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Solubility of 2,2′,4,4′,6,6′-hexanitrostilbene in binary solvent of N,N-dimethylformamide and acetonitrile

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ABSTRACT

The solubility of 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) in binary solvents of (N,N-dimethylformamide + acetonitrile) was measured using a laser monitoring observation technique. In this study, the solubility of HNS in (DMF + CAN) mixtures was measured over the temperature range from (298.15 to 338.15) K under atmospheric pressure. From the experimental results, the solubility of HNS in DMF was found to increase with increasing temperature and mass fraction of DMF. The experimental values were correlated with the CNIBS/R–K model, modified Apelblat equation and Jouyban–Acree model. The effect of solvent composition and temperature on the solubility was discussed. The standard dissolution enthalpy, standard dissolution entropy and the Gibbs energy were calculated according to the experimental solubility data. The solubility data, correlation equations and thermodynamic property obtained from this study would be invoked as basic data and models regarding the crystallization process of HNS.

1. Introduction

The compound 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) is one of the prominent heat resistant explosives used in high performance explosive compositions for demolitions, warheads, and other charges. It demonstrates outstanding resistance to shock, percussion, heat, and friction. Because of its high melting point, it has excellent thermal stability, making it well suitable for intercontinental missile warheads or components, artillery shells, rockets, and high velocity explosives projectiles. HNS is also widely used in warheads for air-to-ground missiles, air-to-air missiles, and cruise missiles [1–4].

For HNS, solution crystallization, in which solvents are used, is the primary method of crystallization. Solubility can affect the capacity of the crystallization process, as well as its ability to reject undesired compounds and minimize loss in the mother liquor [5]. Hopefully, spheroidization of HNS is recrystallization from N,N-dimethylformamide (DMF) and acetonitrile (ACN). Few experimental studies of the solubility of HNS have been reported. To make an in-depth study on the crystallization process, it is necessary to know its solubility in the mixture solvents. Therefore, in this work, the solubility of HNS in DMF and ACN mixtures from T = (298.15 to 338.15 K) has been determined to provide essential data for process design.

As we know, methods of measuring the solubility of a solid in a liquid mixture can be classified either as a dynamic method or balancing method. Compared to the balancing method, the dynamic method is much faster and more readily produces solubility values [6–8]. The dynamic method involves weighing or measuring the individual components to obtain a system with a known composition, determining the state in which the solid phase just disappears. The disappearance of the solid phase can be achieved either by a change in the temperature or by the addition of a known amount of solvent. In this work, the last solid disappearance method, a dynamic method [9–11], was used to determine the solubility of HNS in mixed solvents of DMF and ACN, the disappearance of the solid phase is achieved by adding solvent. The effects of temperature and solvent composition on the solubility of HNS were studied.

A number of methods have been presented in order to estimate the solubility of solutes in solvent mixtures. These can be classified into three groups: theoretical, semi-empirical, and empirical methods [12–14]. The present study applies the combined nearly ideal binary solvent (CNIBS)/Redlich–Kister equation to correlate and predict solubility of HNS in DMF and ACN mixtures, and the modified Apelblat equation to correlate and predict of solubility of HNS in pure DMF.

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2. Experimental

2.1. Materials

Yellow crystals of the trans form of HNS ($C_{14}H_6N_6O_{12}$, molar mass 450.23 $g \cdot mol^{-1}$) obtained from Gansu Yingguang Chemical Industry Group Co. Ltd, China, its mass fraction purity, determined by HPLC, was better than 0.990. It was dried in *vacuo* at $T = 333.15$ K for 24 h and stored in a desiccator. The materials DMF and ACN were analytical grade reagent from Tianjin Chemical Reagent Co. China. The detailed information of reagents used in this experiment are listed in table 1.

