**Article:**
Zhan, N, Zhang, Y and Wang, XZ (2019) Solubility of N-tert-Butylbenzothiazole-2-sulfenamide in Several Pure and Binary Solvents. Journal of Chemical and Engineering Data, 64 (3). pp. 1051-1062. ISSN 0021-9568

https://doi.org/10.1021/acs.jced.8b00954

# Solubility of N-Tert-Butylbenzothiazole-2-Sulfenamide in Several Pure and Binary Solvents

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## ABSTRACT:

The solubility of N-tert-butylbenzothiazole-2-sulfenamide (TBBS) in six pure solvents (methanol, ethanol, toluene, 2-propanol, 1-butanol and tert-butylamine) and three binary solvents (methanol + water, ethanol + water and tert-butylamine + water) was measured in a temperature range between 273.2 K and 313.2 K using a gravimetric determination under a pressure of 0.101 MPa. The initial mole fraction of methanol, ethanol or tert-butylamine in the binary solvents was in the range of 0.4 to 1.0. The experimental data show that the solubility of TBBS increases with the increasing temperature in both the pure and binary solvents. The solubility of TBBS in the six pure solvents has the following sequence: $x_{1,\ \text{tert-butylamine}} > x_{1,\ \text{toluene}} > x_{1,\ \text{1-butanol}} > x_{1,\ \text{ethanol}} > x_{1,\ \text{2-propanol}} > x_{1,\ \text{methanol}}$. The high-temperature solubility of TBBS in tert-butylamine at 318.2 K − 343.2 K under a pressure from 0.156 MPa to 0.213 MPa was also determined using an approach based on turbidity measurement. The experimental solubility data can be correlated by the following four thermodynamic models: the modified Apelblat equation, the $\lambda h$ equation, the CNIBS/R-K model and the NRTL model. The results showed that the solubility of TBBS fitted best with the modified Apelblat equation in both the pure and binary solvents.

## 1. INTRODUCTION

N-tert-butylbenzothiazole-2-sulfenamide (TBBS, $C_{11}H_{14}N_2S_2$, CAS No. 95-31-8), as shown in Figure 1, is an important sulfonamide vulcanization accelerator. It has the advantage of fast sulfation and coking resistance[1, 2]. It is widely used in the synthetic rubber and tire industry because it does not generate the toxic chemical nitrosamine; therefore, it often replaces N-oxydiethylene-2-benzothiazolylsulfenamide[3, 4]. Several methods for synthesizing TBBS from 2-mercaptobenzothiazole and tert-butylamine using different oxidants and catalysts were proposed in the last century[5-7]. However, little attention was paid to the refinement of TBBS via crystallization. The current method for TBBS purification is crystallization with water being used as an anti-solvent[8-11]. This method results in a large amount of salinity wastewater which requires costly treatment in order to meet environmental standards[12]. Therefore, it is of great value to develop an alternative, greener process design for product purification, e.g., possible use of cooling crystallization, or combination of cooling and anti-solvent crystallization, or change of solvent.

In solvent selection and design and optimization of the crystallization processes, it is essential to have one of the most fundamental physicochemical properties, solubility of the solute in solvents[13]. At present, such solubility data for TBBS is not available in the literature.

In this work, the solubility of TBBS in six pure solvents (methanol, ethanol, toluene, 2-propanol, 1-butanol and tert-butylamine) and three binary solvents (methanol + water, ethanol + water and tert-butylamine + water) was determined using a gravimetric method in the temperature range of 273.2 K to 313.2 K under atmospheric pressure. The modified Apelblat equation, the $\lambda h$ equation, the CNIBS/R-K model and the NRTL model were

applied to correlate the experimental solubility data of TBBS. Additionally, the solubility data of TBBS in tert-butylamine at a high temperature range from 318.2 K to 343.2 K under a pressure of 0.156 MPa – 0.213 MPa was measured by a turbidity method[14, 15] due to the needs of industrial crystallization. Accurate high-temperature solubility data are of practical application in process design for cooling crystallization with direct impact on the yield and the solvent usage. This part of the experiment was conducted in a 1-L magnetic agitated autoclave because the atmospheric boiling point of the solvent tert-butylamine is 317.7 K.

## 2. MATERIALS AND EXPERIMENTS

### 2.1. Materials

The TBBS used in this study was provided by Jiangsu Sinorgchem Technology Co.,Ltd., China and had a mass fraction purity greater than 0.99. The solvents purchased from several reagent factories, including methanol, ethanol, toluene, 2-propanol, 1-butanol and tert-butylamine, were of analytical grade and used without further purification. The deionized water used in the experiments was obtained in the laboratory. The detailed information of all the utilized materials was listed in Table 1.

### 2.2. Melting Properties Measurements

For the purpose of understanding the melting properties of TBBS, including the melting temperature ($T_m$) and the enthalpy of fusion ($\Delta_{fus}H$), differential scanning calorimetry (DSC) (type DSC214, Netzsch, Germany) was conducted after standard indium and zinc calibration. At least 5 mg TBBS was needed, and the measurement was performed at a heating rate of 10

K/min under a nitrogen atmosphere at temperature from 303.15 K to 473.15 K. The standard uncertainties of the melting temperature and the enthalpy of fusion were $u(T_m)$ = 0.30 K and $u(\Delta_{fus}H)$ = 0.10 kJ·mol$^{-1}$, respectively.

### 2.3. X-ray Powder Diffraction

X-ray powder diffraction (XRPD) (Bruker, Germany) was applied to test the polymorphism of TBBS during the solubility experiments. The XRPD was performed under the conditions of 40 mA, 40 kV over the scan range from 5° to 35°, with a step size ($\Delta 2\theta$) of 0.0131°. Both raw material and excess undissolved solids in the selected solvents were measured by XRPD to make sure there is no polymorphic transformation.

### 2.4. Solubility Measurement

The solubility of TBBS was determined by two methods, namely, a gravimetric method and a turbidity method. The former was conducted to measure the solubility of TBBS in different pure and binary solvents from 273.2 K to 313.2 K under atmospheric pressure, while the latter was applied to measure the solubility of TBBS in tert-butylamine from 318.2 K to 343.2 K under a pressure between 0.156 MPa and 0.213 MPa.

The gravimetric method was conducted in a 150-mL jacketed beaker, where excessive TBBS was put in to prepare saturated solution. Quantitative solvents (ethanol, methanol or tert-butylamine and water) were measured for the preparation of the binary solvent mixtures. The temperature was kept at a desired value using a circulating thermostatic water bath (type DC-2006, Ningbo Scientz Biotechnology Co., Ltd.) with an accuracy of 0.1 K. The

suspension was continuously stirred using a magnetic stirrer, during which the concentration of the supernatant was measured every hour until the value was unchanged. It was demonstrated that the solution systems could reach equilibrium in 6 h. When stirring stopped, the solution was kept standing for more than 3 h, and then approximately 3 mL supernatant was filtered rapidly using a 5-mL injector equipped with an organic membrane (0.22 $\mu$m) and placed into a preweighed weighing bottle. Finally, the bottle with the sample solution was quickly reweighed and dried in the vacuum drying oven (type DZF-6020, Shanghai Hasuc Instrument Manufacture Co., Ltd.) at 40℃ until the weight remained constant. The above samples were all weighed by an electronic balance (type AL204, Mettler Toledo) with an uncertainty of 0.1 mg. Each solubility value was measured three times, and the average value was taken.

The turbidity method was employed in a 1-L magnetic agitated autoclave (type BR4000, Weihai Control the Reaction Kettle Co., Ltd.) with a pressure gage (uncertainty of 0.001 MPa). A thermosensor was inserted into the inner of the autoclave, so that the temperature of the solution could be controlled and recorded in real time by the circulating thermostatic water bath (type FP51, JULABO, Germany). A turbidity probe (PharmaVision (Qingdao) Intelligent Technology Ltd., China) was applied to determine the point of complete dissolution of the solute in the solvent. First, TBBS and tert-butylamine were weighed and put into the autoclave (TBBS was excessive). The samples were measured by an electronic balance (type PL2002, Shanghai Precision Instruments Co., Ltd.) with an uncertainty of 0.01 g. The suspension was heated at a rate of 0.05 $K \cdot min^{-1}$ until the TBBS completely dissolved (turbidity of the solution reached its minimum). The current temperature of the solution was

1 considered as the dissolving temperature corresponding to its current concentration.

2 For pure solvents, the mole fraction solubility $x_1$ of TBBS was calculated by eq 1 as
3 follows:

4 $$x_1 = \frac{m_1 / M_1}{m_1 / M_1 + m_2 / M_2} \quad (1)$$

5 where $m_1$ and $m_2$ are the masses of TBBS and the pure solvents, respectively. $M_1$ and $M_2$
6 refer to the corresponding molecular masses.

7 For binary solvents, the mole fraction solubility $x_A$ of TBBS in binary solvents and the
8 initial mole fraction $x_B$ of methanol, ethanol or tert-butylamine in binary solvents without
9 solute were defined as follows:

10 $$x_A = \frac{m_A / M_A}{m_A / M_A + m_B / M_B + m_C / M_C} \quad (2)$$

11 $$x_B = \frac{m_B / M_B}{m_B / M_B + m_C / M_C} \quad (3)$$

12 where $m_A$, $m_B$, and $m_C$ stand for the masses of TBBS, (methanol, ethanol or
13 tert-butylamine) and water, respectively. $M_A$, $M_B$, and $M_C$ are the corresponding
14 molecular masses of them.

15

16 **2.5. Method Verification**

17 In order to ensure the reliability and accuracy of the gravimetric method, the mole
18 fraction solubility of 2,2'-azobisisobutyronitrile (AIBN) in ethanol was measured as a
19 validation experiment. The validation measurement results were compared with the
20 literature values[16], as presented in Table 2. The relative deviations between the experimental
21 data and the literature data, defined as eq 4, were less than 5%. Therefore, the experimental

data have a good consistency with the literature values, which indicates the reliability of the measurement method used in this work.

$$RD = \frac{x_1^{exp} - x_1^{cal}}{x_1^{exp}} \quad (4)$$

## 3. THERMODYNAMIC MODELS

### 3.1. The Modified Apelblat Equation

The modified Apelblat equation[17-19], which is derived by the Clausius-Clapeyron equation, was widely used to describe the relationship between the solubility and temperature, as shown in eq 5 as follows:

$$\ln x_1 = A + \frac{B}{T} + C \ln T \quad (5)$$

where A, B and C are the model parameters. A and B represent the change of solution activity coefficient, C represents the effect of temperature on the fusion enthalpy.

### 3.2. The $\lambda h$ Equation

The $\lambda h$ equation[20-22] also builds a connection between the solubility and temperature as follows:

$$\ln\left(1 + \frac{\lambda(1 - x_1)}{x_1}\right) = \lambda h\left(\frac{1}{T} - \frac{1}{T_m}\right) \quad (6)$$

where $\lambda$ and $h$ are the parameters of the model, $T$ is the absolute temperature while $T_m$ is the melting temperature of TBBS which has been obtained by DSC.

