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Solubility, thermodynamic modeling and Hansen solubility parameter of a new type of explosive in four binary solvents (benzene + ethanol, *n*-propanol, *n*-butanol and isoamyl alcohol) from 283.15 K to 323.15 K

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ABSTRACT

The solubility of 3,4-dinitropyrazole (DNP) in four binary solvents (benzene + ethanol, *n*-propanol, *n*-butanol and isoamyl alcohol) was measured by a dynamic laser monitoring at the temperature from 283.15 K to 323.15 K at pressure of 0.1 MPa. The solubility of DNP increased positively with increasing temperature, while increased with decreasing molar fraction of benzene in each binary system. Moreover, the experimental solubility values of DNP in this work were correlated well with four thermodynamic models namely "the modified Apelblat equation, Jouyban-Acree model, NRTL model and Wilson model" obtaining average root-mean-square deviation (10^4RMSD) lower than 98.93 for correlative studies. In addition, Hansen solubility parameters were used to explain and predict the solubility behavior. Finally, mixing thermodynamic properties were estimated and analyzed based on solubility data and the Wilson model, and it's easy to understand that the dissolution was a spontaneous process from the results.

1. Introduction

At present, due to the simple charge process of TNT-based melt-cast explosives, the price is cheap, and it can adapt to various shapes of drug rooms. It has good comprehensive performance and is widely used in conventional weapons. Therefore, it is the most widely used military hybrid explosive in the world [1]. But such explosives have obvious defects [2]. 2-Methyl-1,3,5-trinitrobenzene (TNT) is toxic to humans and cannot meet the requirements in the standard test of insensitive ammunition. In addition, it has high sensitivity and poor safety during transportation. 3,4-Dinitropyrazole (DNP, $C_3H_2O_4N_4$, 158.09, Fig. 1) is a five-membered nitrogen heterocyclic nitro compound with (4n + 2) electrons, which has certain aromaticity, and the structure contains N–N, C–N, N–O and other heights generate thermal groups to make the material have a higher energy (energy output of 8210.32 kJ·cm^{-3}). In addition, due to high nitrogen (35.67%), high oxygen (40.67%), low carbon (22.93%) and other characteristics, the density of DNP is higher than TNP (DNP of 1.87 g·cm^{-3}, TNT of 1.64 g·cm^{-3}), and it is easy to reach oxygen balance (25.48%). Compared with cyclotrimethylenetrinitramine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and other explosives, it is a high-energy, low-melting and low-explosive explosive, which is a potential melt-cast explosive carrier and can replace TNT [3,4]. Furthermore, the single crystal structure and spatial structure have been studied [5] and the results showed that DNP was monoclinic and the space group was $P2_1/c$, with unit cell parameters of a = 9.9801(8) Å, b = 11.9959(9) Å, c = 9.7192(7) Å, β = 94.232(1) °, V = 1160.41(15) Å^3, Z = 8, F(000) = 640, D_c = 1.80969 g·cm^{-3}. Due to the large number of intermolecular hydrogen bonds and the π-π stacking interactions between the DNP molecules, the structure of DNP is very stable. The structure of DNP have been characterized [6], and the experimental values of explosion heat and explosion velocity were 4326 kJ·kg^{-1} and 7633 m·s^{-1}, respectively.

The solubility of solid substances in different solvents is one of the most important parameters in fundamental research, which can also show the knowledge of physical properties and optimal crystallization conditions. It can help estimate a suitable solvents ratio for maximum solubility, playing an important role in the determination of appropriate solvents for the crystallization process [7]. Moreover, many studies have focused on the synthesis of DNP [8–10], but only a few have attempted to establish purification methods to obtain products with high purity and yield. The industrial crystallization process based on the solubility data has many advantages, such as high efficiency, high yield, low energy consumption, low pollution, high product purity, etc. Furthermore, it is especially suitable for industrial fields of solid products, such as fine

