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# Investigation of $SO_2$ solubilities in some biobased solvents and their thermodynamic properties

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ABSTRACT

Solubilities of $SO_2$ have been determined in four biobased solvents (BBSs) at temperatures between 293.15 K and 323.15 K with 10 K intervals and pressure scope of (0–120.0) kPa using isochoric saturation method. The BBSs were selected from butyl lactate (BL), glyceryl triacetate (GT), triethyl citrate (TEC), and acetyl triethyl citrate (ATEC). Henry's constants and thermodynamic properties such as Gibbs free energy, enthalpy and entropy of dissolution were derived from the solubility data. The gravimetric solubilities of $SO_2$ in BBSs were in the range of (0.07–8.52) $mol.kg^{-1}$ and changed with the sequence of GT > BL > TEC ≈ ATEC. All the dissolution enthalpies were negative at each condition. The performances of $SO_2$ absorption in these solvents were further compared with those in some ionic liquids as well as common absorbents. The results illustrated that present BBSs possessed the potentiality as $SO_2$ absorbents due to their relatively large absorption ability, small absorption enthalpy, low toxicity, and biodegradability.



## 1. Introduction

Sulfur dioxide ($SO_2$), a typical contaminant emitted from the burning of fossil fuels, is the main component to form acid rain and smog which bring harmful influence to public health and human productive activity. Therefore, how to control or reduce $SO_2$ emission has attracted more and more concern around the world. Currently, wet limestone-gypsum flue gas desulfurization (FGD) is widely used in practical industry [1,2]. However, such method produces large amounts of $CaSO_4$ and wastewater. The high investment and energy penalty are also evitable disadvantages. Furthermore, the chemical FGD technologies transferred valuable sulfur resource into low-value products. Thus, developing green, economical, and reversible absorbent for $SO_2$ is still in demand.

In the past two decades, ionic liquids (ILs) have been explored to absorb or separate $SO_2$ from flue gas due to their low volatility, high thermal and chemical stability, and good performance [3–7]. Recently, deep eutectic solvents (DESs) were also proposed as the analogues of ILs [8]. However, high viscosity, large energy consumption, or expensive price will greatly restrict their large-scale application in FGD technology [9]. Moreover, the gravimetric solubility of $SO_2$ is relatively small because of the large molecular weight of IL or DES. Conversely, a physical absorption method using organic solvent with high boiling point and low molecular weight has low volatility and high gravimetric absorption capacity. It has the merits of chemical and thermal stability, easy regeneration, low vapor pressure, high absorption capacity and selectivity for $SO_2$, and low toxicity. Up to now, many organic solvents have been reported as absorbents for $SO_2$ in literatures [10–24], mainly includes sulfolane, propylene carbonate, *N*-methylpyrrolidone, N-alkylated imidazoles, methyl cyanoacetate, nitrile-functionalized tertiary amines and submitted aniline, *N*, *N*-dimethylformamide, dimethyl sulfoxide, ethylene glycerol, phosphate ester, and polyethylene glycol. For practical considerations, high boiling point absorbents are preferred because of the reduction of absorbent loss during regeneration.

The structure-property relationship has important influence on the solubility of $SO_2$ in organic absorbents. It is well known that $SO_2$ is an acid anhydride with the tendency to accept electron. Then, the absorbents rich in carbonyl, ester and ether groups have the potential ability to interact with $SO_2$ because of their lone pair electron in the oxygen atom. As an important aspect of Green Chemistry, replacing hazardous and toxic materials by green chemicals has became a preferential target [25]. According to abovementioned ideas, four biobased solvents (BBSs) such as butyl lactate (BL), glyceryl triacetate (GT), triethyl citrate (TEC), and acetyl triethyl citrate (ATEC) were chosen as $SO_2$ absorbents and the solubility data were determined. The selected BBSs have the advantages of high boiling point, chemical inertness and thermal stability, and low toxicity. Such good properties mean that they

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have the superiority in recycling of absorbent, practical operation, and equipment selection. In addition, the abundant oxygen atoms in the molecules of these BBSs are helpful for absorbing acidic $SO_2$. Although the BBSs derived from biomass have attracted increasing concerns as chemical reaction mediums because of their biodegradability, sustainability and low toxicity [26], the researches on BBSs as absorption solvents for $SO_2$ are relatively lacking. In present work, we hope to extend BBSs as absorbents in the $SO_2$ removal technology. New solubility data of $SO_2$ in four BBSs were determined at temperature of (293.15–323.15) K and pressures up to 120.0 kPa. Henry's constants and thermodynamic properties such as standard dissolution Gibbs free energy, enthalpy and entropy were calculated. Moreover, the absorption capacity and absorption enthalpy between present BBSs and other solvents from the literatures were systematically compared.

## 2. Experimental

### 2.1. Chemicals

$SO_2$ was supplied by Jingong Special Gas Co., Ltd. (Hangzhou, China). Butyl lactate (BL), glyceryl triacetate (GT), triethyl citrate (TEC), and acetyl triethyl citrate (ATEC) were purchased from Aladdin Industrial Corporation (Shanghai, China). All chemicals were used directly as received, with the detailed information listed in Table 1. The chemical structures of the four BBSs are illustrated in Fig. 1. An electronic balance (Mettler-Toledo AL204) with the standard uncertainty of 0.0002 g was used to weight the mass of the absorbent.