### 3.3. The CNIBS/R-K Model

The Combined Nearly Ideal Binary Solvents/Redlich-Kister (CNIBS/R-K) model[23, 24] is commonly applied to understand the effect of solvent composition on the experimental solubility data of TBBS as follows:

$$\ln x_1 = x_2 \ln\left(x_1\right)_2 + x_3 \ln\left(x_1\right)_3 + x_2 x_3 \sum_{i=0}^{N} s_i \left(x_2 - x_3\right)^i \quad (7)$$

where $x_1$ and $(x_1)_i$ are the mole fraction solubility of TBBS in binary solvents and mono solvents of i, respectively. $x_2$ refers to the initial mole fraction composition of methanol, ethanol or tert-butylamine, $x_3$ refers to the mole fraction composition of water. $S_i$ is a constant of the model, N is the number of solvents which is 2 in this work. $x_3 = 1 - x_2$, hence, eq 7 can be expressed as follows[25]:

(8)

The CNIBS/R-K model can be finally expressed as eq 9 after further simplified:

$$\ln x_1 = B_1 + B_2 x_2 + B_3 x_2^2 + B_4 x_2^3 + B_5 x_2^4 \quad (9)$$

where $B_1$, $B_2$, $B_3$, $B_4$, $B_5$ are the model constants calculated by the solubility data correlating.

### 3.4. The NRTL Model

According to the phase equilibrium theory, a solute should have the same fugacity in the liquid and solid phases at a fixed temperature T and pressure p of system.

$$f_i^l\left(T, p, x_i\right) = f_i^s\left(T, p\right) \quad (10)$$

A generalized equation to correlate the experimental solubility data was derived as eq 11 as follows:

$$\ln x_1 = \frac{\Delta_{fus}H}{R}\left(\frac{1}{T_m}-\frac{1}{T}\right)-\frac{\Delta C_p}{R}\left(\ln\frac{T_m}{T}-\frac{T_m}{T}+1\right)-\ln\gamma_1 \quad (11)$$

where $\Delta C_p$ is the heat capacity difference between the liquid and solid phases of the solute, $\gamma_1$ is the activity coefficient of the solute.

The term of $\Delta C_p$ has less impact and normally can be ignored, thus, a simplified equation was obtained as follows[26, 27]:

$$\ln x_1 = \frac{\Delta_{fus}H}{R}\left(\frac{1}{T_m}-\frac{1}{T}\right)-\ln\gamma_1 \quad (12)$$

The solubility data of a solute in solvents can be determined by eq 12 after the activity coefficient is calculated from an appropriate model. In this work, the NRTL model[28] was chosen to calculate the activity coefficient of TBBS in pure and binary solvents, as shown by eqs 13 and 14, respectively.

$$\ln\gamma_1 = x_2^2\left[\frac{\tau_{21}G_{21}^2}{\left(x_1+G_{21}x_2\right)^2}+\frac{\tau_{12}G_{12}}{\left(x_2+G_{12}x_1\right)^2}\right] \quad (13)$$

where $G_{12}$, $G_{21}$, $\tau_{12}$, $\tau_{21}$ are the model parameters.

$$\ln\gamma_i = \frac{\sum_{j=1}^{N}\tau_{ji}G_{ji}x_j}{\sum_{i=1}^{N}G_{ij}x_i}+\sum_{j=1}^{N}\frac{x_jG_{ij}}{\sum_{i=1}^{N}G_{ij}x_i}\left[\tau_{ij}-\frac{\sum_{i=1}^{N}x_i\tau_{ij}G_{ij}}{\sum_{i=1}^{N}G_{ij}x_i}\right] \quad (14)$$

where $G_{ij}$ and $\tau_{ij}$ are the model parameters, which can be defined as eqs 15 and 16 as follows:

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right) \quad (15)$$

$$\tau_{ij} = \frac{g_{ij}-g_{jj}}{RT} = \frac{\Delta g_{ij}}{RT} \quad (16)$$

where $\Delta g_{ij}$ represents the Gibbs energy of cross interaction, $\alpha_{ij}$ represents a criterion of the nonrandomness of the system.

## 4. RESULTS AND DISCUSSION

### 4.1. Melting Properties Analysis

The melting properties of TBBS, including the melting temperature ($T_m$) and the enthalpy of fusion ($\Delta_{fus}H$), were determined by DSC. The plot was shown in Figure 2. There appeared an endothermic peak at temperature from 376 K to 395 K. The tangent line at the beginning of the peak and the baseline intersected at a point, which was determined as the onset temperature. The onset point was used as the melting temperature of TBBS, in this work, $T_m$ = 382.45 ± 0.30 K. The enthalpy of fusion was calculated based on the integration method, $\Delta_{fus}H$ = 26.84 ± 0.10 kJ·mol$^{-1}$. The melting temperature and the fusion enthalpy of TBBS were investigated by da Costa et al.[29] previously, and the values were 383.55 K and 26.03 kJ·mol$^{-1}$, respectively. The slight differences between the experimental results and the literature values could attribute to the different purities and DSC conditions of TBBS. Additionally, the entropy of fusion $\Delta_{fus}S$ of TBBS was calculated as 70.18 ± 0.33 J·mol$^{-1}$·K$^{-1}$ by eq 17:

$$\Delta_{fus}S = \frac{\Delta_{fus}H}{T_m} \tag{17}$$

### 4.2. X-ray Powder Diffraction Analysis

The XRPD patterns of raw material and residual solids of TBBS from different solvents were characterized and plotted in Figure 3. Here, we can observe that the XRPD patterns of TBBS in pure solvents and binary solvents highly agree with the pattern of the raw material. This result illustrates that no polymorphic transformation appeared throughout the solubility measurements of TBBS.

### 4.3. Solubility Data and Data Correlation in Pure and Binary Solvents

The solubility data of TBBS in the six pure solvents and three binary solvents of methanol + water, ethanol + water and tert-butylamine + water were summarized in Tables 3 – 6 and graphically plotted in Figures 4 – 7. It was observed that the solubility of TBBS increases with the rising temperature. Furthermore, the solubility data of TBBS in the six pure solvents show the following sequence: $x_{1,\text{ tert-butylamine}} > x_{1,\text{ toluene}} > x_{1,\text{ 1-butanol}} > x_{1,\text{ ethanol}} > x_{1,\text{ 2-propanol}} > x_{1,\text{ methanol}}$. It is well established that solubility is directly related to solvent polarity. The polarity order of the above solvents is toluene < 1-butanol < 2-propanol < ethanol < methanol, illustrating that the solubility order of TBBS is not absolutely accordance with the solvent polarity. Therefore, other factors exist to affect the solubility of TBBS, such as intermolecular interactions between solute and solvents, steric effects and the degree of solvent-solvent association[30, 31]. It is noteworthy that both TBBS and tert-butylamine have a tert-butyl group, leading to the high solubility of TBBS in tert-butylamine, which can be explained by the "like dissolves like" principle.

In binary solvents (methanol + water, ethanol + water or tert-butylamine + water), the solubility of TBBS at a fixed composition increases as temperature increases. Likewise, the solubility of TBBS at a fixed temperature increases with a rising solvent composition $x_B$. Thus, the solubility of TBBS in pure solvents of methanol, ethanol and tert-butylamine possesses the maximum value.

To assess the accuracy of the correlation models for TBBS, the average relative deviation

(ARD) and the root-mean-square deviation (RMSD) were calculated. They were calculated using eqs 18 and 19[32], as follows:

$$\mathrm{ARD} = \frac{1}{\mathrm{N}} \sum_{\mathrm{i}=1}^{\mathrm{N}} \left| \frac{\mathrm{x}_1^{\mathrm{exp}} - \mathrm{x}_1^{\mathrm{cal}}}{\mathrm{x}_1^{\mathrm{exp}}} \right| \tag{18}$$

$$\mathrm{RMSD} = \sqrt{\frac{1}{\mathrm{N}} \sum_{\mathrm{i}=1}^{\mathrm{N}} \left( \mathrm{x}_1^{\mathrm{exp}} - \mathrm{x}_1^{\mathrm{cal}} \right)^2} \tag{19}$$

where N is the number of experimental points in a specific solvent, $x_1^{\mathrm{exp}}$ and $x_1^{\mathrm{cal}}$ refer to the experimental and calculated solubility data of TBBS, respectively.

The correlated parameters of each model in pure and binary solvents together with ARD and RMSD were listed in Tables 6 – 10. It was observed that the values of ARD and RMSD of these models for TBBS in pure and binary solvents were lower than 9.288% and 2.954 × $10^{-3}$, respectively, indicating that the calculated solubility data of these models were in accordance with the experimental data in both the pure and binary solvents.

For the six pure solvents, the average ARD of the modified Apelblat equation, the *λh* equation, and the NRTL model were 1.190%, 1.669% and 1.217%, respectively. For the binary solvents, the average ARD of the modified Apelblat equation, the *λh* equation, the CNIBS/R-K model and the NRTL model were 1.969%, 4.031%, 2.477% and 5.860%, respectively. The results showed that the modified Apelblat equation produced a better fitting effect than the others in both the pure and binary solvents.

### 4.4. Solubility Data and Data Correlation in Tert-butylamine in the Temperature range of 318.2 K – 343.2 K under a pressure of 0.156 MPa – 0.213 MPa

Using the turbidity method, the solubility data of TBBS in tert-butylamine were obtained

up to 343.2 K, well exceeding the atmospheric boiling point of tert-butylamine (317.7 K). To verify the reliability and the accuracy of the turbidity method, the solubility data of TBBS in tert-butylamine from 273.2 K – 313.2 K at atmosphere pressure was also determined by this method, and the results were compared to the value of gravimetric method, as shown in Figure 9. The solubility data of turbidity method were determined by judging the point at which the solute disappeared entirely in the solution. It took some time for TBBS to completely dissolve in tert-butylamine at a certain temperature. However, the temperature in turbidity method was kept growing (though the heating rate was quite slow of 0.05 $K \cdot min^{-1}$), it may not afford the heat required to completely dissolve TBBS when temperature reached the real value. The dissolving temperatures measured were higher than the real values, in other words, the solubility data obtained by the turbidity method were lower than the gravimetric method. However, the differences were relatively small indicating the reliability of the turbidity method. The results and the corresponding experimental pressure were listed in Table 11. It was observed that the slope of the solubility curve was much steeper in the temperature range of 318.2 K – 343.2 K than that of 273.2 K – 313.2 K. Consider a cooling crystallization of TBBS in tert-butylamine, the theoretical yield was limited to 51.9% when cooling from 313.2 K to 273.2 K. Increasing the upper temperature to 343.2 K (TBBS decomposes easily above this point) could improve the theoretical yield to 73.7%.

Gibson[33] reported that the effect of pressure on the solubility of a solid was significant only in very rare cases, which were concluded by the empirical and theoretical considerations as: (i) solutions of sparingly soluble substances in water, e.g., the sulfates, sulfides, fluorides, carbonates, the rare earths and the heavy metals; (ii) great increasement of pressure, roughly

on the order of 1000 atmospheres. Therefore, the modified Apelblat equation, the $\lambda h$ equation and the NRTL model can also be applied to correlate the solubility data of TBBS in tert-butylamine at temperature from 318.2 K to 343.2 K[34]. The fitting parameters of the models together with ARD and RMSD were listed in Table 12. We can see that ARD of the modified Apelblat equation, the $\lambda h$ equation and the NRTL model were 0.2547%, 0.4560% and 0.3422%, respectively. RMSD of the modified Apelblat equation, the $\lambda h$ equation and the NRTL model were $1.045 \times 10^{-3}$, $1.451 \times 10^{-3}$ and $1.310 \times 10^{-3}$, respectively. The results showed that the modified Apelblat equation fitted better for TBBS in tert-butylamine at high temperature.

