J. Chem. Thermodynamics 80 (2015) 7–12

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Thermodynamic models for determination of the solubility of dibenzothiophene in (methanol + acetonitrile) binary solvent mixtures

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ARTICLE INFO

Article history:
Received 29 May 2014
Received in revised form 7 August 2014
Accepted 21 August 2014
Available online 27 August 2014

Keywords:
Dibenzothiophene
Apelblat equation
CNIBS/R-K
Jouyban–Acree model
Van't Hoff analysis

ABSTRACT

In this paper, we focused on solubility and solution thermodynamics of dibenzothiophene. By the gravimetric method, the solubility of dibenzothiophene was measured in (methanol + acetonitrile) binary solvent mixtures at temperatures from (278.15 to 333.15) K under atmosphere pressure. The solubility data were fitted using a 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 free energy, enthalpy, and entropy, were calculated by the van't Hoff analysis. The experimental results showed that methanol could be used as effective anti-solvents in the crystallization process.

1. Introduction

At the present time, the deepening strict regulations of national environmental requirements and the increasing demand for 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 sulfides that are the most difficult to remove sulfur. Meanwhile, realizing desulfurization in 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 figure 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 importantly, it is also an important model compound in the study of hydro-desulfurization 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 aluminum 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 data for industrial production. To determine selection of proper solvents and to design an optimized production process, it is necessary to know the solubility of DBT in different solvents [3–5,17]. To our knowledge, we find no report of the solubility of DBT in (methanol + acetonitrile) binary solvent mixtures.

In this work, the solubility of DBT in (methanol + acetonitrile) binary solvent mixtures was measured at temperatures from (278.15 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 the experimental results. This is the first attempt at modeling the solubility of DBT in (methanol + acetonitrile) binary solvent mixtures using these specific thermodynamic models. The thermodynamic properties of the dissolution process, including enthalpy, entropy and Gibbs free energy, were calculated by means of the 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

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http://dx.doi.org/10.1016/j.jct.2014.08.012
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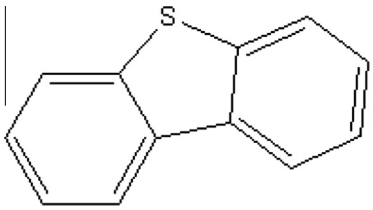

FIGURE 1. Chemical structure of dibenzothiophene.

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 $T = 373.15$ K. This melting point falls within the temperature range of (370.15 to 373.15) K values reported in the literature [6–9]. Methanol and acetonitrile 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 0.997. 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 (avoided 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.). The actual temperature was measured by a thermometer (uncertainty of ±0.05 K) inside the vessel. For each measurement, some excess DBT was 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 to achieve static state [10–12]. The supernatant fluid was taken, filtered, and poured into a volumetric flask pre-weighed by using an analytical balance (Sartorius, BS210s, Germany) with a resolution of ±0.1 mg. Finally, 1 mL solution supernatant was transferred into a 5 mL beaker with a cover and weighted immediately. This breaker had been pre-weighted. All beakers 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 taken.

The mole fraction solubility of DBT (x) in (methanol + acetonitrile) binary solvent mixtures is calculated by equation (1). The mole fraction of methanol (x_A) in the binary solvent mixtures is calculated by equation (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, methanol, acetonitrile, and M_1, M_2, M_3 represent the molar mass of the DBT, methanol, acetonitrile, respectively.

3. Results and discussion

3.1. Solubility data and thermodynamic models

The solubility data of DBT (x) in (methanol + acetonitrile) binary solvent mixtures with the temperature ranging from (278.15 to 333.15) K are presented in table 2, and graphically showed in figure 2. The solubility data are similar to those reported by Ramirez-Verduzco et al. in general [6]. The mole fraction solubility of DBT in acetonitrile at $T = 303.7$ K is 0.0189 which compares well with the reported value of 0.0199; while at $T = 323.1$ K, the mole fraction solubility of 0.0506 compares well with the reported value of 0.0522. But there is an inconsistency issue around $T = 333.0$ K. Values of mole fraction solubility of DBT in acetonitrile are 0.08393 ($T = 333.15$ K, our experimental data) and 0.1021 ($T = 332.0$ K, the literature data), respectively [6], perhaps because the process of experimental operation is non-standard. We have checked the data by another experiment to verify the correctness. The latest results are consistent with the previous data.

3.2. Modified Apelblat equation

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

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

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 acetonitrile under isothermal conditions 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 equation (4):

$$\ln x = x_A \ln X_A + x_B \ln X_B + x_A x_B \sum_{i=0}^{N} S_i (x_A - x_B)^i, \tag{4}$$

where x represents the mole fraction solubility of DBT. The x_A and x_B represent the initial mole fraction composition of the binary solvent when the solute was not added; X_A and X_B respectively represent

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
Methanol	Shanghai Shenbo Chemical Co., Ltd	⩾0.997	67-56-1
Acetonitrile	Shanghai Shenbo Chemical Co., Ltd	⩾0.997	75-05-8