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Measurement and correlation of solubility of ε-CL-20 in solvent mixtures of (chloroform + ethyl acetate) and (m-xylene + ethyl acetate) at temperatures from 278.15 K to 313.15 K

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ABSTRACT

The solubility of ε-CL-20 in (chloroform + ethyl acetate) and (m-xylene + ethyl acetate) solvent mixtures was measured at atmospheric pressure (0.1 MPa) for the temperature range from 278.15 K to 313.15 K using a gravimetric method. The results indicate that the molar solubility of ε-CL-20 in the two binary solvents shows a negative correlation with temperature when the mole fraction of chloroform or m-xylene is low, but a positive correlation when the mole fraction is high. The solubility data were fitted using the Apelblat equation, CNIBS/R-K, Van't Hoff–Jouyban–Acree, and Jouyban–Acree models. Mixing thermodynamic properties of ε-CL-20 in the binary solvents were also calculated. The reported solubility and dissolution properties of ε-CL-20 in these two binary solvent mixtures can provide essential support for industrial design of ε-CL-20 systems and further theoretical studies.

1. Introduction

CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexazaisowurtzitane; CAS: 135285-90-4), shown in Fig. 1, is the most powerful commercially available explosive at present [1,2]. It has the highest crystal density and the highest detonation velocity among highly energetic materials and is widely applied in the military and aerospace industries. It occurs in several polymorphic forms, of which ε-CL-20 is the most stable [3]. The purity of energetic materials is a crucial factor that determines processes for their testing, storage, and usage [4]. Like other energetic materials, the density, sensitivity, and applications of ε-CL-20 are strongly affected by its crystal quality. Control of crystallization is usually considered a potential way to save energy and improve crystal quality [5–8]. Solubility is one of the most significant physicochemical properties affecting design and optimization of the crystallization process, which will dictate the product purity, yield, and crystal size distribution. Knowledge of solubility data is therefore extremely useful in the design of separation processes and for the development of thermodynamic models.

During purification of ε-CL-20 via solution crystallization, understanding of its solubility and thermodynamic properties in different solvents is indispensable. Despite this, to the best of our knowledge, there have been few studies that have focused on the solubility of ε-CL-20. Holtz et al. [9] investigated the solubility of ε-CL-20 in some selected materials but primarily concentrated on polyurethane binder systems and gelled materials because of the utility of extrusion cast explosives and paste extrudable explosives. Simon et al. [10] and Veera et al. [11] examined the solubility of CL-20 in plasticizers and polymers and in supercritical fluids, respectively. To date, however, no studies regarding the solubility of ε-CL-20 in binary mixtures have been reported in the literature.

In this work, the solubility of ε-CL-20 in binary solvent mixtures of (chloroform + ethanol acetate) and (m-xylene + ethyl acetate) was investigated at temperature range from 278.15 K to 313.15 K at atmospheric pressure. In order to correlate the effects of temperature and solvent composition with solubility, the modified Apelblat and (CNIBS)/R-K equations and two Jouyban–Acree-based models were utilized. To further understand the dissolving process, solution thermodynamics data for the molar enthalpy, entropy, and Gibbs energy were also calculated and analyzed. Additionally, to ensure that the crystal form remains constant during the experimental process, the identification of ε-CL-20 crystal was verified by using X-ray powder diffraction (XRPD).

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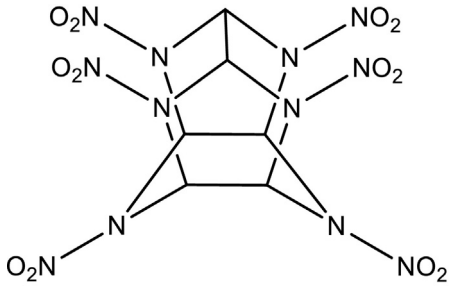

Fig. 1. Chemical structure of CL-20.

2. Experimental

2.1. Materials

Raw ε-CL-20 was synthesized in our laboratory [12] and purified by recrystallization using a solvent–antisolvent method [13]. The mass fraction purity of CL-20 exceeded 0.995 when analyzed by high-performance liquid chromatography, as shown in Fig. 2. The organic solvents (ethyl acetate, chloroform, and m-xylene) were all of analytical-reagent grade. More detailed properties of the materials are listed in Table 1. All chemicals were used as-received and were not subjected to further purification.