## 5. CONCLUSION

The solubility of TBBS was found to increase with the increasing temperature in pure solvents in the temperature range between 273.2 K and 313.2 K, and it shows a decreasing order as: $x_{1,\text{ tert-butylamine}} > x_{1,\text{ toluene}} > x_{1,\text{ 1-butanol}} > x_{1,\text{ ethanol}} > x_{1,\text{ 2-propanol}} > x_{1,\text{ methanol}}$. The solubility of TBBS increases as the temperature and the initial mole fraction of methanol/ ethanol/ tert-butylamine rise in binary solvents. Furthermore, the solubility of TBBS in tert-butylamine at a high temperature range from 318.2 K to 343.2 K under a pressure of 0.156 MPa − 0.213 MPa was also measured by turbidity method for the requirement of industrial application. The modified Apelblat equation, the $\lambda h$ equation, the CNIBS/R-K model and the NRTL model were applied to correlate the TBBS solubility. The calculated solubility data were in good accordance with the experimental solubility data. In conclusion, these results can function as a guidance of practical crystallization process optimization of

TBBS.

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### Funding

The work described in this paper received support from the National Natural Science Foundation of China (NNSFC) (grant references: 91434126, 61633006), the Natural Science Foundation of Guangdong Province (grant reference: 2014A030313228, 2017A030310262), the Guangdong Provincial Science and Technology Projects under the Scheme of Applied Science and Technology Research Special Funds (grant reference: 2015B020232007), and the Fundamental Research Funds for the Central Universities (grant reference: 2017MS092).


### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGEMENTS


The authors would like to extend their thanks to Dr. Jianguo Cao of Pharmavision

(Qingdao) Intelligent Technology Limited (www. pharmavision-ltd.com) who provided the turbidity probe.

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## Tables

**Table 1.** The Sources and Mass Fraction Purity of Materials Used.

| Chemical Name | Molecular Mass ($g \cdot mol^{-1}$) | Source | Mass Fraction Purity | Analysis Method |
|---|---|---|---|---|
| N-tert-butylbenzothiazole-2-sulfenamide | 238.37 | Jiangsu Sinorgchem Technology Co.,Ltd. | ≥0.99 | HPLC[a] |
| 2,2'-azobisisobutyronitrile | 164.21 | Shanghai Aladdin Bio-Chem Technology Co., Ltd. | ≥0.99 | HPLC[a] |
| methanol | 32.04 | Guangzhou Chemical Reagent Factory | ≥0.995 | GC[b] |
| ethanol | 46.07 | Guangzhou Chemical Reagent Factory | ≥0.995 | GC[b] |
| toluene | 92.14 | Shanghai Aladdin Bio-Chem Technology Co., Ltd. | ≥0.995 | GC[b] |
| 2-propanol | 60.06 | Shanghai Aladdin Bio-Chem Technology Co., Ltd. | ≥0.995 | GC[b] |
| 1-butanol | 74.12 | Guangzhou Chemical Reagent Factory | ≥0.995 | GC[b] |
| tert-butylamine | 73.14 | Shanghai Aladdin Bio-Chem Technology Co., Ltd. | ≥0.990 | GC[b] |
| deionized water | 18.02 | Laboratory | none | none |

[a] High performance liquid chromatography (type Lc-20A, Shimadzu, Japan).

[b] Gas chromatography.

**Table 2.** Comparison of the experimental solubility of AIBN in ethanol from 273.2 K to 313.2 K with the literature data ($p = 0.101$ MPa).

| T (K) | $10^3 x_1^{exp}$ | $10^3 x_1^{lit}$ | 100 RD |
|---|---|---|---|
| 278.6 | 2.720 | 2.625 | 3.493 |
| 284.4 | 3.901 | 4.081 | -4.614 |
| 289.0 | 5.288 | 5.114 | 3.290 |
| 293.2 | 6.612 | 6.666 | -0.817 |
| 297.9 | 9.540 | 9.378 | 1.698 |
| 303.0 | 12.72 | 12.83 | -0.865 |
| 307.7 | 16.21 | 16.45 | -1.487 |
| 312.6 | 22.59 | 22.10 | 2.169 |

$x_1^{exp}$ is the experimental solubility of AIBN in ethanol and $x_1^{lit}$ is mole fraction solubility of AIBN in ethanol reported by Li et al.[16] . RD is the relative deviation between the experimental data and the literature data. The standard uncertainties of temperature and pressure are respective u(T) = 0.1 K and u(P) = 1 kPa. The relative standard uncertainty of mole fraction solubility is $u_r(x_1) = 0.01$.

**Table 3.** Mole Fraction Solubility ($x_1$) of TBBS in Different Pure Solvents from 273.2 K to 313.2 K ($p =$ 0.101 MPa).

| T (K) | $10^2 x_1^{exp}$ | $10^2 x_1^{cal}$ | | | T (K) | $10^2 x_1^{exp}$ | $10^2 x_1^{cal}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | | eq 4 | eq 5 | eq 12 | | | eq 4 | eq 5 | eq 12 |
| | | Methanol | | | | | 2-Propanol | | |
| 273.2 | 0.591 | 0.591 | 0.547 | 0.589 | 273.2 | 0.844 | 0.818 | 0.826 | 0.815 |
| 278.2 | 0.707 | 0.702 | 0.676 | 0.704 | 278.2 | 0.938 | 0.997 | 1.00 | 0.961 |
| 283.2 | 0.834 | 0.838 | 0.831 | 0.840 | 283.2 | 1.22 | 1.21 | 1.21 | 1.22 |
| 288.2 | 0.991 | 1.01 | 1.02 | 1.01 | 288.2 | 1.50 | 1.46 | 1.46 | 1.50 |
| 293.2 | 1.23 | 1.21 | 1.24 | 1.22 | 293.2 | 1.76 | 1.75 | 1.75 | 1.78 |
| 298.2 | 1.48 | 1.47 | 1.50 | 1.47 | 298.2 | 2.08 | 2.10 | 2.09 | 2.12 |
| 303.2 | 1.78 | 1.79 | 1.81 | 1.78 | 303.2 | 2.50 | 2.51 | 2.50 | 2.52 |
| 308.2 | 2.19 | 2.18 | 2.19 | 2.18 | 308.2 | 2.98 | 2.98 | 2.97 | 2.96 |
| 313.2 | 2.66 | 2.67 | 2.63 | 2.68 | 313.2 | 3.52 | 3.53 | 3.53 | 3.46 |
| | | Ethanol | | | | | 1-Butanol | | |
| 273.2 | 0.951 | 0.940 | 0.876 | 0.940 | 273.2 | 1.77 | 1.76 | 1.70 | 1.76 |
| 278.2 | 1.11 | 1.12 | 1.08 | 1.12 | 278.2 | 2.02 | 2.04 | 2.01 | 2.04 |
| 283.2 | 1.33 | 1.34 | 1.33 | 1.34 | 283.2 | 2.37 | 2.38 | 2.38 | 2.38 |
| 288.2 | 1.57 | 1.60 | 1.62 | 1.60 | 288.2 | 2.80 | 2.77 | 2.79 | 2.78 |
| 293.2 | 1.98 | 1.93 | 1.97 | 1.94 | 293.2 | 3.25 | 3.24 | 3.27 | 3.24 |
| 298.2 | 2.36 | 2.33 | 2.38 | 2.33 | 298.2 | 3.75 | 3.79 | 3.83 | 3.78 |
| 303.2 | 2.78 | 2.83 | 2.86 | 2.80 | 303.2 | 4.44 | 4.44 | 4.47 | 4.43 |
| 308.2 | 3.44 | 3.44 | 3.44 | 3.43 | 308.2 | 5.24 | 5.21 | 5.21 | 5.21 |
| 313.2 | 4.19 | 4.19 | 4.13 | 4.21 | 313.2 | 6.10 | 6.12 | 6.07 | 6.13 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Toluene | | | | | Tert-butylamine | | | |
| 273.2 | 2.73 | 2.82 | 2.79 | 2.84 | 273.2 | 9.52 | 9.64 | 9.56 | 9.70 |
| 278.2 | 3.55 | 3.44 | 3.41 | 3.45 | 278.2 | 10.7 | 10.5 | 10.5 | 10.5 |
| 283.2 | 4.22 | 4.17 | 4.15 | 4.16 | 283.2 | 11.5 | 11.4 | 11.4 | 11.4 |
| 288.2 | 5.18 | 5.03 | 5.01 | 5.01 | 288.2 | 12.4 | 12.5 | 12.5 | 12.5 |
| 293.2 | 6.05 | 6.04 | 6.03 | 6.00 | 293.2 | 13.5 | 13.6 | 13.7 | 13.6 |
| 298.2 | 6.91 | 7.21 | 7.21 | 7.15 | 298.2 | 14.9 | 14.9 | 14.9 | 14.9 |
| 303.2 | 8.40 | 8.57 | 8.58 | 8.54 | 303.2 | 16.5 | 16.3 | 16.3 | 16.3 |
| 308.2 | 10.2 | 10.1 | 10.2 | 10.2 | 308.2 | 17.6 | 17.9 | 17.9 | 18.0 |
| 313.2 | 12.2 | 11.9 | 12.0 | 12.1 | 313.2 | 19.8 | 19.6 | 19.6 | 19.7 |

eq 4, eq 5, eq 12 refers to the modified Apelblat equation, the $\lambda h$ equation and the NRTL model, respectively. $x_1^{exp}$ is the experimental solubility and $x_1^{cal}$ is the calculated solubility. The standard uncertainties of temperature and pressure are respective u(T) = 0.1 K and u(P) = 1 kPa. The relative standard uncertainty of mole fraction solubility is $u_r(x_1) = 0.05$.

