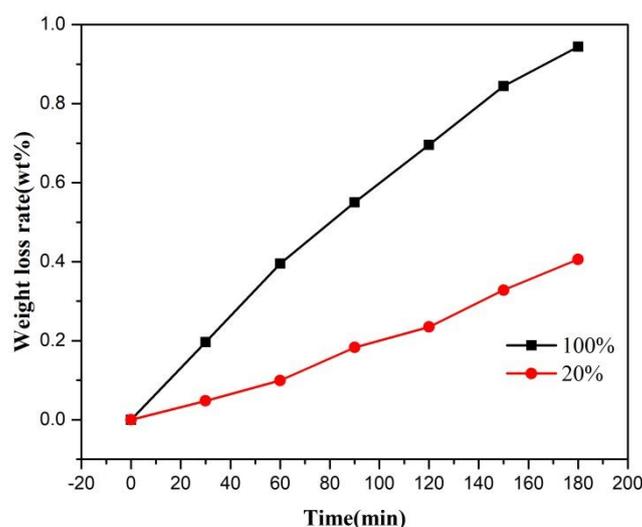


Figure 4. Effects of DTSMA concentration on the weight loss rate.

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Table 1 Viscosity of the reported absorbents.

Absorbent	T (K)	η (before absorption) (mPa·s)	η (after absorption) (mPa·s)	Ref
DTSMA/DSO solution (40 wt% DTSMA)	318	2.63		This work
DTSMA	298	2.01	29.46	This work
	318	1.29	9.51	This work
Im-H ₂ O	318	1.30	5.67	32
TMGL	338	418	810	33
MEAL	338	794	2000	33
[N ₂₂₂₂][FA]/PEG200	303.1	85.70		34
	5			
[Ch][FA]/PEG200	303.1	143.79		34
	5			
[Et ₂ NEMim][SCN]	303.1	1284.31		35
	5			
[C ₂ OHMim][SCN]	303.1	112.15		35
	5			
N ₄₄₄₄ Cl:Pyr (1:2)	298.2	106.40		36
[NH ₂ mim][OAc]	298	2810		37

[bmim][OH]	298	125		37
2-	298.2	118		38
hydroxyethylammoniu				
m formate				
Im-Gly	338	149	470	39
[P ₄₄₄₂][BTFA]	293	803.30		40
[P ₄₄₄₂][TTFA]	293	1116.40		40
EU/BmimCl (1:2)	303.1	375.90		41
	5			
BmimCl:4CH ₃ -Im(1:2)	298.2	195.40		36

3.4 Analysis of absorption product and phase change mechanism

In order to determine the SO₂ absorption mechanism of DTSMA, the absorption product was characterized by NMR and FTIR (Figure 5). After absorption of SO₂, the number of proton peaks did not change but shifted to lower field. Among them, the protons H-1 (2.32 ppm), H-5 (1.89 ppm) in two methylene groups connected to N were shifted to H-1' (2.68 ppm), H-5' (2.19 ppm), respectively. Protons in other locations have smaller chemical shifts when compared to H-1 and H-5, due to their longer distances to N atom. These results indicated that there was an N→S charge-transfer interaction between DTSMA and SO₂ [42]. SO₂ is an electron-withdrawing group, and could lead to reduction of the electron clouds density around N atoms, so the shielding effect of around the proton was weakened. The ¹³C NMR spectrum also confirmed this speculation. Due to the charge interaction, chemical shift of the C atoms (C-1, C-5) in

the two methylene groups connected to N are moved. The C at other locations are far away from N atom, so their chemical shifts exhibited almost no change.

