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Determination and correlation of solubility of 2,2′,4,4′,6,6′-hexanitro-1,1′-biphenyl and 2,2′,2″,4,4′,4″,6,6′,6″-Nonanitro-1,1′:3′,1″-terphenyl in six pure solvents

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Solubility
Correlation
Gravimetric method

A B S T R A C T

The knowledge of solubility and dissolution thermodynamics for 2,2′,4,4′,6,6′-hexanitro-1,1′-biphenyl (HNBP) and 2,2′,2″,4,4′,4″,6,6′,6″-Nonanitro-1,1’:3′,1″-terphenyl (NONA) in different solvents is not only significant for its crystallization and further theoretical studies, but also important to the use of HNBP and NONA in the related fields. In this paper, the gravimetric method was used to determine the solubility of HNBP and NONA in benzene, toluene, xylene, chlorobenzene, anisole and epichlorohydrin at temperatures ranging from (313.15–353.15) K under atmospheric pressure. The experimental results show that the solubility of HNBP and NONA monotonously increase with the temperature increasing in all selected solvents. Meanwhile, under the same conditions the solubility and solubility changes with temprature of HNBP are greater than that of NONA. To fit and extend the application range of the experimental solubility data, the modified Apelblat equation, λh equation, polynomial empirical equation and ideal van't Hoff model were used to correlate the experimental values of HNBP and the modified Apelblat equation, polynomial empirical equation and ideal van't Hoff model were used to correlate the experimental values of NONA. It was found that the correlated results of selected correlation equations are all in good agreement with the experimental values. And the polynomial empirical equation provided better correlation results than the other models. Furthermore, the standard dissolution enthalpy, standard dissolution entropy and Gibbs energy were calculated from the experimental molar fraction solubility data. The calculated thermodynamic parameters indicated that the dissolution of HNBP and NONA in the selected solvents is a favorable process and endothermic process.

1. Introduction

2,2′,4,4′,6,6′-Hexanitro-1,1′-biphenyl (HNBP, cas: 4433-16-3, formula weight: 424.2 g mol^{-1}, structure shown in Fig. 1),2′,2″,4,4′,4″,6,6′,6″-Nonanitro-1,1’:3′,1″-terphenyl (NONA, cas: 51460-84-5, formula weight: 635.3 g mol^{-1}, structure shown in Fig. 1) are a kind of polynitrobenzene explosives, which not only has a high melting point but also has a good energy performance. Its excellent overall performance, such as high density, high melting point and appropriate sensitivity [1–3], indicates that HNBP and NONA can be used as an important component of heat resistant explosives used in the field of oil drilling and aerospace [4].

From the first report of NHBP and NONA to the present, a great deal of research has been done on the performance of the above compounds [5,6]. It is well known that the performance of explosives in use is not only related to their own properties but also related to their external states, such as purity, morphology and particle sizes of explosives. In the application of explosives, the high-purity and regular morphology of the explosive particles tend to have better performance and more safety. Recrystallization is a simple and effective method to obtain the solid compound with regular morphology and high purity. But not all solvents capable of dissolving the solid compound can be used to the recrystallization of the compound, and only those solvents that dissolve other organic impurities and have a large change in the solubility with respect to the target compound when temperature changes can be consider as a preferable recrystallization reagent. Therefore, the choice of solvent is crucial for the recrystallization of the solid compound. Unfortunately, it is difficult to obtain the solubility data

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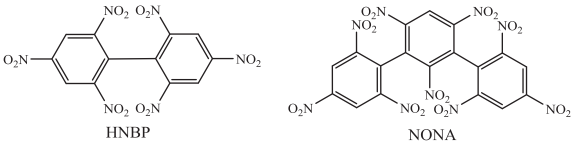

Fig. 1. Molecular structures of HNBP and NONA.

of these two explosives from the available literature. At the same time, HNBP is also the main byproduct for the synthesis of NONA [7,8]. It is also a simpler method to separate and purify NONA by using the difference in solubility of the two substances in same solvent at the same temperatures. Therefore, it is important to test the solubility of HNBP and NONA in different solvents.

In this work, the solubility data of HNBP and NONA in benzene, toluene, xylene, chlorobenzene, anisole and epichlorohydrin at temperatures ranging from (313.15–353.15)K under atmospheric pressure were measured through the gravimetric method [9,10]. To obtain the precise melting temperature of HNBP and NONA used in this paper the differential scanning calorimetry was used. And, to correct and expand the range of experimental solubility data of HNBP and NONA, four correlation equations were used, including the modified Apelblat equation, λh equation, polynomial empirical equation and ideal van't Hoff model. In addition, to obtain the thermodynamic parameters of the dissolution process, the standard dissolution enthalpy, standard dissolution entropy and the Gibbs energy were also calculated from the experimental data.