**Table 4.** Mole Fraction Solubility ($x_A$) of TBBS in Methanol ($x_B$) + Water Solvents from 273.2 K to 313.2 K ($p = 0.101$ MPa).

| T (K) | $10^3 x_A^{exp}$ | $10^3 x_A^{cal}$ | | | | T (K) | $10^3 x_A^{exp}$ | $10^3 x_A^{cal}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | eq 4 | eq 5 | eq 8 | eq 13 | | | eq 4 | eq 5 | eq 8 | eq 13 |
| | | $x_2$ = 0.40 | | | | | | $x_2$ = 0.80 | | | |
| 273.2 | 0.0261 | 0.0242 | 0.0211 | 0.0261 | 0.0246 | 273.2 | 1.63 | 1.70 | 1.58 | 1.56 | 1.55 |
| 278.2 | 0.0396 | 0.0418 | 0.0396 | 0.0407 | 0.0449 | 278.2 | 2.18 | 2.14 | 2.05 | 2.06 | 2.02 |
| 283.2 | 0.0660 | 0.0722 | 0.0725 | 0.0678 | 0.0800 | 283.2 | 2.88 | 2.70 | 2.62 | 2.61 | 2.62 |
| 288.2 | 0.121 | 0.125 | 0.130 | 0.123 | 0.139 | 288.2 | 3.46 | 3.39 | 3.34 | 3.30 | 3.35 |
| 293.2 | 0.222 | 0.216 | 0.229 | 0.224 | 0.237 | 293.2 | 4.12 | 4.24 | 4.23 | 3.90 | 4.25 |
| 298.2 | 0.399 | 0.373 | 0.395 | 0.402 | 0.397 | 298.2 | 5.16 | 5.30 | 5.32 | 4.90 | 5.37 |
| 303.2 | 0.670 | 0.645 | 0.669 | 0.673 | 0.653 | 303.2 | 6.44 | 6.61 | 6.66 | 6.28 | 6.73 |
| 308.2 | 1.12 | 1.12 | 1.12 | 1.11 | 1.06 | 308.2 | 8.04 | 8.23 | 8.31 | 8.30 | 8.40 |
| 313.2 | 1.83 | 1.92 | 1.83 | 1.80 | 1.70 | 313.2 | 10.7 | 10.2 | 10.3 | 11.0 | 10.3 |
| | | $x_2$ = 0.50 | | | | | | $x_2$ = 0.90 | | | |
| 273.2 | 0.129 | 0.127 | 0.137 | 0.127 | 0.0987 | 273.2 | 3.56 | 3.68 | 3.01 | 3.67 | 2.92 |
| 278.2 | 0.191 | 0.191 | 0.203 | 0.179 | 0.156 | 278.2 | 4.39 | 4.19 | 3.77 | 4.63 | 3.70 |
| 283.2 | 0.284 | 0.283 | 0.295 | 0.254 | 0.240 | 283.2 | 4.82 | 4.86 | 4.70 | 5.28 | 4.65 |
| 288.2 | 0.388 | 0.414 | 0.425 | 0.360 | 0.364 | 288.2 | 5.74 | 5.74 | 5.82 | 6.04 | 5.80 |
| 293.2 | 0.598 | 0.596 | 0.604 | 0.576 | 0.545 | 293.2 | 6.94 | 6.89 | 7.18 | 7.23 | 7.20 |
| 298.2 | 0.883 | 0.846 | 0.849 | 0.858 | 0.803 | 298.2 | 8.29 | 8.39 | 8.81 | 8.60 | 8.87 |
| 303.2 | 1.24 | 1.19 | 1.18 | 1.22 | 1.17 | 303.2 | 10.2 | 10.4 | 10.8 | 10.4 | 10.9 |
| 308.2 | 1.59 | 1.64 | 1.63 | 1.64 | 1.67 | 308.2 | 13.1 | 13.0 | 13.2 | 12.7 | 13.3 |
| 313.2 | 2.24 | 2.25 | 2.24 | 2.40 | 2.37 | 313.2 | 16.6 | 16.5 | 16.0 | 16.0 | 16.2 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $x_2$ = 0.60 | | | | | | $x_2$ = 1.00 | | | |
| 273.2 | 0.310 | 0.299 | 0.201 | 0.313 | 0.305 | 273.2 | 5.91 | 5.91 | 5.47 | 5.88 | 5.57 |
| 278.2 | 0.389 | 0.399 | 0.311 | 0.427 | 0.438 | 278.2 | 7.07 | 7.02 | 6.76 | 6.98 | 6.90 |
| 283.2 | 0.515 | 0.542 | 0.474 | 0.601 | 0.620 | 283.2 | 8.34 | 8.38 | 8.31 | 8.15 | 8.49 |
| 288.2 | 0.744 | 0.749 | 0.711 | 0.828 | 0.868 | 288.2 | 9.91 | 10.1 | 10.2 | 9.77 | 10.4 |
| 293.2 | 1.10 | 1.05 | 1.05 | 1.15 | 1.20 | 293.2 | 12.3 | 12.1 | 12.4 | 12.2 | 12.6 |
| 298.2 | 1.54 | 1.49 | 1.54 | 1.59 | 1.64 | 298.2 | 14.8 | 14.7 | 15.0 | 14.6 | 15.3 |
| 303.2 | 2.13 | 2.15 | 2.23 | 2.18 | 2.23 | 303.2 | 17.8 | 17.9 | 18.1 | 17.7 | 18.4 |
| 308.2 | 3.07 | 3.14 | 3.20 | 2.94 | 3.00 | 308.2 | 21.9 | 21.8 | 21.9 | 22.0 | 22.1 |
| 313.2 | 4.64 | 4.62 | 4.53 | 4.14 | 4.05 | 313.2 | 26.6 | 26.7 | 26.3 | 26.9 | 26.4 |
| | | $x_2$ = 0.70 | | | | | | | | | |
| 273.2 | 0.651 | 0.676 | 0.621 | 0.667 | 0.746 | | | | | | |
| 278.2 | 0.923 | 0.915 | 0.863 | 0.902 | 1.01 | | | | | | |
| 283.2 | 1.29 | 1.23 | 1.19 | 1.25 | 1.36 | | | | | | |
| 288.2 | 1.77 | 1.65 | 1.62 | 1.70 | 1.81 | | | | | | |
| 293.2 | 2.10 | 2.20 | 2.18 | 2.11 | 2.37 | | | | | | |
| 298.2 | 2.77 | 2.91 | 2.91 | 2.80 | 3.09 | | | | | | |
| 303.2 | 3.75 | 3.84 | 3.87 | 3.76 | 4.01 | | | | | | |
| 308.2 | 5.14 | 5.04 | 5.09 | 5.18 | 5.17 | | | | | | |
| 313.2 | 6.73 | 6.59 | 6.67 | 7.12 | 6.62 | | | | | | |

eq 4, eq 5, eq 8, eq 13 refers to the modified Apelblat equation, the $\lambda h$ equation, the CNIBS/R-K model and the NRTL model, respectively. $x_1^{exp}$ is the experimental solubility and $x_1^{cal}$ is the calculated solubility. The standard uncertainties of temperature and pressure are respective u(T) = 0.1 K and u(P) = 1 kPa. The relative standard uncertainty of the solvent composition is $u_r(x_B)$ = 0.01. The relative standard uncertainty of mole fraction solubility is $u_r(x_A)$ = 0.13.

**Table 5.** Mole Fraction Solubility ($x_A$) of TBBS in Ethanol ($x_B$) + Water Solvents from 273.2 K to 313.2 K ($p = 0.101$ MPa).

| T (K) | $10^3 x_A^{exp}$ | $10^3 x_A^{cal}$ | | | | T (K) | $10^3 x_A^{exp}$ | $10^3 x_A^{cal}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | eq 4 | eq 5 | eq 8 | eq 13 | | | eq 4 | eq 5 | eq 8 | eq 13 |
| | | $x_2$ = 0.40 | | | | | | $x_2$ = 0.80 | | | |
| 273.2 | 0.344 | 0.348 | 0.249 | 0.346 | 0.380 | 273.2 | 5.71 | 5.88 | 5.13 | 4.95 | 4.90 |
| 278.2 | 0.457 | 0.459 | 0.369 | 0.457 | 0.514 | 278.2 | 6.78 | 6.61 | 6.20 | 6.23 | 6.01 |
| 283.2 | 0.629 | 0.613 | 0.541 | 0.627 | 0.690 | 283.2 | 7.79 | 7.55 | 7.47 | 7.21 | 7.31 |
| 288.2 | 0.841 | 0.826 | 0.781 | 0.842 | 0.921 | 288.2 | 8.96 | 8.75 | 8.95 | 8.39 | 8.85 |
| 293.2 | 1.12 | 1.13 | 1.12 | 1.11 | 1.22 | 293.2 | 9.96 | 10.3 | 10.7 | 9.61 | 10.6 |
| 298.2 | 1.54 | 1.55 | 1.58 | 1.55 | 1.61 | 298.2 | 11.5 | 12.2 | 12.7 | 11.0 | 12.7 |
| 303.2 | 2.13 | 2.14 | 2.21 | 2.14 | 2.12 | 303.2 | 14.6 | 14.7 | 15.1 | 14.6 | 15.2 |
| 308.2 | 2.88 | 2.99 | 3.06 | 2.92 | 2.76 | 308.2 | 19.2 | 17.9 | 18.0 | 17.6 | 18.1 |
| 313.2 | 4.34 | 4.20 | 4.20 | 4.41 | 3.62 | 313.2 | 21.3 | 21.9 | 21.3 | 20.4 | 21.3 |
| | | $x_2$ = 0.50 | | | | | | $x_2$ = 0.90 | | | |
| 273.2 | 1.20 | 1.23 | 0.944 | 1.19 | 0.935 | 273.2 | 7.11 | 7.44 | 7.92 | 7.68 | 7.01 |
| 278.2 | 1.50 | 1.42 | 1.23 | 1.52 | 1.21 | 278.2 | 9.49 | 8.92 | 9.19 | 9.90 | 8.52 |
| 283.2 | 1.66 | 1.68 | 1.59 | 1.70 | 1.55 | 283.2 | 10.9 | 10.6 | 10.6 | 11.3 | 10.3 |
| 288.2 | 2.02 | 2.03 | 2.05 | 2.02 | 1.98 | 288.2 | 12.2 | 12.4 | 12.3 | 12.6 | 12.3 |
| 293.2 | 2.46 | 2.50 | 2.61 | 2.43 | 2.52 | 293.2 | 14.5 | 14.5 | 14.2 | 14.9 | 14.7 |
| 298.2 | 3.23 | 3.14 | 3.31 | 3.22 | 3.18 | 298.2 | 15.2 | 16.7 | 16.3 | 15.5 | 17.4 |
| 303.2 | 3.96 | 3.99 | 4.18 | 3.89 | 3.99 | 303.2 | 20.8 | 19.1 | 18.8 | 20.9 | 20.6 |
| 308.2 | 5.06 | 5.17 | 5.25 | 4.79 | 4.99 | 308.2 | 21.4 | 21.7 | 21.7 | 22.9 | 24.2 |
| 313.2 | 6.88 | 6.78 | 6.58 | 6.44 | 6.25 | 313.2 | 24.5 | 24.5 | 25.0 | 25.6 | 28.3 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $x_2$ = 0.60 | | | | | | $x_2$ = 1.00 | | | |
| 273.2 | 2.23 | 2.30 | 1.99 | 2.15 | 1.85 | 273.2 | 9.51 | 9.40 | 8.76 | 9.35 | 9.48 |
| 278.2 | 2.74 | 2.63 | 2.45 | 2.62 | 2.34 | 278.2 | 11.1 | 11.2 | 10.8 | 11.0 | 11.4 |
| 283.2 | 3.11 | 3.05 | 2.99 | 2.92 | 2.93 | 283.2 | 13.3 | 13.4 | 13.3 | 13.2 | 13.7 |
| 288.2 | 3.58 | 3.59 | 3.65 | 3.49 | 3.64 | 288.2 | 15.7 | 16.0 | 16.2 | 15.6 | 16.3 |
| 293.2 | 3.97 | 4.27 | 4.42 | 4.01 | 4.50 | 293.2 | 19.8 | 19.3 | 19.7 | 19.7 | 19.4 |
| 298.2 | 5.43 | 5.15 | 5.35 | 5.39 | 5.55 | 298.2 | 23.6 | 23.3 | 23.8 | 23.5 | 22.8 |
| 303.2 | 6.15 | 6.27 | 6.45 | 6.33 | 6.78 | 303.2 | 27.8 | 28.3 | 28.6 | 27.8 | 26.8 |
| 308.2 | 7.71 | 7.71 | 7.77 | 8.19 | 8.27 | 308.2 | 34.4 | 34.4 | 34.4 | 33.8 | 31.3 |
| 313.2 | 9.62 | 9.57 | 9.34 | 10.6 | 10.1 | 313.2 | 41.9 | 41.9 | 41.3 | 41.3 | 36.4 |
| | | $x_2$ = 0.70 | | | | | | | | | |
| 273.2 | 2.87 | 2.96 | 2.36 | 3.22 | 3.17 | | | | | | |
| 278.2 | 3.58 | 3.48 | 3.07 | 3.91 | 3.93 | | | | | | |
| 283.2 | 4.10 | 4.17 | 3.95 | 4.51 | 4.83 | | | | | | |
| 288.2 | 5.09 | 5.07 | 5.05 | 5.42 | 5.92 | | | | | | |
| 293.2 | 6.05 | 6.24 | 6.42 | 6.16 | 7.20 | | | | | | |
| 298.2 | 7.65 | 7.79 | 8.10 | 7.92 | 8.72 | | | | | | |
| 303.2 | 9.93 | 9.84 | 10.2 | 9.76 | 10.5 | | | | | | |
| 308.2 | 12.5 | 12.6 | 12.7 | 12.8 | 12.7 | | | | | | |
| 313.2 | 16.4 | 16.2 | 15.9 | 15.8 | 15.2 | | | | | | |

eq 4, eq 5, eq 8, eq 13 refers to the modified Apelblat equation, the $\lambda h$ equation, the CNIBS/R-K model and the NRTL model, respectively. $x_1^{exp}$ is the experimental solubility and $x_1^{cal}$ is the calculated solubility. The standard uncertainties of temperature and pressure are respective u(T) = 0.1 K and u(P) = 1 kPa. The relative standard uncertainty of the solvent composition is $u_r(x_B)$ = 0.01. The relative standard uncertainty of mole fraction solubility is $u_r(x_A)$ = 0.15.