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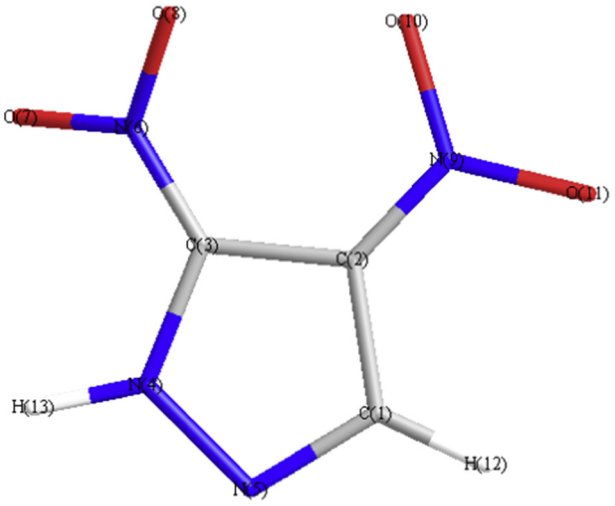

Fig. 1. The molecular structure of DNP.

chemicals and biopharmaceuticals. At the same time, the study of solubility data defines the separation limit for the crystallization separation process, and provides basic data for the design of the equipment structure size and the determination of operating conditions, which is an important prerequisite for realizing chemical production. The solubility data of DNP has important research significance for the crystallization process of DNP.

The solubility of DNP in four binary solvent mixtures has been determined at temperatures ranging from (283.15 to 323.15) K with a dynamic laser monitor. The solubility data was regressed with different thermodynamic models including the modified Apelblat equation, Jouyban-Acree model, NRTL model and Wilson model. Hansen solubility parameters of DNP and mixed binary solvents were applied to investigate the dissolution behavior. Besides, the mixing thermodynamic properties of DNP in different binary solvent mixtures, including mixing enthalpy, mixing entropy and mixing Gibbs energy, were calculated and discussed by Wilson model. Additionally, the identification of DNP crystal was verified by using X-ray diffraction (XRD).

2. Experimental

2.1. Chemical materials

DNP was synthesized from pyrazole by a three-step reaction of nitration, rearrangement and nitration [11], and the synthetic route is showed in Fig. 2. It was purified by crystallization in benzene and its mass fraction purity, measured by High Performance Liquid Chromatography (HPLC), was 0.990. All solvents used in this experiment, such as benzene, ethanol, *n*-propanol, *n*-butanol and isoamyl alcohol, were purchased from local reagent factories without further purification, and their mass fraction purity was not less than 0.990. More information of all the materials used in this experiment is presented in Table 1.

2.2. Differential scanning calorimetry

The differential scanning calorimetry (DSC 1/500, Mettler-Toledo, Switzerland) was used to determine the melting temperature (T_m) and fusion enthalpy ($\Delta_{fus}H$) of DNP. The standard uncertainties of the measurement were a temperature of 0.5 K and a fusion enthalpy of 400 $J \cdot mol^{-1}$. Fig. 3 indicates that the fusion enthalpy is 11.744 $kJ \cdot mol^{-1}$ and the melting temperature is 360.98 K.

2.3. X-ray diffraction

Since the solubility may change with the crystal structure, it is necessary to confirm the crystal structure before the measurement of its solubility. The DNP crystal used to measure the solubility was identified by X-ray diffraction (XRD) using Bruker D8 Advance (Bruker Corporation, Germany). The data was carried out in the range of 2θ from 5° to 80°, with a voltage of 45 kV and a scanning rate of $10° \cdot min^{-1}$. The XRD curves of DNP in binary solvents were showed in Fig. 4. The results showed that no polymorph transformation of DNP was identified.

2.4. Hansen solubility parameter

The concept of Hansen solubility parameter (HSP) has been widely used for selecting suitable solvents for solute [12]. The basis of the HSP approach is to assume that the total cohesive energy (E_t) of a pure compound consists of three parts, including nonpolar (dispersion) interactions (E_d), polar (dipole-dipole and dipole-induced dipole) interactions (E_p) and hydrogen bonding or other specific association interactions including Lewis acid-base interactions (E_h):

$$E_t = E_d + E_p + E_h \tag{1}$$

Dividing each contribution by the molar volume:

$$\frac{E_t}{V} = \frac{E_d}{V} + \frac{E_p}{V} + \frac{E_h}{V} = {\delta_d}^2 + {\delta_p}^2 + {\delta_h}^2 \tag{2}$$