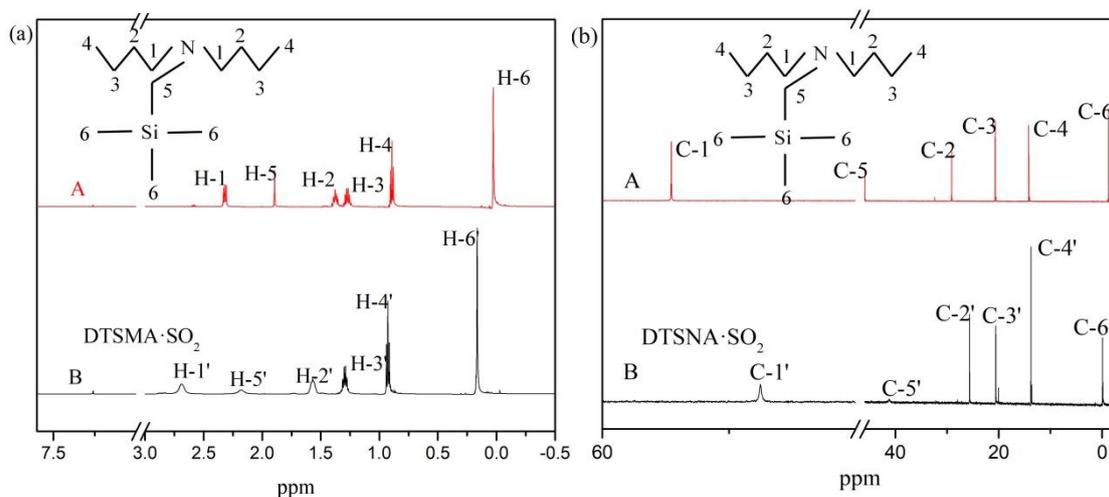
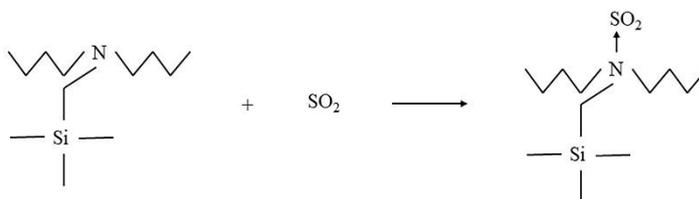


Figure 5. (a) ¹H NMR (600 MHz, CDCl₃) and (b) ¹³C NMR (600 MHz, CDCl₃) spectra for DTSMA before and after absorption of SO₂.

FTIR spectroscopy (Figure S8) further confirmed that the absorption product was DTSMA·SO₂. The asymmetric and symmetric stretching vibration modes of gaseous SO₂ appeared at 1351 and 1150 cm⁻¹, respectively [43]. After absorption, these stretching vibration modes of SO₂ in complex shifted to lower wavenumbers. It showed characteristic peaks of the charge transfer complex at 1189 and 1098 cm⁻¹. The reaction equation of the electron transfer product was showed in Scheme 2.



Scheme 2. Reaction between DTSMA and SO₂ to form DTSMA·SO₂ product.

The SO₂ phase change mechanism of the switchable solvent was mainly attributed to the polarity change of the solution before and after absorption, which has been

reported in previously reported literature [23]. In order to determine whether the phase change mechanism of this absorption solution was the same as with that in the literature, the polarity of the solution before and after absorption of SO₂ was studied by an UV absorption method. As shown in Figure 6, the maximum absorption wavelength of the solution before and after absorption (1 mol SO₂/mol DTSMA) were 520 and 533 nm, respectively. This indicated the change of polarity of the solution was the phase change mechanism of this silicone system.

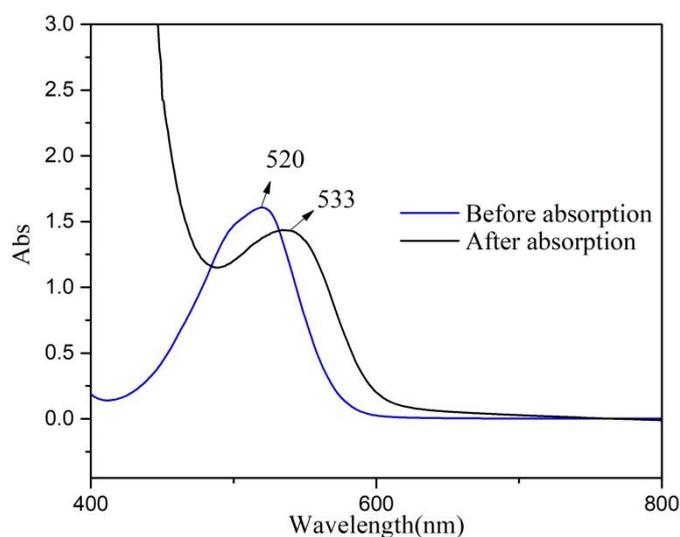


Figure 6. UV spectra of Nile red in DTSMA before and after absorption of SO₂.

