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Thermodynamic analysis for determination of solid–liquid equilibrium of dibenzothiophene in a binary solvent of formic acid and butan-1-ol between (278.15 and 333.15) K

Qi Zhang [a], Yonghong Hu [a, *], Yang Yang [a], Cuicui Cao [a], Limin Cheng [a], Ying Shi [b], Wenge Yang [a]

[a] State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing 210009, China
[b] Taiyuan Qiaoyou Chemical Industrial Co. Ltd., Taiyuan 030025, China

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ABSTRACT

In this paper, we focused on solubility and solution thermodynamics of dibenzothiophene. By gravimetric method, the solubility of dibenzothiophene was measured in (formic acid + butan-1-ol) binary solvent mixtures from 278.15 K to 333.15 K under atmosphere pressure. The solubility data were fitted using modified Apelblat equation, a variant of the combined nearly ideal binary solvent/Redich–Kister (CNIBS/R–K) model and Jouyban–Acree model. Computational results showed that the modified Apelblat equation was superior to the other two equations. In addition, the thermodynamic properties of the solution process, including the Gibbs energy, enthalpy, and entropy were calculated by the van't Hoff analysis. The experimental results showed that formic acid could be used as effective anti-solvents in the crystallization process.

1. Introduction

At the present time, the deepening strict of national environmental requirements and the increasing demand of clean fuel bring new challenges to the development of deep desulfurization technologies [1,2]. Thus, the ultra-deep desulfurization methods of oil have become hot point in research. Dibenzothiophene and its derivatives are regarded as the sulphides that are the most difficult to desulfurate. Meanwhile, realizing desulfurization in the industrial production generates the necessity to have date about the physicochemical properties of these materials.

Dibenzothiophene ($C_{12}H_8S$, CASRN: 132-65-0, shown in Fig. 1), or DBT for short, is a colorless or white needle-like crystal, which is widely used as an important intermediate in the production of cosmetics and pharmaceuticals. DBT can be used as additives in rose-scented perfume. More important, it is also an important model compound in the study of hydrodesulfurization reaction for diesel oil. DBT is the organosulfur compound consisting of two benzene rings fused to a central thiophene ring, which can be obtained by the reaction of biphenyl with sulfur dichloride in the presence of aluminium trichloride [1,2]. The solubilities of organic compounds in different solvents play an important role for understanding the solid–liquid equilibria (SLE) or phase equilibria in the development of a crystallization process, or liquid–liquid equilibria in extraction and extractive or azeotropic distillation processes [3–5]. More particularly, knowledge of an accurate solubility is needed for the design of separation processes such as extractive crystallization and the safety of operating different processing units such as distillation columns, absorption units, and extraction plants. The solubility of DBT can also supply basic and theoretical date for industrial production. To determine proper solvents and to design an optimized production process, it is necessary to know the solubilities of DBT in different solvents [3–5]. To our knowledge, we find no report of the solubility of DBT in (formic acid + butan-1-ol) binary solvent mixtures.

In this work, the solubility of DBT in (formic acid + butan-1-ol) binary solvent mixtures was measured from 278.15 K to 333.15 K under atmosphere pressure. The modified Apelblat equation, a variant of the combined nearly ideal binary solvent/Redich–Kister (CNIBS/R–K) model and Jouyban–Acree model were applied to correlate with the experimental data. This is the first attempt at

* Corresponding author.
E-mail address: yonghonghu11@126.com (Y. Hu).

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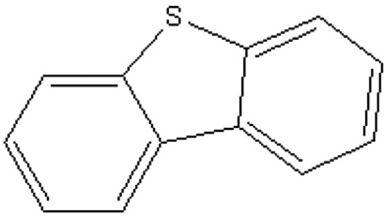

Fig. 1. Chemical structure of dibenzothiophene.

modeling the solubility of DBT in (formic acid + butan-1-ol) binary solvent mixtures using these specific thermodynamic models. The thermodynamic properties of the dissolution process, including enthalpy, entropy and Gibbs energy, were calculated by means of van't Hoff analysis and Gibbs equation.