### 2.2. Measurement of density and viscosity

Density and viscosity of the BBSs were determined at $T$ = (293.15–338.15) K under 101.3 kPa in a thermostatic water-bath with the standard uncertainty of 0.05 K. The density was determined using pycnometer (its volume was calibrated at each experimental temperature with double distilled water as standard substance). The viscosity was detected by Pinkevitch method according to GB/T10247-2008 with high purity ethylene glycol as calibrating substance for the viscometer. Each measurement was repeated at least 3 runs, and the average value was calculated for the further study.

### 2.3. Measurement of $SO_2$ solubility

$SO_2$ solubility data was determined using an isochoric saturation method. Detailed description of the experimental apparatus was available in our previous works [27]. It was composed mainly of a gas equilibrium cell (EC) and a gas reservoir (GR), with the volumes of 141.61 $cm^3$ and 370.99 $cm^3$, respectively. The temperature of solutions in the EC and GR was maintained at a certain value using thermostatic water bath with the standard uncertainty of 0.05 K. Two pressure transmitters (Fujian WIDEPLUS Precision Instruments Co., Ltd, WIDEPLUS-8) with the standard uncertainty of 0.6 kPa were used to record the experimental pressures. At beginning of the measurement, a certain amount of BBSs ($w$) was added into the EC and the whole system was evacuated to pressure $p_0$. Then, GR was charged with $SO_2$ from the cylinder to a pressure $p_1$. The initial pressure in the EC was recorded to be $p_v$ when the temperature of EC reached the experimental value. With the needle valve between GR and EC was opened, $SO_2$ was loaded into EC from GR to be absorbed by solvents while magnetic stirring. Gas liquid equilibrium is assumed to reach if the pressure of EC keeps stable at least 2 h. The final pressure was recorded as $p_2$ for GR and $p_3$ for EC. Then, the equilibrium partial pressure of $SO_2$ in the EC was denoted as following,

$$p_s = p_3 - p_v \tag{1}$$

$p_v$ was the sum of residual gas pressure and saturated vapor pressure of the solvent. Generally, its value was within the standard uncertainty of the pressure. The $SO_2$ uptake of $n$ ($p_s$) was calculated by the following equation,

$$n(p_s) = \rho_g(p_1,T)V_{GR} - \rho_g(p_2,T)V_{GR} - \rho_g(p_s,T)(V_{EC} - w/\rho_{sol}) \tag{2}$$

where $\rho_g$ ($p_i$, $T$) represents the density of $SO_2$ in mol/$cm^3$ at $p_i$ ($i$ = 1, s) and $T$, and is obtained from NIST standard reference database [28]. $\rho_{sol}$ is the density of BBS in g/$cm^3$ at $T$. $V_{EC}$ and $V_{GR}$ represent the volumes of EC and GR in $cm^3$, respectively. The liquid phase molality ($m_{SO_2}$) of $SO_2$ can be easily calculated by following equation,

$$m_{so_2} = n_{SO_2}/w \tag{3}$$

where $w$ is the mass of BBS loaded at the beginning of each experiment.

## 3. Results and discussion

### 3.1. Physical properties of BBSs

Densities and dynamic viscosities of four BBSs at the temperatures of (293.15–338.15) K and 101.3 kPa were listed in Table 2 and firstly compared with the data taken from literatures in Figs. 2 and 3. It is evident that the majority of relative deviations for density and viscosity (expressed as the deviation between experimental and literature data divided by experimental value) are less than 0.3% and 3.0%, respectively. Such result means the good consistency between experimental and literature data.

Furthermore, the densities and viscosities were graphically depicted in Fig. 4. As expected, the density of each BBS decreased linearly with increasing temperature. The dynamic viscosity also decreased with the increasing temperature, but in a non-linear model. The temperature dependences of density and viscosity were fitted by linear and VFT equations [43,44], respectively.

$$\rho = a + bT \tag{4}$$

**Table 1**
Description of chemicals used in present work.

| Chemicals | Source | Purification method | Mass fraction purity[a] | Analysis method |
|---|---|---|---|---|
| Sulfur dioxide ($SO_2$) | Jingong Special Gas Co., Ltd. | – | 0.999 | – |
| Butyl lactate (BL) (DL-mixture) | Aladdin Industrial Co., Ltd. | None | 0.980 | GC[b] |
| Glyceryl triacetate (GT) | Aladdin Industrial Co., Ltd. | None | 0.985 | GC[b] |
| Triethyl citrate (TEC) | Aladdin Industrial Co., Ltd. | None | 0.980 | GC[b] |
| Acetyl triethyl citrate (ATEC) | Aladdin Industrial Co., Ltd. | None | 0.970 | GC[b] |
| Ethylene glycol | Aladdin Industrial Co., Ltd. | None | 0.999 | GC[b] |

[a] Data declared by the supplier;
[b] Gas-liquid chromatography