3.5 Impact of absorption conditions on absorption capacity

The effects of temperature on absorption capacity were investigated by using a 40 wt% DTSMA/DSO solution under 1 atm (Figure 7a). The absorption capacity of SO₂ gradually decreased from 2.26 to 1.39 mol SO₂/mol DTSMA with the rising temperature from 20 to 50 °C. It demonstrated that low temperature was beneficial to achieving maximum absorption capacity of SO₂. Besides, the SO₂ absorption capacity of the solution with various DTSMA mass ratio was also investigated (Figure 7b). The absorption capacity of the solution with 20 wt% DTSMA can reach to 2.20 mol

SO₂/mol DTSMA, while the solution with 80 wt% DTSMA decreased to 1.76 mol SO₂/mol DTSMA. This is because DSO has a small amount of physical absorption capacity. Moreover, the partial pressure also has a great impact on the absorption capacity (Figure 7c), *i.e.*, when the partial pressure was decreased from 1 to 0.002 atm, the absorption capacity decreased from 1.90 to 0.17 mol SO₂/mol DTSMA. In other words, the absorption capacity of SO₂ decreases with the decreasing of partial pressure. It should be noted that the absorption capacity of the solution with 40wt% of DTSMA can still reach to 0.57 mol SO₂/mol DTSMA at just 0.02 atm.