**Table 6.** Mole Fraction Solubility ($x_A$) of TBBS in Tert-butylamine ($x_B$) + Water Solvents from 273.2 K to 313.2 K ($p = 0.101$ MPa).

| T (K) | $10^2 x_A^{exp}$ | $10^2 x_A^{cal}$ | | | | T (K) | $10^2 x_A^{exp}$ | $10^2 x_A^{cal}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | eq 4 | eq 5 | eq 8 | eq 13 | | | eq 4 | eq 5 | eq 8 | eq 13 |
| | | $x_2$ = 0.40 | | | | | | $x_2$ = 0.80 | | | |
| 273.2 | 0.637 | 0.633 | 0.591 | 0.636 | 0.597 | 273.2 | 5.72 | 5.68 | 5.58 | 5.71 | 5.44 |
| 278.2 | 0.728 | 0.732 | 0.710 | 0.727 | 0.717 | 278.2 | 6.28 | 6.32 | 6.29 | 6.24 | 6.23 |
| 283.2 | 0.849 | 0.852 | 0.849 | 0.850 | 0.857 | 283.2 | 7.05 | 7.06 | 7.07 | 6.98 | 7.07 |
| 288.2 | 0.993 | 0.998 | 1.01 | 0.993 | 1.02 | 288.2 | 7.77 | 7.89 | 7.94 | 7.69 | 8.01 |
| 293.2 | 1.19 | 1.18 | 1.20 | 1.19 | 1.21 | 293.2 | 8.76 | 8.84 | 8.91 | 8.71 | 8.99 |
| 298.2 | 1.38 | 1.39 | 1.42 | 1.39 | 1.44 | 298.2 | 10.3 | 9.92 | 9.98 | 10.1 | 9.97 |
| 303.2 | 1.68 | 1.66 | 1.68 | 1.69 | 1.70 | 303.2 | 11.1 | 11.1 | 11.2 | 11.1 | 11.2 |
| 308.2 | 1.98 | 1.99 | 1.99 | 1.98 | 2.00 | 308.2 | 12.5 | 12.5 | 12.5 | 12.5 | 12.4 |
| 313.2 | 2.37 | 2.39 | 2.35 | 2.37 | 2.35 | 313.2 | 14.1 | 14.1 | 14.0 | 14.1 | 13.6 |
| | | $x_2$ = 0.50 | | | | | | $x_2$ = 0.90 | | | |
| 273.2 | 1.28 | 1.29 | 1.25 | 1.28 | 1.29 | 273.2 | 7.56 | 7.58 | 7.37 | 7.57 | 7.18 |
| 278.2 | 1.53 | 1.50 | 1.48 | 1.53 | 1.52 | 278.2 | 8.33 | 8.27 | 8.19 | 8.36 | 8.16 |
| 283.2 | 1.74 | 1.74 | 1.74 | 1.73 | 1.78 | 283.2 | 9.04 | 9.07 | 9.10 | 9.11 | 9.25 |
| 288.2 | 2.01 | 2.03 | 2.04 | 2.01 | 2.08 | 288.2 | 9.89 | 9.99 | 10.1 | 9.95 | 10.4 |
| 293.2 | 2.36 | 2.37 | 2.39 | 2.36 | 2.42 | 293.2 | 11.1 | 11.1 | 11.2 | 11.2 | 11.6 |
| 298.2 | 2.79 | 2.77 | 2.79 | 2.76 | 2.81 | 298.2 | 12.3 | 12.3 | 12.4 | 12.5 | 12.9 |
| 303.2 | 3.22 | 3.24 | 3.26 | 3.21 | 3.25 | 303.2 | 13.6 | 13.6 | 13.7 | 13.7 | 14.2 |
| 308.2 | 3.82 | 3.80 | 3.80 | 3.81 | 3.76 | 308.2 | 15.2 | 15.2 | 15.2 | 15.2 | 15.6 |
| 313.2 | 4.44 | 4.45 | 4.42 | 4.46 | 4.33 | 313.2 | 17.1 | 17.0 | 16.9 | 17.1 | 17.0 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $x_2$ = 0.60 | | | | | | $x_2$ = 1.00 | | | |
| 273.2 | 2.38 | 2.39 | 2.31 | 2.37 | 2.37 | 273.2 | 9.52 | 9.64 | 9.56 | 9.52 | 8.88 |
| 278.2 | 2.77 | 2.73 | 2.69 | 2.75 | 2.75 | 278.2 | 10.7 | 10.5 | 10.5 | 10.7 | 9.98 |
| 283.2 | 3.09 | 3.12 | 3.12 | 3.11 | 3.19 | 283.2 | 11.5 | 11.4 | 11.4 | 11.5 | 11.2 |
| 288.2 | 3.56 | 3.58 | 3.61 | 3.55 | 3.68 | 288.2 | 12.4 | 12.5 | 12.5 | 12.4 | 12.6 |
| 293.2 | 4.11 | 4.12 | 4.16 | 4.09 | 4.22 | 293.2 | 13.5 | 13.6 | 13.7 | 13.5 | 14.0 |
| 298.2 | 4.81 | 4.75 | 4.80 | 4.87 | 4.82 | 298.2 | 14.9 | 14.9 | 14.9 | 14.9 | 15.5 |
| 303.2 | 5.44 | 5.49 | 5.53 | 5.47 | 5.50 | 303.2 | 16.5 | 16.3 | 16.3 | 16.4 | 16.9 |
| 308.2 | 6.37 | 6.36 | 6.36 | 6.38 | 6.25 | 308.2 | 17.6 | 17.9 | 17.9 | 17.6 | 18.7 |
| 313.2 | 7.39 | 7.38 | 7.32 | 7.35 | 7.08 | 313.2 | 19.8 | 19.6 | 19.6 | 19.8 | 20.1 |
| | | $x_2$ = 0.70 | | | | | | | | | |
| 273.2 | 3.88 | 3.84 | 3.75 | 3.90 | 3.80 | | | | | | |
| 278.2 | 4.30 | 4.34 | 4.30 | 4.34 | 4.38 | | | | | | |
| 283.2 | 4.92 | 4.91 | 4.92 | 4.93 | 5.01 | | | | | | |
| 288.2 | 5.46 | 5.57 | 5.62 | 5.51 | 5.73 | | | | | | |
| 293.2 | 6.24 | 6.33 | 6.40 | 6.28 | 6.49 | | | | | | |
| 298.2 | 7.47 | 7.21 | 7.28 | 7.49 | 7.29 | | | | | | |
| 303.2 | 8.26 | 8.24 | 8.28 | 8.24 | 8.23 | | | | | | |
| 308.2 | 9.43 | 9.42 | 9.41 | 9.42 | 9.22 | | | | | | |
| 313.2 | 10.7 | 10.8 | 10.7 | 10.7 | 10.3 | | | | | | |

eq 4, eq 5, eq 8, eq 13 refers to the modified Apelblat equation, the $\lambda h$ equation, the CNIBS/R-K model and the NRTL model, respectively. $x_1^{exp}$ is the experimental solubility and $x_1^{cal}$ is the calculated solubility. The standard uncertainties of temperature and pressure are respective u(T) = 0.1 K and u(P) = 1 kPa. The relative standard uncertainty of the solvent composition is $u_r(x_B)$ = 0.01. The relative standard uncertainty of mole fraction solubility is $u_r(x_A)$ = 0.06.

**Table 7.** Fitting Parameters of TBBS in Six Pure Solvents ($p$ = 0.101 MPa).

| Solvents | Parameters | Methanol | Ethanol | Toluene | 2-Propanol | 1-Butanol | Tert-butylamine |
|---|---|---|---|---|---|---|---|
| modified | A | -240.69 | -219.89 | -17.90 | -42.89 | -152.91 | -94.32 |
| Apelblat | B | 7598.58 | 6732.45 | -1963.65 | -958.03 | 4275.98 | 2747.95 |
| equation | C | 37.03 | 33.97 | 3.836 | 7.413 | 23.75 | 14.60 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | $10^2$ARD | 0.6781 | 1.149 | 2.158 | 1.628 | 0.5546 | 0.9736 |
| | $10^3$RMSD | 0.1018 | 0.2712 | 1.612 | 0.2691 | 0.2194 | 1.520 |
| | $\lambda$ | 0.1350 | 0.2124 | 0.6453 | 0.1500 | 0.1910 | 0.1709 |
| $\lambda h$ | $h$ | 22959.16 | 14497.94 | 4679.65 | 18782.15 | 12459.28 | 5382.66 |
| equation | $10^2$ARD | 2.211 | 2.061 | 2.189 | 1.599 | 0.9976 | 0.9585 |
| | $10^3$RMSD | 0.2673 | 0.4493 | 1.552 | 0.2748 | 0.3916 | 1.601 |
| | $10^3\alpha$ | 54.77 | 23.16 | 9.049 | 170.68 | 7.700 | 0.01931 |
| NRTL | $\Delta g_{12}$ | -17613.09 | -25011.73 | -29852.36 | 33545.72 | -52877.26 | 1326661.63 |
| model | $\Delta g_{21}$ | 31217.21 | 35411.83 | 34105.85 | 96461.38 | 64950.66 | -1314692.43 |
| | $10^2$ARD | 0.6803 | 1.355 | 2.057 | 1.523 | 0.5513 | 1.137 |
| | $10^3$RMSD | 0.1068 | 0.2815 | 1.274 | 0.3180 | 0.2055 | 1.736 |

**Table 8.** Fitting Parameters of the Modified Apelblat Equation for TBBS in the (Methanol + Water), (Ethanol + Water) and (Tert-butylamine + Water) Binary Solvents ($p = 0.101$ MPa).