2. Experimental

2.1. Materials

Dibenzothiophene (98% wt) was purchased from Aladdin (China). Its purity was measured by high performance liquid chromatography (HPLC type DIONEX P680 DIONEX Technologies), and the melting point of dibenzothiophene was measured by digital melting point system (type WRS-1B, Shanghai Precision & Scientific Instrument Co., Ltd.) at 373.15 K. This melting point falls within the range of (370.15–373.15)K values reported in the literature [6–9]. Formic acid and butan-1-ol for dissolving were supplied by Shanghai Shenbo Chemical Co., Ltd., China. The purities of the solvents were determined in our laboratory by gas chromatography and their mass fraction purities were higher than 0.980. Meanwhile, all chemicals were used received without further purification. The properties of these solvents are presented in Table 1.

2.2. Apparatus and procedures

The solubility of DBT was investigated, in various solvents, by the analytical stirred-flask method, and we used the gravimetric method to measure the compositions of the saturated solutions. Saturated solutions of DBT, which were produced by 8 mL solvent mixtures and some excess DBT, were prepared in a spherical, 10 mL Pyrex glass flask with a bottle stopper (avoid evaporation of solvent during experimental steps). The flask was maintained in a jacket glass vessel full of water at the desired temperature through circulating water, whose temperature was controlled by a thermostat with an accuracy of ±0.1 K that was supplied from a constant-temperature water bath (type HWC-52, ShangHai Cany Precision Instrument Co., Ltd.). And the actual temperature was measured by a thermometer (uncertainty of ±0.05 K) inside the vessel. For each measurement, some excess DBT were added to a known volume of solvent mixtures. Continuous stirring was achieved for fully mixing the suspension using a magnetic stirrer at the required temperature. The stirring continued for about 12 h to ensure the solid–liquid equilibrium and the solution was allowed to settle for 3 h or more before sampling for achieving a static state [10–12]. The supernatant was taken, filtered, and poured into a volumetric flask preweighed by using an analytical balance (Sartorius, BS210s, Germany) with a resolution of ±0.1 mg. At last, 1 mL solution supernatant (preheat the tips of pipettor to 345.15 K, avoid solute residual) was transferred into 5 mL breaker with a cover and weighted immediately. This breaker had been weighted before. All breakers were put into a dryer at room temperature and weighted weekly until reaching constant weight. All determinations were repeated three times to check reproducibility, and then an average value was given.

The mole fraction solubility of DBT (x) in (formic acid + butan-1-ol) binary solvent mixtures is calculated by Eq. (1). The mole fraction of formic acid (x_A) in the binary solvent mixtures is calculated by Eq. (2).

$$x = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \tag{1}$$

$$x_A = \frac{m_2/M_2}{m_2/M_2 + m_3/M_3} \tag{2}$$

where m_1, m_2, m_3 represent the mass of DBT, formic acid, butan-1-ol, and M_1, M_2, M_3 represent the molar mass of the DBT, formic acid, butan-1-ol, respectively.

3. Results and discussions

3.1. Solubility data and thermodynamic models

The solubility data of DBT (x) in (formic acid + butan-1-ol) binary solvent mixtures with the temperature ranging from 278.15 K to 333.15 K are presented in Table 2, and graphically showed in Fig. 2.

3.2. Modified Apelblat equation

The changing trends of solubility against temperature in the solvent with same ratio are described by modified Apelblat equation. This model is firstly used by Apelblat [13,14], which can give a relatively accurate correlation with three parameters:

$$\ln x = A + \frac{B}{T/K} + C\ln(T/K) \tag{3}$$

where x represents the mole fraction solubility of DBT, T is the experimental temperature in K, and A, B and C are the regression curve parameters in the equation which are listed in Table 3.

3.3. CNIBS/R–K model

The changing trends of solubility against different ratio of butan-1-ol under isothermal condition are described by the Combined Nearly Ideal Binary Solvent/Redich–Kister (CNIBS/R–K) model [15–19], which is one of the theoretical models for calculating the solute solubility in binary solvents and represented in Eq. (4):

Table 1
Mass fraction purities of dibenzothiophene and solvents with CAS registry number.

Compound	Source	Mass fraction purity	CAS No.
Dibenzothiophene	Aladdin Reagent Co., Ltd	≥0.980	132-65-0
Butan-1-ol	Shanghai Shenbo Chemical Co., Ltd	≥0.997	71-36-3
Formic acid	Shanghai Shenbo Chemical Co., Ltd	≥0.980	64-18-6