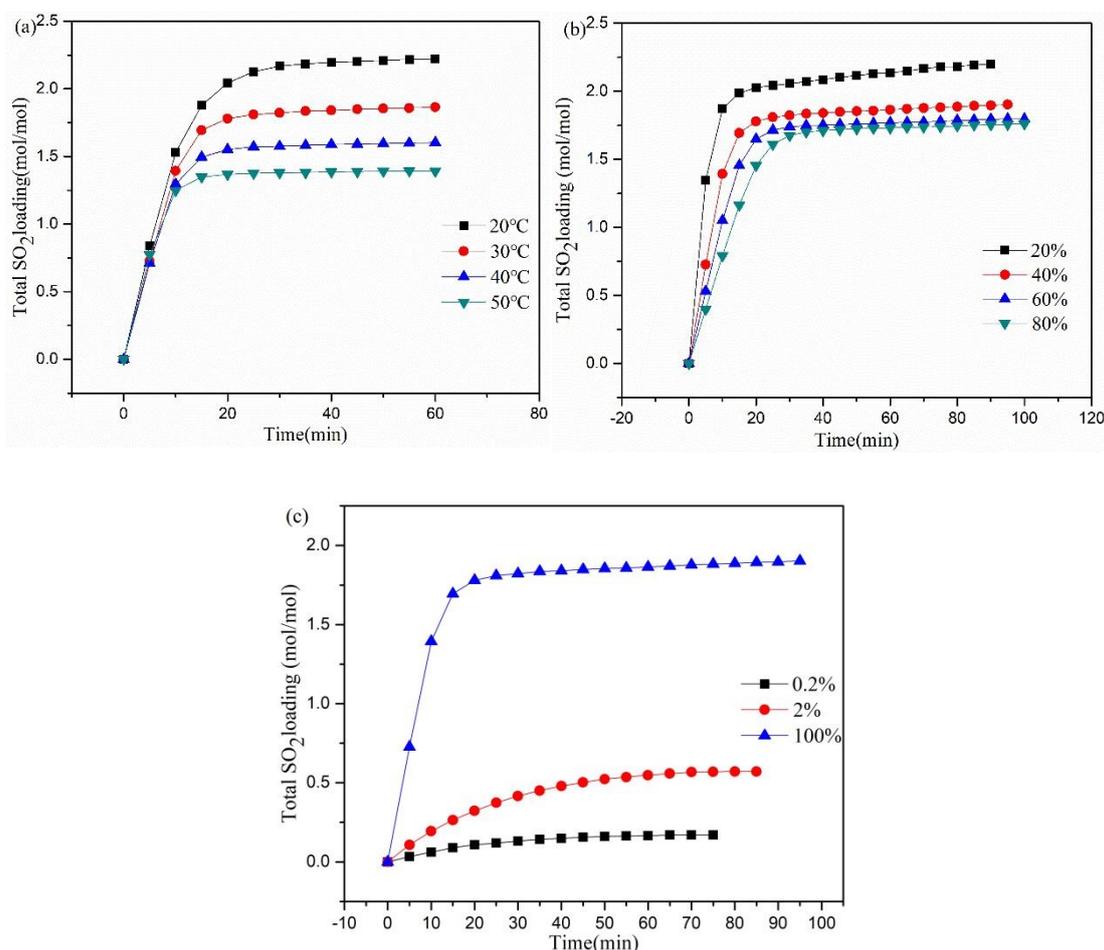


Figure 7. Effects of temperature (a), DTSMA mass fraction (b) and pressure (c) on the absorption capacity of SO₂.

Table 2 listed the absorption capacity of different absorbents reported in the literature. Although some ILs and Deep Eutectic Solvents exhibited high absorption capacity under low SO₂ pressure, the high viscosity of these absorbents also limited their practical applications. For example, the absorption capacity of BmimCl:4CH₃-Im(1:2), EmimCl-NFM (1:1), [P₄₄₄₂][BTFA] and [P₄₄₄₂][TTFA] is 1.07mol/mol, 1.30mol/mol, 1.34 mol/mol and 1.26 mol/mol, but exhibited high viscosity of 195.40, 375.90, 803.30 and 1116.40 mPa·s, respectively. And it can be concluded that the absorption capacity of DTSMA was better than some of the absorbents, for example, the absorption capacity of Bet-EG (1:3), [TMG][Ac], [MEA][Ac] and [P₄₄₄₂][TFSI] was 0.33mol/mol, , 0.49 mol/mol, 0.28 mol/mol and 0.01mol/mol. All these results indicated that the low viscosity DTSMA might serve as a promising absorbent towards SO₂ absorption under various pressures.

Table 2 Comparison of absorption capacities of various absorbents under low partial pressure SO₂.

Absorbents	T (K)	Pressure(atm)	Absorption capacity(mol/mol)	Ref
DTSMA/DSO solution (40 wt% DTSMA)	303	0.02	0.57	This work
BmimCl:4CH ₃ -Im (1:2)	293	0.02	1.07	36
EmimCl-NFM (1:1)	293.15	0.01	0.90	44

				View Article Online DOI: 10.1039/D0NJ04500D
Bet-EG (1:3)	313.20	0.02	0.33	45
EU/BmimCl (1:2)	293.15	0.02	1.30	41
[TMG][Ac]	323	0.03	0.49	46
[TMG][PhCOO]	323	0.03	0.70	46
[MEA][Ac]	323	0.03	0.28	46
[P ₄₄₄₂][TFSI]	293	0.01	0.01	40
[P ₄₄₄₂][BTFA]	293	0.01	1.34	40
[P ₄₄₄₂][TTFA]	293	0.01	1.26	40
[N ₂₂₂₂][P]	313	0.03	0.87	47
[N ₂₂₂₂] ₂ [succinate]	313	0.03	1.32	47

3.6 The effects of SO₂ absorption capacity on the distribution two phases

Under the absorption conditions of 30 °C and 1 atm, the DTAMA/DSO (40wt%/60wt%) solution was selected to study the effects of SO₂ absorption capacity on the distribution of DTSMA, DSO, and SO₂ in upper and lower phases, and the results were analyzed by gas chromatography (Figure 8). With the absorption capacity of SO₂ increased from 0.8 to 1.8 mol SO₂/mol DTSMA, the mass fraction of DTSMA in the upper phase decreased from 35.6 to 7.7 wt%, and the mass fraction of DSO increased from 58.7 to 87.7 wt%. The mass fraction of SO₂ in the upper phase was about 5 wt% and remained almost no change with the increases of SO₂ absorption capacity. On the other hand, with the increases of the absorption capacity of SO₂, the mass fraction of SO₂ in the lower phase solution increased from 12.0 to 22.6 wt%, and the mass fraction of DSO mass fraction decreased from 30.3 to 21.3 wt%. It should be noticed that the

mass fraction of DTSMA changed from 57.7 to 56.0 wt%, which remained essentially unchanged. In a word, the phase separation phenomenon occurs with the increases of absorption capacity of SO_2 , where DTSMA in the upper phase gradually moves to the lower phase, and the DSO in the lower phase gradually moved to the upper phase until the absorption process completed.