| $x_2$ | A | B | C | $10^2$ARD | $10^3$RMSD |
|---|---|---|---|---|---|
| | | Methanol + Water | | | |
| 0.40 | -402.38 | 9279.09 | 63.77 | 4.950 | 0.03485 |
| 0.50 | 41.21 | -7360.44 | -4.143 | 2.304 | 0.02872 |
| 0.60 | -578.15 | 20021.90 | 88.54 | 2.564 | 0.03485 |
| 0.70 | -94.44 | -277.90 | 15.71 | 3.606 | 0.09814 |
| 0.80 | -119.31 | 1718.42 | 19.01 | 3.287 | 0.1996 |
| 0.90 | -489.06 | 18460.34 | 74.13 | 1.592 | 0.1306 |
| 1.00 | -240.69 | 7598.58 | 37.03 | 0.6781 | 0.1018 |

| | | | | | |
|---|---|---|---|---|---|
| | | Ethanol + Water | | | |
| 0.40 | -441.56 | 14497.80 | 67.83 | 1.681 | 0.05864 |
| 0.50 | -570.29 | 21596.42 | 86.37 | 2.189 | 0.06934 |
| 0.60 | -403.28 | 14816.44 | 61.13 | 2.738 | 0.1520 |
| 0.70 | -455.56 | 16621.50 | 69.32 | 1.684 | 0.1120 |
| 0.80 | -407.91 | 15259.84 | 61.84 | 3.406 | 0.5792 |
| 0.90 | 88.59 | -6228.51 | -12.60 | 3.949 | 0.8035 |
| 1.00 | -219.89 | 6732.45 | 33.97 | 1.149 | 0.2712 |
| | | Tert-butylamine + Water | | | |
| 0.40 | -249.06 | 8291.85 | 38.08 | 0.6369 | 0.1074 |
| 0.50 | -149.61 | 4134.56 | 23.20 | 0.7137 | 0.1738 |
| 0.60 | -164.57 | 5011.02 | 25.40 | 0.6612 | 0.3230 |
| 0.70 | -145.61 | 4374.25 | 22.52 | 1.147 | 1.044 |
| 0.80 | -120.42 | 3506.75 | 18.66 | 1.006 | 1.395 |
| 0.90 | -157.03 | 5301.80 | 24.07 | 0.4395 | 0.5543 |
| 1.00 | -94.32 | 2747.95 | 14.60 | 0.9736 | 1.520 |

**Table 9.** Fitting Parameters of the $\lambda h$ Equation for TBBS in the (Methanol + Water), (Ethanol + Water) and (Tert-butylamine + Water) Binary Solvents ($p = 0.101$ MPa).

| $x_2$ | $\lambda$ | $h$ | $10^2$ARD | $10^3$RMSD |
|---|---|---|---|---|
| | | Methanol + Water | | |
| 0.40 | 0.4537 | 21025.61 | 4.597 | 0.005606 |
| 0.50 | 0.06576 | 89776.38 | 4.155 | 0.02835 |
| 0.60 | 0.2054 | 32271.17 | 9.237 | 0.08197 |
| 0.70 | 0.1129 | 44133.41 | 4.666 | 0.09744 |
| 0.80 | 0.08484 | 45077.72 | 4.111 | 0.2064 |
| 0.90 | 0.09559 | 34889.76 | 6.022 | 0.4533 |
| 1.00 | 0.1350 | 22959.16 | 2.210 | 0.2673 |

| | | | | |
|---|---|---|---|---|
| Ethanol + Water | | | | |
| 0.40 | 0.1302 | 46001.62 | 9.288 | 0.09694 |
| 0.50 | 0.05917 | 67129.63 | 7.430 | 0.1972 |
| 0.60 | 0.04414 | 68078.26 | 5.371 | 0.2458 |
| 0.70 | 0.1380 | 28299.10 | 6.168 | 0.3692 |
| 0.80 | 0.08264 | 32800.79 | 5.655 | 0.7156 |
| 0.90 | 0.05419 | 36225.01 | 4.573 | 0.8527 |
| 1.00 | 0.2124 | 14497.94 | 2.061 | 0.4493 |
| Tert-butylamine + Water | | | | |
| 0.40 | 0.08365 | 31009.76 | 1.891 | 0.2431 |
| 0.50 | 0.1299 | 17807.02 | 1.151 | 0.2788 |
| 0.60 | 0.1824 | 11351.55 | 1.357 | 0.5728 |
| 0.70 | 0.2250 | 8134.20 | 1.328 | 1.064 |
| 0.80 | 0.2265 | 6651.22 | 1.284 | 1.433 |
| 0.90 | 0.2162 | 5807.70 | 1.144 | 1.358 |
| 1.00 | 0.1709 | 5382.66 | 0.9585 | 1.601 |

**Table 10.** Fitting Parameters of the CNIBS/R-K Model for TBBS in the (Methanol + Water), (Ethanol + Water) and (Tert-butylamine + Water) Binary Solvents ($p = 0.101$ MPa).

| T (K) | $B_1$ | $B_2$ | $B_3$ | $B_4$ | $B_5$ | $10^2$ARD | $10^3$RMSD |
|---|---|---|---|---|---|---|---|
| Methanol + Water | | | | | | | |
| 273.2 | -45.54 | 196.72 | -403.08 | 376.89 | -130.13 | 1.787 | 0.04952 |
| 278.2 | -42.11 | 179.98 | -369.85 | 348.23 | -121.21 | 4.801 | 0.1078 |
| 283.2 | -32.59 | 124.13 | -244.65 | 226.29 | -77.99 | 7.799 | 0.2153 |
| 288.2 | -20.47 | 54.18 | -91.49 | 80.01 | -26.86 | 5.106 | 0.1455 |
| 293.2 | -21.37 | 66.32 | -123.27 | 111.20 | -37.28 | 2.884 | 0.1473 |
| 298.2 | -15.34 | 34.90 | -57.79 | 50.36 | -16.36 | 2.535 | 0.1629 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 303.2 | -8.340 | -3.650 | 24.86 | -27.30 | 10.40 | 1.328 | 0.1014 |
| 308.2 | 2.091 | -63.65 | 155.11 | -149.93 | 52.56 | 2.271 | 0.1884 |
| 313.2 | 5.495 | -80.57 | 190.38 | -182.48 | 63.55 | 4.774 | 0.3797 |
| | | | | Ethanol + Water | | | |
| 273.2 | -36.53 | 159.01 | -319.34 | 289.73 | -97.55 | 5.689 | 0.3882 |
| 278.2 | -39.17 | 179.98 | -373.09 | 347.52 | -119.77 | 3.990 | 0.2945 |
| 283.2 | -29.86 | 126.69 | -259.94 | 243.20 | -84.41 | 4.307 | 0.3120 |
| 288.2 | -23.02 | 86.33 | -170.16 | 156.40 | -53.71 | 2.872 | 0.3023 |
| 293.2 | -21.01 | 77.38 | -153.78 | 142.51 | -49.02 | 1.520 | 0.1922 |
| 298.2 | -13.69 | 30.59 | -40.21 | 23.73 | -4.179 | 1.756 | 0.2642 |
| 303.2 | -11.77 | 25.67 | -41.86 | 37.23 | -12.85 | 1.161 | 0.1179 |
| 308.2 | -0.9646 | -41.77 | 114.52 | -118.79 | 43.62 | 4.590 | 0.8951 |
| 313.2 | 4.313 | -71.91 | 182.85 | -187.36 | 68.93 | 4.487 | 0.7342 |
| | | | | Tert-butylamine + Water | | | |
| 273.2 | -7.316 | 1.001 | 20.75 | -26.89 | 10.10 | 0.2105 | 0.1034 |
| 278.2 | -10.44 | 20.68 | -21.27 | 11.10 | -2.303 | 0.4221 | 0.2484 |
| 283.2 | -8.077 | 7.063 | 8.859 | -17.63 | 7.623 | 0.5077 | 0.3810 |
| 288.2 | -8.802 | 12.75 | -4.106 | -5.318 | 3.384 | 0.4329 | 0.4242 |
| 293.2 | -8.921 | 15.14 | -10.61 | 1.762 | 0.6269 | 0.2677 | 0.2662 |
| 298.2 | -6.994 | 3.305 | 17.69 | -26.83 | 10.92 | 0.8651 | 0.9196 |
| 303.2 | -6.669 | 3.508 | 15.28 | -23.59 | 9.662 | 0.2257 | 0.1850 |
| 308.2 | -7.810 | 11.74 | -3.276 | -5.752 | 3.359 | 0.08932 | 0.08223 |
| 313.2 | -7.340 | 10.28 | -0.6459 | -8.111 | 4.194 | 0.1935 | 0.2147 |

**Table 11.** Fitting Parameters of the NRTL Model for TBBS in the (Methanol + Water), (Ethanol + Water) and (Tert-butylamine + Water) Binary Solvents ($p = 0.101$ MPa).

| Parameters | Methanol + Water | Ethanol + Water | Tert-butylamine + Water |
|---|---|---|---|
| $\alpha_1$ | 0.21 | 0.20 | 0.20 |
| $\alpha_2$ | 0.20 | 0.20 | 0.20 |
| $\alpha_3$ | 0.15 | 0.18 | 0.19 |
| $\Delta g_{12}$ | 11236.83 | 23278.21 | 24946.10 |
| $\Delta g_{21}$ | 180.82 | -67.89 | -5516.29 |
| $\Delta g_{13}$ | -75107.57 | -53457.84 | -11627.84 |
| $\Delta g_{31}$ | 6834.44 | 1411.41 | 14536.08 |
| $\Delta g_{23}$ | -77641.35 | -58764.54 | -25266.33 |
| $\Delta g_{32}$ | -13996.55 | 53336.31 | 1527.45 |
| $10^2$ARD | 7.297 | 7.724 | 2.560 |
| $10^3$RMSD | 0.2693 | 1.158 | 2.954 |

**Table 12.** Mole Fraction Solubility ($x_1$) and Experimental Pressure of TBBS in Tert-butylamine from 318.2 K to 343.2 K by a Turbidity Method.

| T (K) | P (MPa) | $10^2 x_1^{exp}$ | $10^2 x_1^{cal}$ | | |
|---|---|---|---|---|---|
| | | | eq 4 | eq 5 | eq 12 |
| 320.0 | 0.156 | 21.66 | 21.64 | 21.50 | 21.64 |
| 325.2 | 0.164 | 24.38 | 24.31 | 24.34 | 24.27 |
| 332.3 | 0.183 | 28.59 | 28.67 | 28.80 | 28.68 |
| 335.2 | 0.191 | 30.76 | 30.73 | 30.84 | 30.71 |
| 338.8 | 0.202 | 33.77 | 33.55 | 33.57 | 33.51 |
| 342.7 | 0.213 | 36.91 | 36.96 | 36.81 | 36.99 |

eq 4, eq 5 and eq 12 refers to the modified Apelblat equation, the $\lambda h$ equation and the NRTL model, respectively. $x_1^{exp}$ is the experimental solubility and $x_1^{cal}$ is the calculated solubility. The standard uncertainties of temperature and pressure are respective u(T) = 0.1 K and u(P) = 1 kPa. The relative standard uncertainty of mole fraction solubility is $u_r(x_1) = 0.002$.