Therefore, the total solubility parameter (δ_t) can be expressed as:

$$\delta_t = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \tag{3}$$

Where δ_d, δ_p and δ_H represent the Hansen dispersion solubility parameter, polar solubility parameter and hydrogen bonding solubility parameter, respectively. The values of δ_d, δ_p and δ_H for selected solvents can be obtained from literature [12]. The solubility parameter for binary solvents (δ_{mix}) can be expressed as: [13]

$$\delta_{mix} = \alpha\delta_1 + (1-\alpha)\delta_2 \tag{4}$$

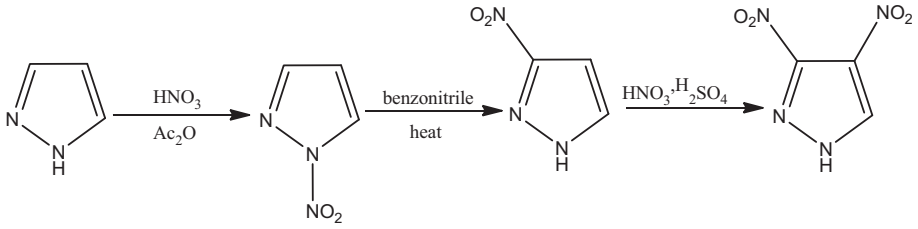

Fig. 2. Synthetic route of DNP.

Table 1
The detailed information of the materials used in this paper.

Material	Molar mass/(g·mol^{-1})	ρ[a]/(g·cm^{-3})	Source	Purity	Purification method	Analysis method
DNP	158.09	1.810	Synthesized by us	0.990	crystallization	HPLC[b]
Benzene	78.11	0.879	Sinopharm Chemical Reagent Co., Ltd	0.995	none	GC[c]
Ethanol	46.07	0.789	Sinopharm Chemical Reagent Co., Ltd	0.995	none	GC[c]
n-propanol	60.11	0.804	Sinopharm Chemical Reagent Co., Ltd	0.990	none	GC[c]
n-butanol	74.12	0.810	Sinopharm Chemical Reagent Co., Ltd	0.990	none	GC[c]
Isoamyl alcohol	88.15	0.809	Sinopharm Chemical Reagent Co., Ltd	0.990	none	GC[c]

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

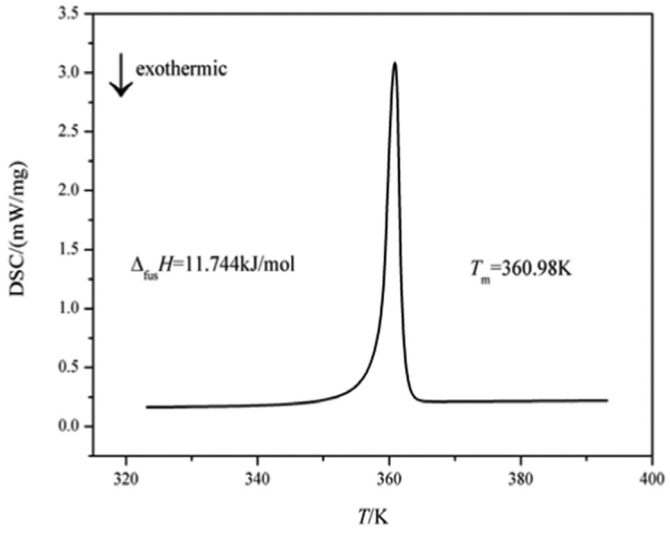

Fig. 3. DSC plot of DNP.

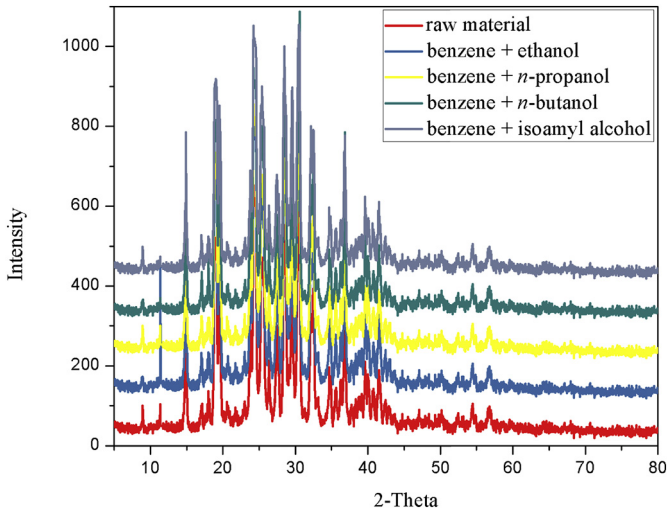

Fig. 4. XRD pattern of DNP.