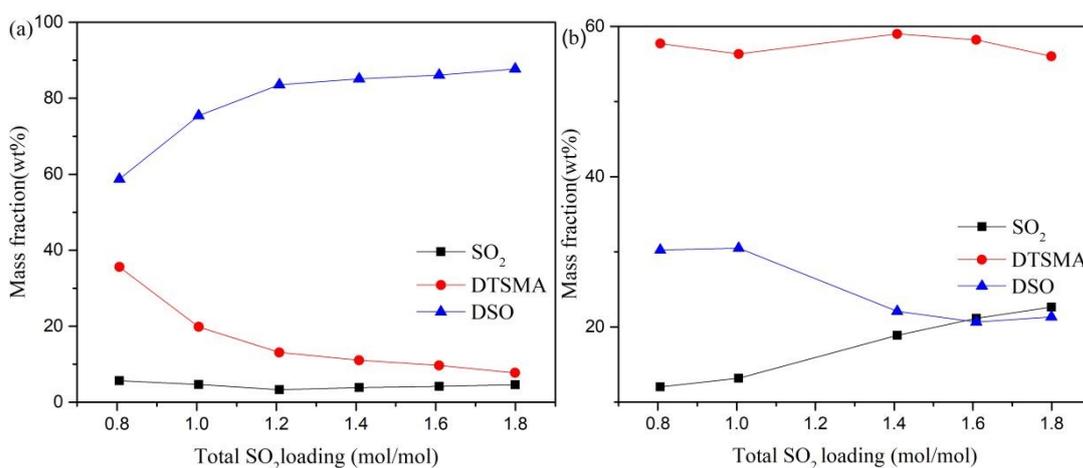


Figure 8. (a) Upper and (b) lower phase distributions of 40% DTAMA+60% DSO solution after absorption of SO_2 at 30 °C and 1 atm.

3.7 SO_2 desulfurization efficiency and DTSMA/DSO cyclic absorption capability

The desulfurization efficiency was measured in an apparatus similar to that of Xu et al's work [25,48]. As shown in Figure 9a, the desulfurization efficiency was higher than 95% within absorption capacity of 1 mol SO_2 /mol DTSMA, this illustrated the excellent SO_2 absorption ability of the solution. Moreover, the selective absorption experiment was performed at 30 °C and 1 atm by using an absorption solution with DTSMA mass fraction of 40 wt% (Figure 9b). It can be seen from the figure that the absorption capacity of CO_2 was only 0.077 mol CO_2 /mol DTSMA, it means that the selectivity coefficient towards SO_2/CO_2 mixture gases was 25. The cyclic SO_2 absorption

performance of the DTSMA/DSO solution was also studied to evaluate its practical use in industrial applications. We performed 5 times absorption/desorption cycle experiments under the conditions of 1 atm and 100 °C. The result was showed in Figure 9c, obviously, the absorption capacity after fifth times of absorption experiment was close to the first absorption capacity, indicated that the absorbent has almost no mass loss during the 5 times absorption experiments. With the increasing of the cycling numbers, the time required for absorption and desorption became longer. The reason is that the electron transfer product cannot be regenerated increased, which resulted in that the mass transfer rate decreased.