2.2. Solubility measurements

Solubility measurements of ε-CL-20 in the (chloroform + ethyl acetate) and (m-xylene + ethyl acetate) mixtures were performed at temperatures ranging from 278.15 K to 313.15 K using the equilibrium method [14,15]. An excess of ε-CL-20 was added to jacketed flasks. The mole fraction of chloroform or m-xylene ranged from 0.1 to 0.9. A condenser was used to prevent evaporation of solvent during the experiments. A thermostatic water bath (Shanghai Bilon Precision Instrument Co., Ltd., China) was used to control the temperature with a uncertainty of 0.01 K. The mixtures of ε-CL-20 and the binary solvents were magnetically stirred in the vessel. The solutions were agitated for 12 h to ensure that solid–liquid equilibrium was established. The agitation was then switched off and the solution allowed to settle for 6 h. Five milliliters of the upper portion of the solution was then sampled and filtered through a membrane (0.22 μm) onto a weighed watch glass. The watch glass was weighed again to record the mass of solution, and the solvent was then dried for a further 12 h under vacuum at 318.15 K. After drying, the watch glass was reweighed to determine the mass of residue solid. Each mass was determined using an analytical balance (Mettler Toledo XS105, Switzerland) with an uncertainty of 0.1 mg. All experiments were repeated three times at each temperature to obtain the reported mean values.

The saturated mole fraction solubility of the solute (x_A) in the binary solvent mixtures was evaluated from Eq. (1); the mole fraction of chloroform or m-xylene (x_1) in the mixed solvent was calculated from Eq. (2):

$$x_A = \frac{m_A/M_A}{m_A/M_A + m_1/M_1 + m_2/M_2}, \tag{1}$$

$$x_1 = \frac{m_1/M_2}{m_1/M_1 + m_2/M_2}, \tag{2}$$

where m_A, m_1, and m_2 represent the masses of the solute, chloroform or m-xylene, and ethyl acetate, respectively, and M_A, M_1, and M_2 represent the respective molar masses.

2.3. X-ray powder diffraction

Powder X-ray diffraction (PXRD) was adopted to identify the polymorphic forms of CL-20. PXRD patterns were obtained using a RD2PHASER (Bruker, Germany) instrument using Cu-Kα radiation (0.154 nm). The measurements were carried out using a step size of 0.02°, a dwell time of 1 s, a voltage of 30 kV, and a current of 100 mA. Purified CL-20 and excess CL-20 in the solvents were analyzed by PXRD; the patterns are shown in Fig. 3.

2.4. High-performance liquid chromatography

The purity of the CL-20 was determined using an Agilent 1260 high-performance liquid chromatograph equipped with an Eclipse XDB C18 chromatographic column. The temperature was held at 303.15 K during the analytical procedure. The wavelength of the ultraviolet detector was set to 230 nm and the sample injection volume was 5 μL. The mobile phase was methanol/water (50/50), injected at a flow rate of 1 mL·min^{-1}.

3. Thermodynamic models

Many models have been used to correlate the solubility of a solid in a mixed solvent [16]. In this work, the solubility of ε-CL-20 in the binary solvent mixtures of (chloroform + ethyl acetate) and (m-xylene + ethyl acetate) was correlated using several models: the modified Apelblat equation, the CNIBS/R-K model, and two types of Jouyban–Acree model, the details of which are discussed below.

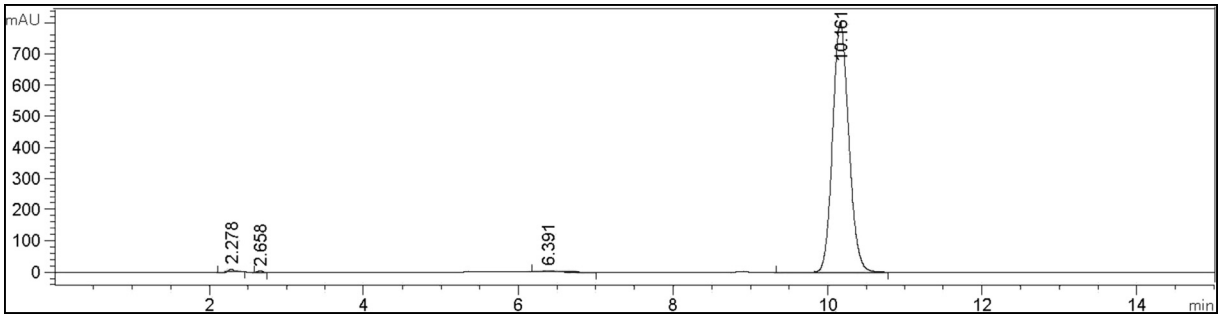

Fig. 2. High-performance liquid chromatograph (HLPC) of ε-CL-20.