2.2. Apparatus and procedure

The apparatus for the solubility measurements (figure 1) is the same as that described in the literature [8]. A laser monitoring system was used to determine the solubility of the solute in the solvent at a known temperature. The system consisted of a laser generator, a photoelectric transformer, and a light intensity display. The apparatus also involves a jacketed glass vessel with water circulated from a water bath with a thermoelectric controller (type SYP, China). The jacket temperature was controlled to be constant (fluctuating within $T = 0.05$ K). Continuous stirring was achieved with a magnetic stirring bar. A condenser was connected with the vessel to prevent the solvents from evaporating. A mercury-in-glass thermometer was inserted into the inner chambers of the vessels for the measurement of the temperature. The thermometer had an uncertainty of $T = 0.02$ K. An analytical balance (Metler Toledo AL104, Switzerland) with an accuracy of 0.0001 g was used during the measurements. A certain amount of solvent was moved into the inner chamber of the glass vessel by a transfer pipette with a standard uncertainty of 0.01 mL. Then excess amount of HNS sample measured by an electronic balance with a standard uncertainty of 0.0001 g was added into the solvent. Then stir the suspension for 2 h. Next, adding solvent by the speed of 2 $mL \cdot h^{-1}$ from a burette with a standard uncertainty of 0.01 mL until the solute was dissolved absolutely, which was judged by the laser monitoring system. When the DNTF particles completely dissolved, the intensity of laser beam reached the maximum. Finally, recording the total volume of solvent permitted the calculation of the concentration of DNTF. To make sure the pressure in the vessel was equal to local atmospheric pressure, a condenser pipe installed on the top of the vessel. The same solubility experiments were conducted three times. The uncertainty of the experimental solubility values is about 5%. The saturated solution mole fraction solubility of the solute (x_A) and the mole fraction of the ACN (x_C) in binary {DMF (B) + ACN (C)} solvent mixtures can be obtained as follows:

$$x_A = \frac{m_A/M_A}{m_A/M_A + m_B/M_B + m_C/M_C}, \quad (1)$$

$$x_C = \frac{m_C/M_C}{m_B/M_B + m_C/M_C}, \quad (2)$$

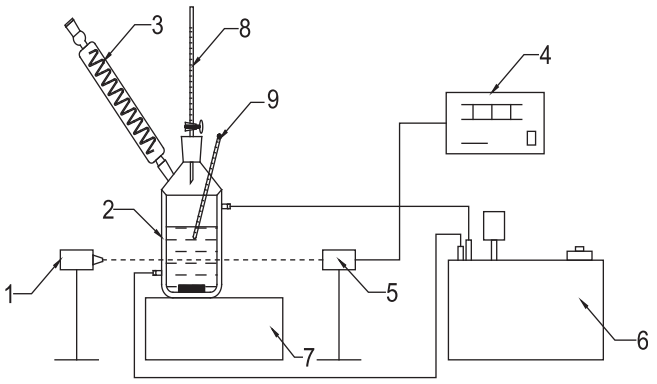

FIGURE 1. Schematic setup for the solubility determination: (1) laser generator, (2) dissolution kettle, (3) condenser, (4) digital display, (5) photoelectric switch, (6) thermostatic bath, (7) magnetic stirrer, (8) stir bar, (9) burette, and (10) thermometer.

in which, m_A, m_B, and m_C represent the mass of solute, DMF, and ACN, respectively. M_A, M_B, and M_C are the molar mass of solute, DMF, and ACN, respectively.

3. Results and discussion

3.1. Measured solubility

The solubility of HNS in binary solvent mixtures (DMF + CAN) from (298.15 to 338.15) K is presented in table 2.

Sitzmann *et al.* have reported the solubility of HNS in pure DMF in 1975 [15], however, some discrepancy, which is graphically shown in figure 2, exists between our values and reference [15]. We consider that the reasons for the discrepancy arise from the difference of the methods. The dynamic laser method has proven to be an accurate method to measure the solubility of solid in liquid during recent decades. We have verified the data of reference [15] by adding 1.5 g HNS in 100 g pure DMF under stirring. After 3 h there were many undissolved HNS particles in the suspension. Values of solubility of reference [15] are greater than those found in this study. The HNS undergoes substantial mechanical loss which arises from dissolving in the solvent whereas the static method is designed to measure solubility. In addition, the authors in reference [15] only reported four temperatures which is not enough for the study of the crystallization process. In addition, our solubility values have been checked many times as we study the recrystallization process.

3.2. Correlation of the solubility values

In order to estimate solubility in pure and binary solvent mixtures, various co-solvency models were used. These models enable us to predict and calculate the suitable solvent composition needed to make an acceptable formulation of the solute. Some of these models are theoretical, *viz.* excess free energy (EFE) [13], CNIBS/R–K [16], and general single model (GSM) [17]; while others are

TABLE 1
Provenance and mass fraction purity of materials studied.

Name	Purification method	Purity (mass fraction)	Analysis method	Source
HNS of trans-form	Recrystallization	>0.990	HPLC[a]	Gansu Yinguang Chemical Industry Group Co. Ltd. China
DMF	None	>0.995	GC[b]	Tianjin Chemical Reagent Co. China
ACN	None	>0.995	GC	Tianjin Chemical Reagent Co. China

[a] High-performance liquid chromatography.
[b] Gas chromatography.