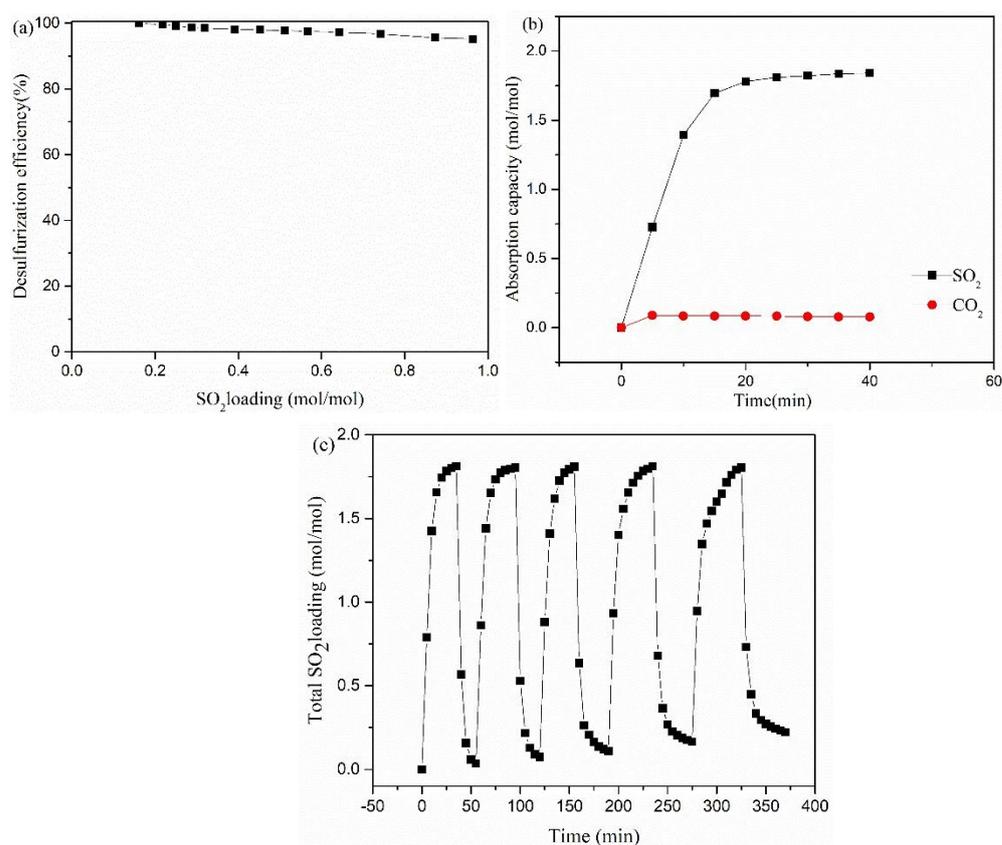


Figure 9. SO₂ desulfurization efficiency (a), selective absorption performance (b) and recyclability (c) of the DTSMA/DSO solution. (Absorption conditions: 30 °C, 1atm with the SO₂ flow rate of 50 mL/min; Desorption conditions: 100 °C, 1 atm with the

N₂ flow rate of 50 mL/min)

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4. CONCLUSIONS

In summary, we reported a facile and eco-friendly approach in synthesizing a novel SO₂ phase change absorbent with low viscosity. Benefiting from this silicon-containing organic substance, the DTSMA exhibited miscible with low-flammability DSO solvent, the integration of low volatility and low viscosity properties of the DTSMA/DSO system was very beneficial to capturing SO₂ into SO₂-lean (upper) and SO₂-rich (lower) immiscible two phases. The absorption capacity of individual DTSMA was 1.9 and 0.57 mol SO₂/mol DTSMA at 1 and 0.2 atm under 30 °C conditions, and the absorption product was found to be an electron transfer complex. Besides, the DTSMA/DSO solution system exhibited selective absorption property towards SO₂ and mild cyclic desorption performance upon N₂. The proposed synthesis approach is not only of profound significance to environmental protection, but also a great promotion to the industrial SO₂ pollutant treatment.

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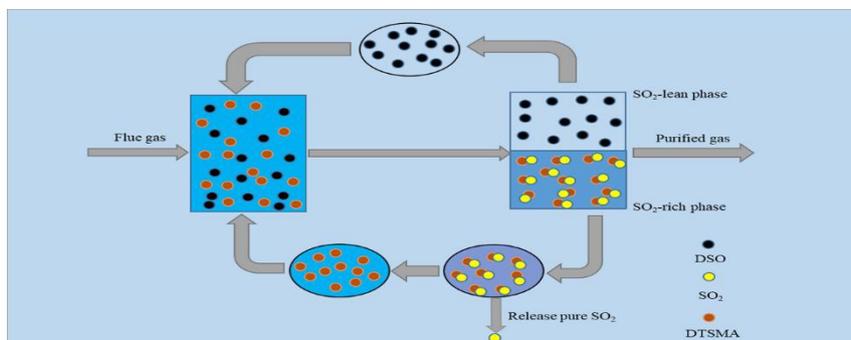
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