**Table 13.** Fitting Parameters of TBBS in Tert-butylamine at High Temperature (318.2 K – 343.2 K).

| Modified Apelblat equation | | $\lambda h$ equation | | NRTL model | |
|---|---|---|---|---|---|
| A | -201.60 | $\lambda$ | 0.4855 | $\alpha$ | 0.9529 |
| B | 7545.04 | $h$ | 4111.72 | $\Delta g_{12}$ | -15120.20 |
| C | 30.60 | $10^2$ARD | 0.4560 | $\Delta g_{21}$ | 1057.23 |
| $10^2$ARD | 0.2547 | $10^3$RMSD | 1.451 | $10^2$ARD | 0.3422 |
| $10^3$RMSD | 1.045 | | | $10^3$RMSD | 1.310 |

## Figures

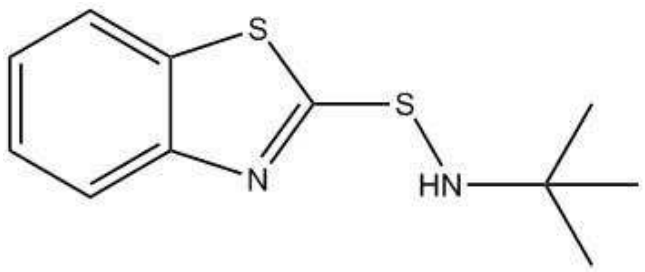


**Figure 1.** Molecular structure of TBBS.

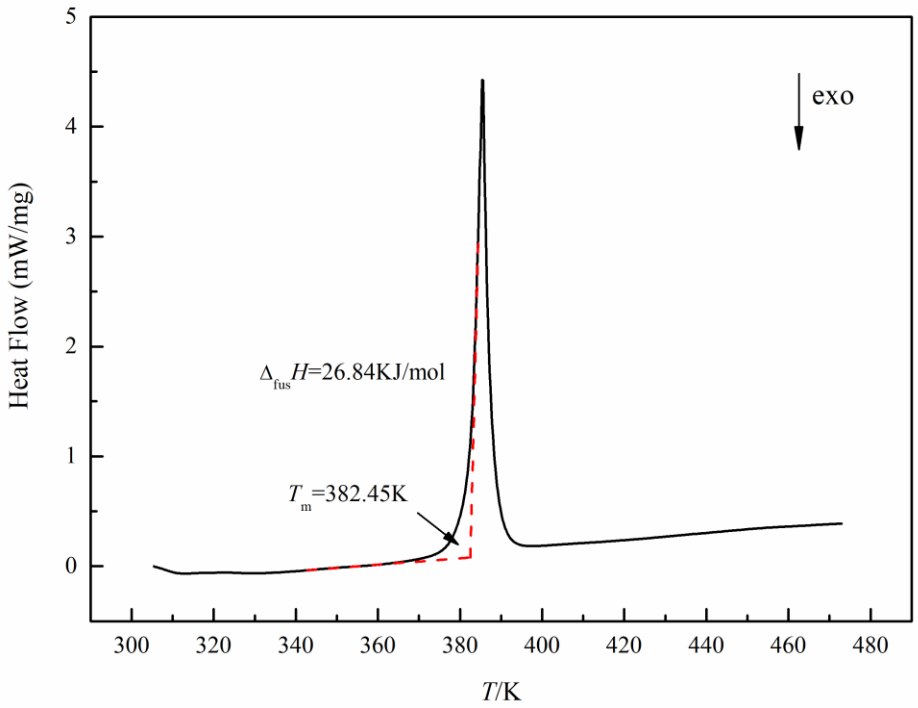


**Figure 2.** Thermal analysis (DSC) of TBBS (the onset point was determined as the intersection of the baseline and the tangent line of the endothermic peak).

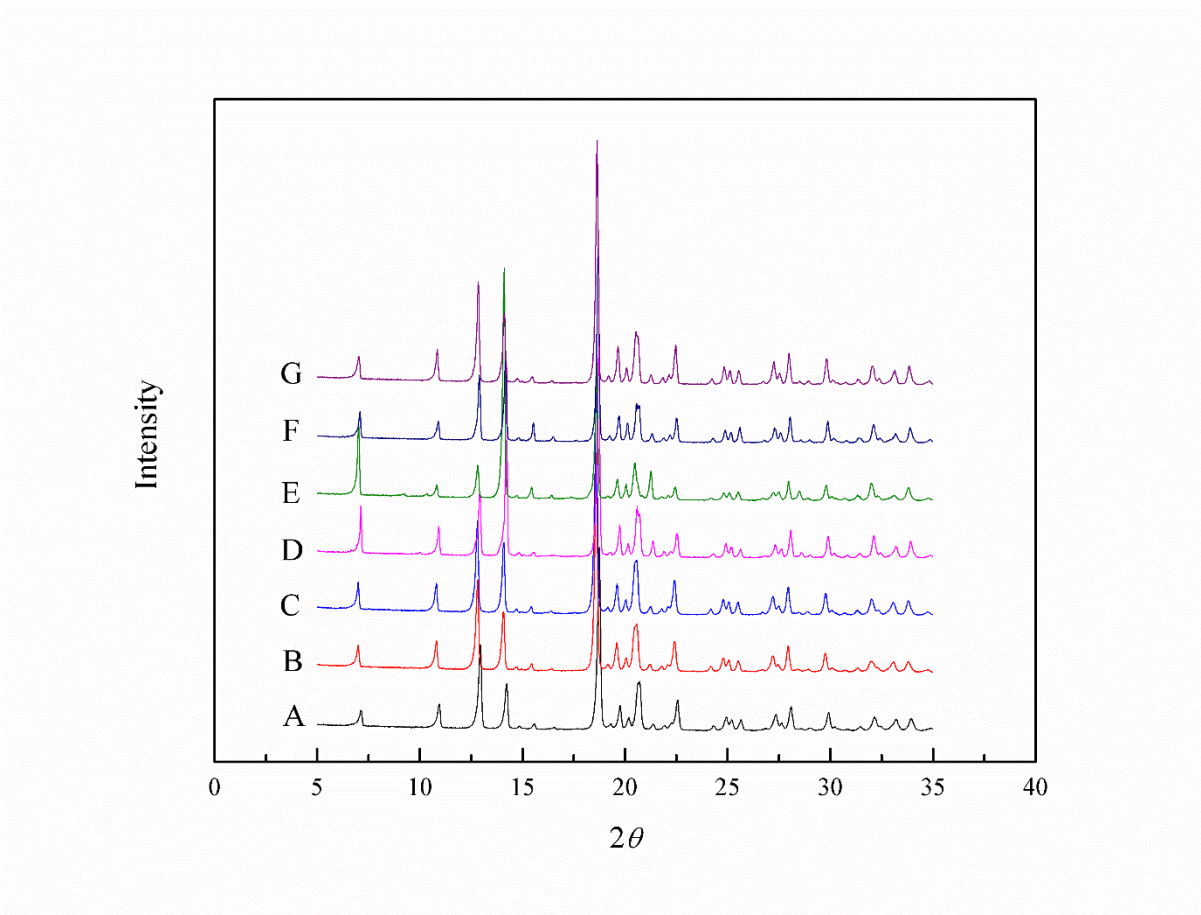


**Figure 3.** XRPD patterns of TBBS in different solvents: (A) raw material; (B) methanol; (C) ethanol; (D) toluene; (E) 2-propanol; (F) 1-butanol; (G) tert-butylamine + water with $x_2 = 0.40$.

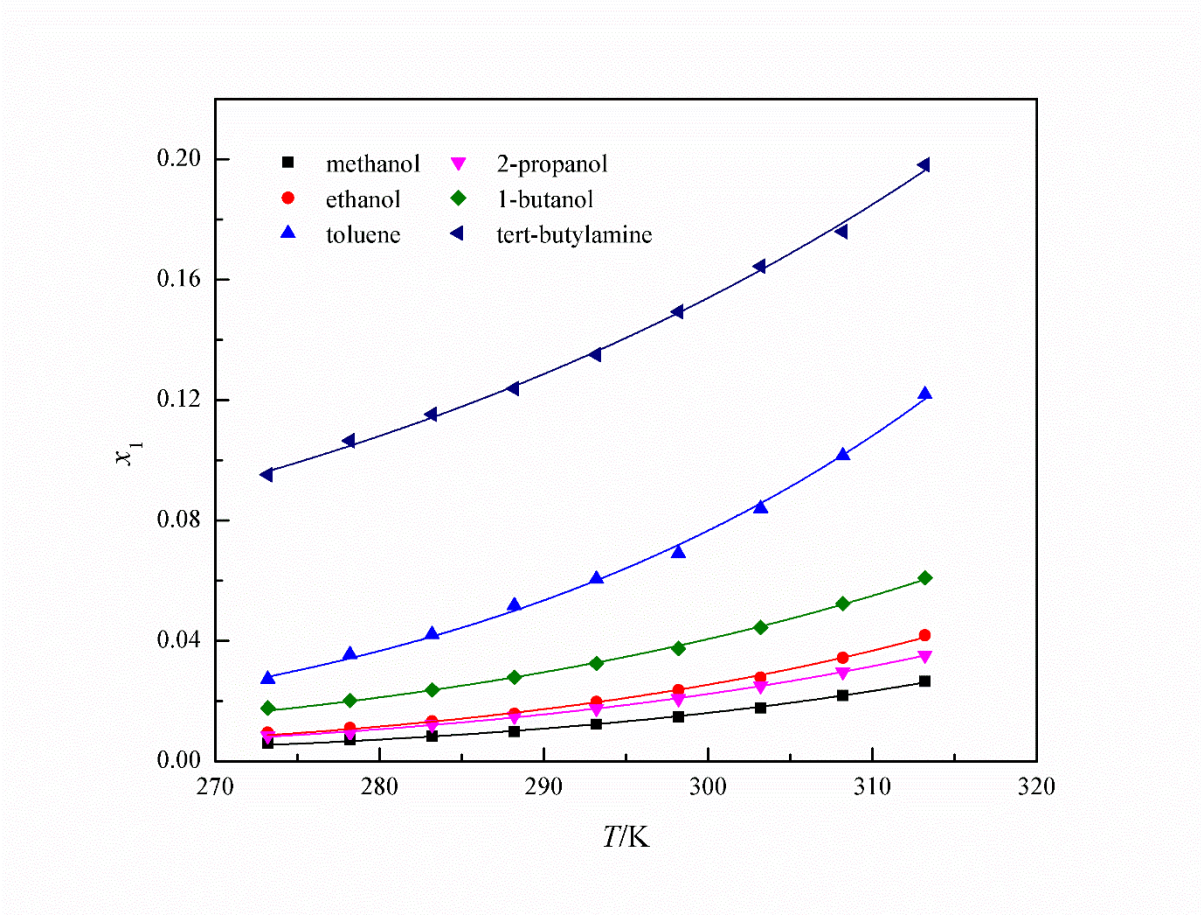


**Figure 4.** Mole fraction solubility ($x_1$) of TBBS in different pure solvents at $p = 0.101$ MPa at temperature from 273.2 K to 313.2 K. The solid lines correspond to the solubility values calculated by the modified Apelblat equation.