Where α stands for the volume fraction of solvent 1 (benzene); δ_1 and δ_2 are the Hansen solubility parameters of solvent 1 (benzene) and solvent 2 (ethanol / *n*-propanol / *n*-butanol / isoamyl alcohol).

The group contribution (Hoftyzer-Van Krevelen) method was used to calculate the values of δ_d, δ_p and δ_H of DNP [14]. The molar volume of DNP, $V_s = 95.0\ cm^3 \cdot mol^{-1}$, was taken from the SciFinder database [15].

In addition, the difference of total solubility parameter between solute and solvent ($\Delta\delta_t$) can be used to estimate the miscibility of two compounds: [16]

$$\Delta\delta_t = |\delta_{t2} - \delta_{t1}| \tag{5}$$

Where δ_{t1} and δ_{t2} are total Hansen solubility parameters of solute and binary solvents, respectively.

2.5. Experimental procedures

In this research work, the solubility of DNP in four selected binary solvents including "benzene + ethanol, *n*-propanol, *n*-butanol and isoamyl alcohol" at 283.15–323.15 K was investigated by laser monitoring method. The experimental approach and apparatus were similar to our previous published paper and briefly described here [17–19]. Firstly, about 50 mL binary solvent was added into a double-layer glass bottle (customized through the glasswork). The temperature of solvent was controlled by circulating water bath (type 501, Gongyi Yuhua Instrument Co., Ltd., China) with an uncertainty of 0.05 K and determined by thermometer mercury. Then, excess amount of solid was added into double-layer glass bottle at the setting temperature. A magnetic agitator was used for accelerating the dissolution rate of DNP in selected binary solvents. The mixture solution was stirred for more than 30 min. After 30 min, the selected binary solvents of known weight were added dropwise into mixture solution by a syringe with the dropping rate of 2–3 drops per minute till the last trace of DNP was dissolved in mixture solution. The mixture solution reached saturation and the electrical signal of laser monitoring arrived at its maximum at this moment. The weights of solute and solvent were weighed by an electronic analytical balance (type AB 204, Mettler Toledo, Switzerland) with an accuracy of 0.0001 g. Three parallel experiments for each temperature point were performed in this work and the average values were considered the final results.

The mole-fraction solubility of DNP (x_1) in binary solvents can be expressed as:

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \tag{6}$$

$$x_2 = \frac{m_2/M_2}{m_2/M_2 + m_3/M_3} \tag{7}$$

$$x_3 = 1 - x_2 \tag{8}$$

$$w_1 = \frac{m_2}{m_2 + m_3} \tag{9}$$

$$w_2 = 1 - w_1 \tag{10}$$

Where x_1 represents the solubility of DNP in binary solvents; x_2 is the mole fraction of benzene in binary mixed solvents; x_3 is the mole fraction of (ethanol / *n*-propanol / *n*-butanol / isoamyl alcohol)

in binary solvents; w_1 is the mass fraction of benzene in binary solvents mixtures; w_2 is the mass fraction of (ethanol / *n*-propanol / *n*-butanol / isoamyl alcohol) in binary solvents; m_1, m_2, m_3, and M_1, M_2, M_3 represent the mass and molar mass of DNP, benzene and (ethanol, *n*-propanol, *n*-butanol and isoamyl alcohol), respectively.

3. Results and discussion

3.1. Solubility models

Since (solid + liquid) equilibrium is usually not available, correlation and prediction schemes are frequently utilized. The modified Apelblat equation, Jouyban-Acree model, NRTL model and Wilson model are used to correlate the experimental values. The root-mean-square deviation (RMSD) of four binary solvents is used to evaluate the fitting results of the correlation models. The RMSD is defined as:

$$RMSD = \left[\frac{\sum_{i=1}^{n}\left(x_i^c - x_i^e\right)^2}{N}\right]^{1/2} \tag{11}$$

Where x^e and x^c denote experimental data and the calculated values, respectively, and N is the number of experimental data.

3.1.1. The modified Apelblat equation

The temperature and solubility of DNP were correlated by the modified Apelblat equation [20–22]. It is simple and commonly to be written as follows:

$$\ln x_1 = A + \frac{B}{T} + C\ln T \tag{12}$$

Where A, B, C are the empirical constants and T is the absolute temperature. The values of A and B reflect the variation of the activity coefficient, C represents the temperature effect upon the fusion enthalpy.