2. Experimental section

2.1. Materials

The sample of HNBP and NONA, synthesized by our own laboratory, was purified by recrystallization in anisole. All of the organic solvents used in this experiment, including benzene, toluene, dimethylbenzene, anisole, chlorobenzene and epichlorohydrin are analytical grade reagents (>0.995 mass fraction purity) which were purchased from local reagent factory and used without further purification. The detailed information on all materials used in this experiment is listed in Table 1. HNBP was synthesized by copper-catalyzed Ullmann reaction at 150 °C with 2-chloro-1,3,5-trinitrobenzene (PiCl) as raw material and nitrobenzene as an inert solvent. After the reaction was completed, chloroform was added dropwise to the reaction mother liquid to precipitate HNBP from nitrobenzene solution, the reaction mixture was filtered off and the filter cake was washed repeatedly with chloroform to obtain HNBP. NONA was also synthesized by Ullmann reaction at 150 °C with 2, 4-dichloro-1, 3, 5-trinitrobenzene (DCTNB) and PiCl as raw materials and nitrobenzene as an inert solvent. After the reaction was completed, ethanol was added dropwise to the reaction mother liquid to precipitate raw product from nitrobenzene solution, the reaction mixture was filtered off and the filter cake was washed repeatedly with benzene, toluene to remove the HNBP, in turn the silica powder was used to separate NONA from polymer.

2.2. Differential scanning calorimetry

In order to get the exact melting point of the experimental sample, the melting temperature T_m of HNBP and NONA was measured by using a differential scanning calorimetric instrument under nitrogen atmosphere. About 1.0 mg of the sample was heated at a heating rate of 5 K min^{-1}; at the temperatures ranging from (300–573) K and (300–733) K, respectively in a closed DSC pan. For each DSC experiment, an empty DSC pan was used as a blank reference. The standard uncertainties of the measurements were 0.5 K for the temperature and 400 J mol^{-1}; for the enthalpy of fusion.

2.3. Solubility measurements

In the present work, the gravimetric method system was applied to determine the solubility of HNBP and NONA. The excess recrystallized sample was charged into the inner chamber of a glassware (100 mL) which connected to a circulating water bath, and equipped with a stirrer for the full contact of mixture, a mercury thermometer with a standard uncertainty of ±0.05 K to measure the actual temperature of suspension and a condenser reflux device to make sure the measurement is performed at the atmospheric pressure. Then an amount of solvent (benzene, toluene, xylene, mesitylene, anisole and chlorobenzene) was added to the glassware. The temperature of the recycled water in the outer

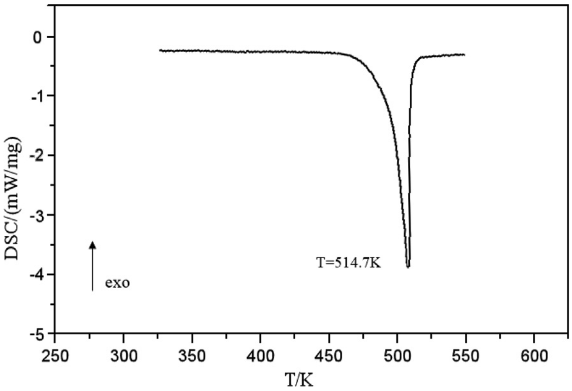

Fig. 2. Thermal analysis (DSC) of HNBP.

Table 1
Provenance and mass fraction purity of materials studied.

Name	Purification	Mass fraction purity	ρ[a] [11]/(g cm^{-3})	Analysis method	Source
HNBP	Recrystallization	>0.990	–	HPLC[b]	Synthesized by us
NONA	Recrystallization	>0.990	–	HPLC	Synthesized by us
Benzene	None	>0.995	0.879	GC[c]	Sinopharm Chemical Reagent Co., Ltd
Toluene	None	>0.995	0.867	GC	Tianjin Shentai Chemical Reagent Co., Ltd
Xylene	None	>0.995	0.860	GC	Sinopharm Chemical Reagent Co., Ltd
Anisole	None	>0.995	0.995	GC	Sinopharm Chemical Reagent Co., Ltd
Chlorobenzene	None	>0.995	1.106	GC	Sinopharm Chemical Reagent Co., Ltd
Epichlorohydrin	None	>0.995	1.181	GC	Tianjin Shentai Chemical Reagent Co., Ltd

[a] The density of solvents at 293.15 K.
[b] High performance liquid chromatography.
[c] Gas chromatography.