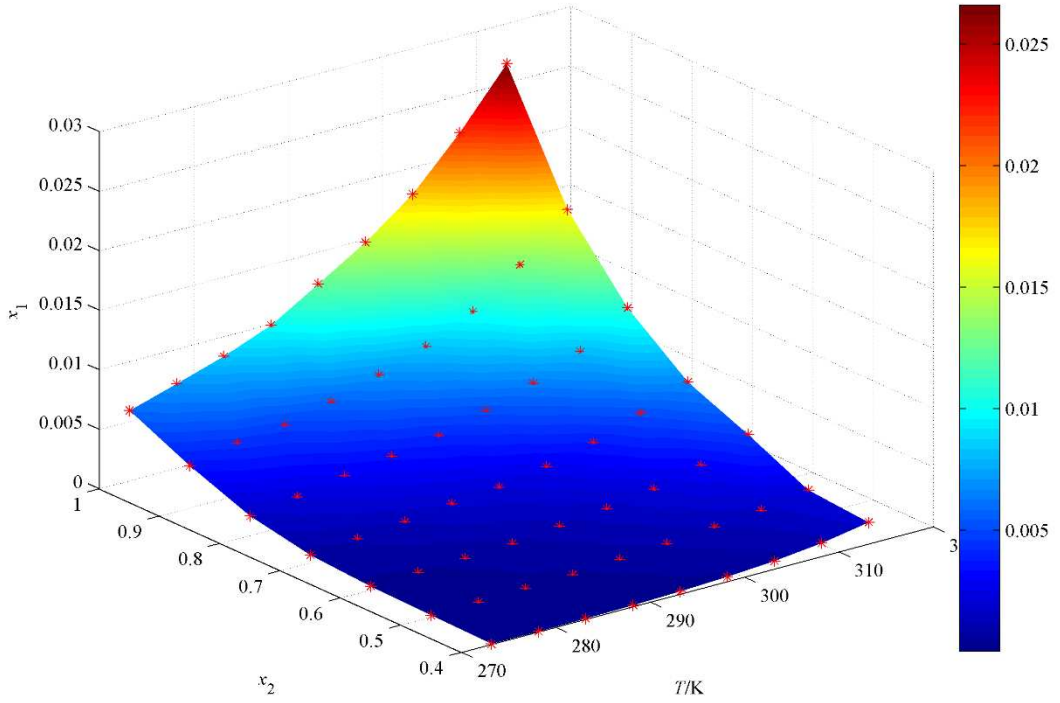


**Figure 5.** Mole fraction solubility ($x_1$) of TBBS in binary solvents (methanol + water) with various solvent compositions ($x_2$) at temperature range from 273.2 K to 313.2K.

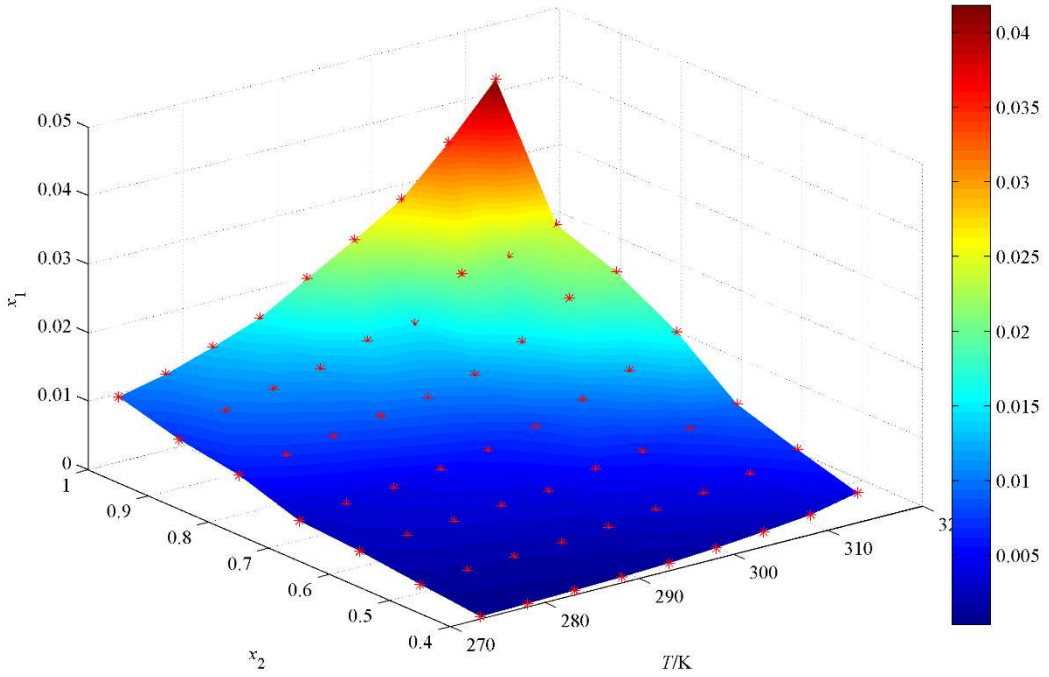


**Figure 6.** Mole fraction solubility ($x_1$) of TBBS in binary solvents (ethanol + water) with various solvent compositions ($x_2$) at temperature range from 273.2 K to 313.2K.

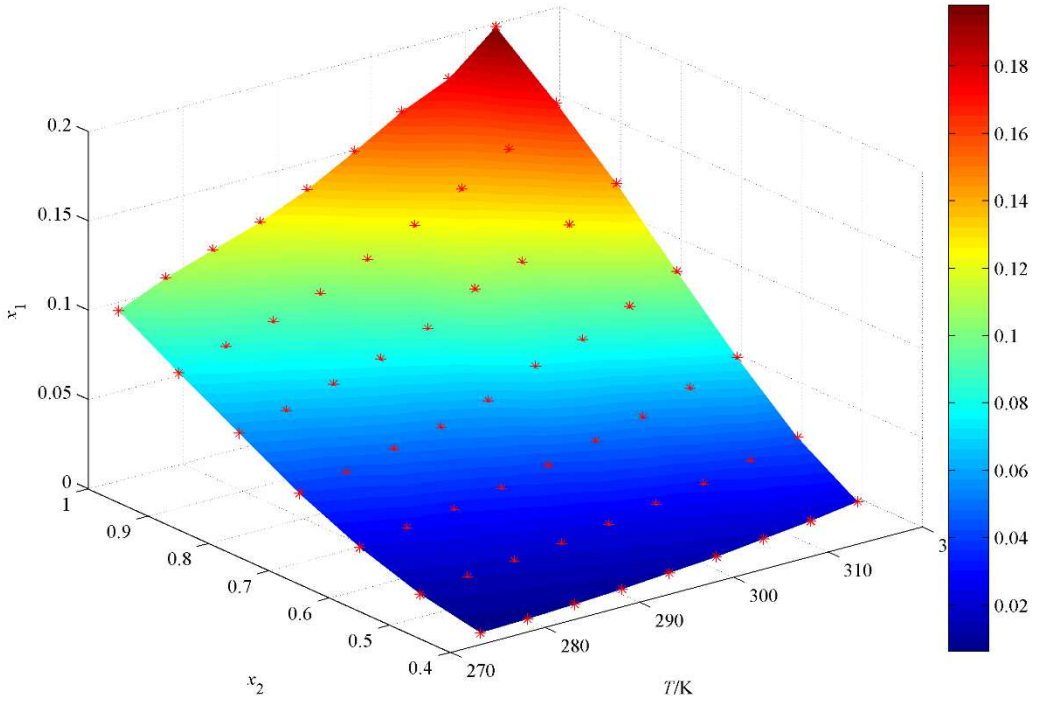


**Figure 7.** Mole fraction solubility ($x_1$) of TBBS in binary solvents (tert-butylamine + water) with various solvent compositions ($x_2$) at temperature range from 273.2 K to 313.2K.

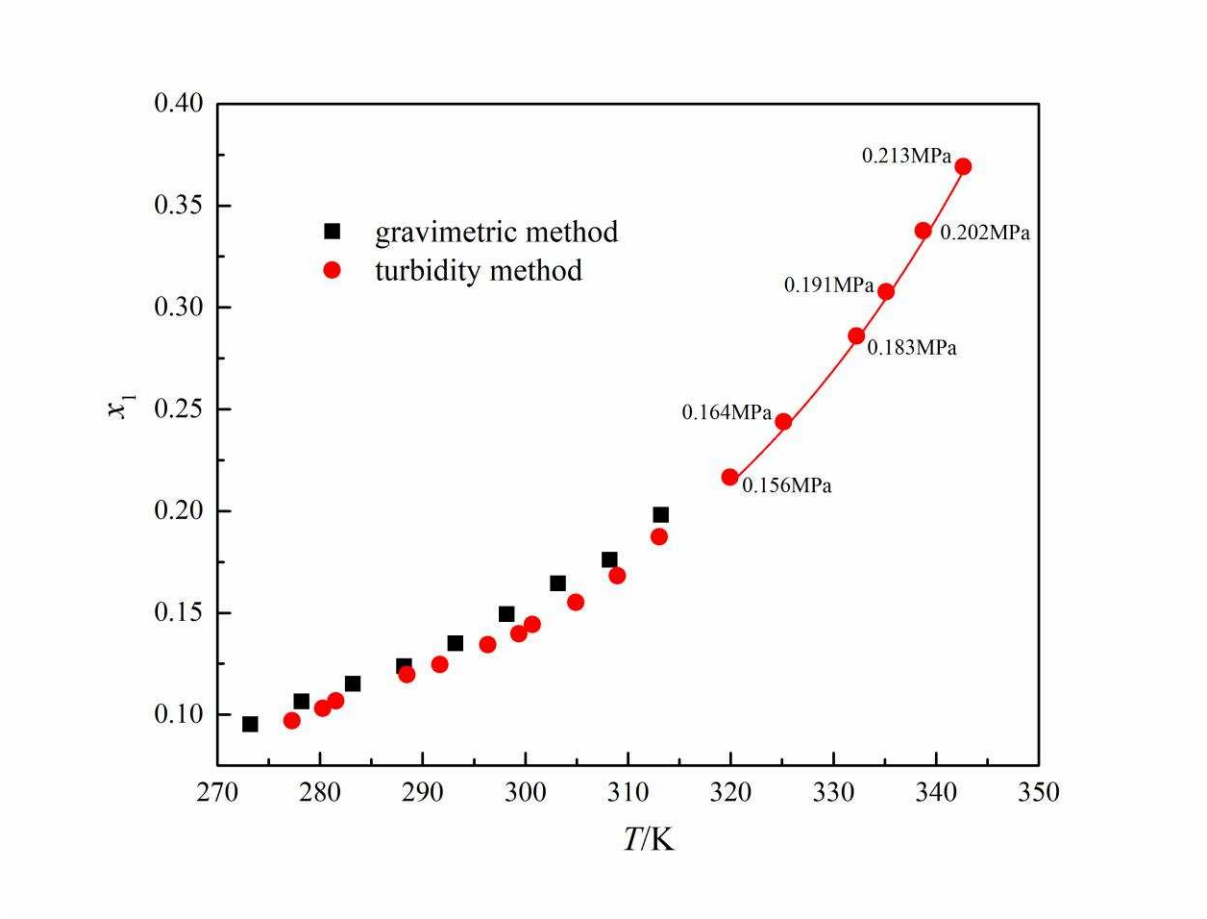


**Figure 8.** Mole fraction solubility of TBBS in tert-butylamine by gravimetric method and turbidity method. Solubility of TBBS at temperature from 273.2 K − 313.2 K was measured under atmospheric pressure ($p$ = 0.101 MPa) while that at temperature from 318.2 K − 343.2 K was measured at pressure of 0.156 MPa − 0.213 MPa. The solid line corresponds to the solubility values calculated by the modified Apelblat equation.

## Graphical abstract