3.1.2. Jouyban-Acree model

The Jouyban-Acree model [23,24] is a semi-empirical thermodynamic model that it is widely used to correlate the relationship between temperature and solvent composition with the solubility. The equation can be expressed as:

$$\ln x_1 = x_2 \ln (x_1)_2 + x_3 \ln (x_1)_3 + x_2 x_3 \sum_{i=0}^{2} \frac{J_i (x_2 - x_3)^i}{T} \tag{13}$$

Where J_i is the model constant.

In order to extent the application of the temperature ranges where non-linear solubility behavior is observed, Jouyban et al. proposed a combination of Jouyban-Acree model and the modified Apelblat equation to correlate the solubility of a solute in binary solvent mixtures at different temperatures. According to the modified Apelblat equation, $\ln(x_1)_2$ and $\ln(x_1)_3$ can be expressed by Eqs. (14) and (15):

$$\ln (x_1)_2 = A_2 + B_2/T + C_2 \ln T \ln (x_1)_2 = A_2 + B_2/T + C_2 \ln T \tag{14}$$

$$\ln (x_1)_3 = A_3 + B_3/T + C_3 \ln T \tag{15}$$

Put Eqs. (14), (15) and $x_3 = 1 - x_2$ into Eq. (13), a new equation can be obtained:

$$\begin{aligned}\ln x_1 = {} & A_2 + B_2/T + C_2 \ln T + (A_2 - A_3)x_2 + (B_2 - B_3 + J_0 - J_1 + J_2)\frac{x_2}{T} \\ & + (3J_1 - J_0 - 5J_2)\frac{{x_2}^2}{T} + (8J_2 - 2J_1)\frac{{x_2}^3}{T} \\ & + (-4J_2)\frac{{x_2}^4}{T} + (C_2 - C_3)x_2 \ln T\end{aligned} \tag{16}$$

When introducing constant term, Eq. (16) can be further simplified as Eq. (17):

$$\begin{aligned}\ln x_1 = {} & A_1 + A_2/T + A_3 \ln T + A_4 x_2 + A_5 x_2/T + A_6 (x_2)^2/T + A_7 (x_2)^3/T \\ & + A_8 (x_2)^4/T + A_9 x_2 \ln T\end{aligned} \tag{17}$$

Where A_1, A_2, A_3, A_4, A_5, A_6, A_7, A_8 and A_9 are empirical model parameters.

3.1.3. NRTL model

Based on Scott's two-liquid approach, Renon and Prausnitz's NRTL model has some similarities to Guggenheim's quasi-chemical approach [25,26]. Rather than using interaction potential energies and volume fractions, NRTL model was described by using Gibbs energies of interaction (G_{ij} and G_{ii}), mole fractions and a non-randomness parameter of the molecular distribution (α_{ij} and α_{ji}). The NRTL expression of g^E for ternary mixture can be given by:

$$\frac{g^E}{RT} = \sum_{i=1}^{3} x_i \frac{\tau_{ji} x_j G_{ji}}{\sum_{l=1}^{3} x_l G_{li}} \tag{18}$$

Where the adjustable parameters (τ_{ij} and τ_{ji}) can be expressed by using the difference between energy parameter characteristics (Δg_{ij} and Δg_{ji}) as:

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} = \frac{\Delta g_{ij}}{RT} \tag{19}$$

Table 2
Hansen solubility parameter of selected binary solvents and solute.

w_1	δ_d $(MPa)^{0.5}$	δ_p $(MPa)^{0.5}$	δ_H $(MPa)^{0.5}$	δ_t $(MPa)^{0.5}$	$\Delta\delta_t$ $(MPa)^{0.5}$
benzene + ethanol					
0.86	17.3	2.1	4.5	18.0	9.8
0.72	17.1	3.2	6.9	18.7	9.1
0.60	16.9	4.1	9.0	19.6	8.2
0.52	16.7	4.7	10.4	20.3	7.5
0.40	16.5	5.7	12.5	21.5	6.3
0.30	16.3	6.5	14.3	22.6	5.2
0.21	16.2	7.2	15.8	23.7	4.1
benzene + *n*-propanol					
0.88	17.4	1.7	3.8	17.9	9.9
0.77	17.2	2.3	5.5	18.2	9.6
0.66	17.0	3.0	7.2	18.7	9.1
0.56	16.9	3.6	8.8	19.3	8.5
0.46	16.7	4.1	10.3	20.0	7.8
0.36	16.5	4.7	11.9	20.9	6.9
0.26	16.3	5.3	13.4	21.8	6.0
benzene + *n*-butanol					
0.90	17.4	1.5	3.4	17.8	10.0
0.80	17.3	1.9	4.8	18.0	9.8
0.70	17.1	2.4	6.1	18.3	9.5
0.60	17.0	2.9	7.5	18.8	9.0
0.50	16.8	3.4	8.9	19.3	8.5
0.40	16.6	3.8	10.3	19.9	7.9
0.30	16.5	4.3	11.7	20.6	7.2
benzene + isoamyl alcohol					
0.75	17.2	1.8	5.0	17.9	9.9
0.65	17.0	2.2	6.1	18.2	9.6
0.55	16.8	2.5	7.3	18.5	9.3
0.45	16.6	2.8	8.5	18.9	8.9
0.34	16.4	3.2	9.8	19.4	8.4
0.23	16.2	3.5	11.1	20.0	7.8
0.12	16.0	3.9	12.4	20.6	7.2
DNP	18.0	18.2	10.8	27.8	0.0

Table 3
Mole fraction solubility (x_1) of DNP in binary solvent mixtures at different temperatures from 283.15 K to 323.15 K and $P = 0.1$ MPa[a,b].

T/K	x_1^{exp}	x_1^{AP}	x_1^{IA}	x_1^{NRTL}	x_1^{Wilson}
benzene + ethanol ($w_1 = 0.86/x_2 = 0.8426$)					
283.15	0.07206	0.07342	0.07177	0.07209	0.07495
288.15	0.08252	0.08443	0.08099	0.08246	0.08474
293.15	0.09708	0.09680	0.09191	0.09712	0.09679
298.15	0.1141	0.1106	0.1049	0.1142	0.1109
303.15	0.1320	0.1261	0.1202	0.1319	0.1269
308.15	0.1394	0.1433	0.1385	0.1394	0.1401
313.15	0.1590	0.1624	0.1601	0.1590	0.1597
318.15	0.1813	0.1835	0.1859	0.1814	0.1825
323.15	0.2098	0.2069	0.2165	0.2098	0.2109
benzene + ethanol ($w_1 = 0.72/x_2 = 0.6914$)					
283.15	0.1190	0.1195	0.1166	0.1190	0.1210
288.15	0.1297	0.1353	0.1308	0.1296	0.1335
293.15	0.1588	0.1524	0.1474	0.1588	0.1529
298.15	0.1721	0.1711	0.1671	0.1721	0.1688
303.15	0.1936	0.1912	0.1902	0.1936	0.1891
308.15	0.2139	0.2128	0.2175	0.2139	0.2107
313.15	0.2292	0.2360	0.2497	0.2292	0.2319
318.15	0.2598	0.2608	0.2877	0.2598	0.2622
323.15	0.2901	0.2872	0.3326	0.2901	0.2951
benzene + ethanol ($w_1 = 0.60/x_2 = 0.5665$)					
283.15	0.1693	0.1644	0.1705	0.1693	0.1659
288.15	0.1849	0.1854	0.1903	0.1849	0.1857
293.15	0.2069	0.2100	0.2134	0.2068	0.2094
298.15	0.2332	0.2387	0.2405	0.2332	0.2369
303.15	0.2717	0.2723	0.2724	0.2717	0.2718
308.15	0.3125	0.3117	0.3097	0.3126	0.3112
313.15	0.3643	0.3578	0.3535	0.3642	0.3599
318.15	0.4125	0.4118	0.4049	0.4125	0.4117
323.15	0.4721	0.4751	0.4653	0.4721	0.4749
benzene + ethanol ($w_1 = 0.52/x_2 = 0.4856$)					
283.15	0.2126	0.2077	0.2057	0.2127	0.2091
288.15	0.2319	0.2338	0.2290	0.2318	0.2339
293.15	0.2601	0.2644	0.2563	0.2601	0.2636
298.15	0.3009	0.3001	0.2882	0.3009	0.3007
303.15	0.3368	0.3419	0.3255	0.3369	0.3395
308.15	0.3948	0.3907	0.3691	0.3947	0.3915
313.15	0.4504	0.4480	0.4201	0.4504	0.4479
318.15	0.5169	0.5150	0.4797	0.5169	0.5153
323.15	0.5909	0.5936	0.5496	0.5909	0.5938
benzene + ethanol ($w_1 = 0.40/x_2 = 0.3674$)					
283.15	0.2294	0.2235	0.2434	0.2294	0.2275
288.15	0.2501	0.2530	0.2706	0.2501	0.2537
293.15	0.2808	0.2867	0.3024	0.2808	0.2853
298.15	0.3253	0.3254	0.3394	0.3252	0.3248
303.15	0.3684	0.3698	0.3825	0.3684	0.3676
308.15	0.4252	0.4207	0.4326	0.4252	0.4203
313.15	0.4810	0.4791	0.4911	0.4810	0.4778
318.15	0.5454	0.5459	0.5593	0.5454	0.5451
323.15	0.6213	0.6226	0.6388	0.6213	0.6252
benzene + ethanol ($w_1 = 0.30/x_2 = 0.2719$)					
283.15	0.2562	0.2561	0.2592	0.2563	0.2551
288.15	0.2842	0.2840	0.2883	0.2842	0.2843
293.15	0.3115	0.3166	0.3221	0.3113	0.3158
298.15	0.3596	0.3547	0.3614	0.3598	0.3574
303.15	0.3999	0.3993	0.4071	0.4000	0.3999
308.15	0.4556	0.4513	0.4601	0.4556	0.4528
313.15	0.5117	0.5122	0.5218	0.5116	0.5111
318.15	0.5739	0.5834	0.5935	0.5741	0.5778
323.15	0.6717	0.6667	0.6769	0.6717	0.6704
benzene + ethanol ($w_1 = 0.21/x_2 = 0.1881$)					
283.15	0.2800	0.2816	0.2720	0.2798	0.2813
288.15	0.3103	0.3134	0.3027	0.3108	0.3127
293.15	0.3522	0.3498	0.3382	0.3520	0.3505
298.15	0.3940	0.3913	0.3794	0.3938	0.3916
303.15	0.4415	0.4386	0.4272	0.4414	0.4385
308.15	0.4961	0.4927	0.4826	0.4962	0.4925
313.15	0.5523	0.5544	0.5468	0.5526	0.5522
318.15	0.6125	0.6249	0.6212	0.6123	0.6190
323.15	0.7132	0.7053	0.7077	0.7132	0.7134

(continued on next page)

Table 3 (*continued*)

T/K	x_1^{exp}	x_1^{AP}	x_1^{IA}	x_1^{NRTL}	x_1^{Wilson}
benzene + *n*-propanol ($w_1 = 0.88/x_2 = 0.8495$)					
283.15	0.07112	0.07219	0.06632	0.07127	0.07389
288.15	0.08188	0.08262	0.07616	0.08178	0.08335
293.15	0.09504	0.09455	0.08747	0.09502	0.09453
298.15	0.1105	0.1076	0.1003	0.1105	0.1077
303.15	0.1230	0.1222	0.1152	0.1230	0.1210
308.15	0.1360	0.1384	0.1321	0.1360	0.1358
313.15	0.1569	0.1563	0.1515	0.1569	0.1554
318.15	0.1737	0.1759	0.1737	0.1738	0.1750
323.15	0.1991	0.1975	0.1991	0.1991	0.2009
benzene + *n*-propanol ($w_1 = 0.77/x_2 = 0.7204$)					
283.15	0.1045	0.1062	0.1065	0.1045	0.1106
288.15	0.1193	0.1227	0.1219	0.1192	0.1237
293.15	0.1421	0.1406	0.1394	0.1421	0.1406
298.15	0.1654	0.1598	0.1595	0.1655	0.1594
303.15	0.1817	0.1805	0.1824	0.1816	0.1774
308.15	0.2079	0.2024	0.2086	0.2079	0.2011
313.15	0.2155	0.2255	0.2384	0.2155	0.2186
318.15	0.2454	0.2498	0.2725	0.2455	0.2481
323.15	0.2805	0.2751	0.3113	0.2805	0.2834
benzene + *n*-propanol ($w_1 = 0.66/x_2 = 0.5990$)					
283.15	0.1501	0.1484	0.1474	0.1501	0.1500
288.15	0.1672	0.1697	0.1684	0.1671	0.1698
293.15	0.1990	0.1946	0.1924	0.1990	0.1967
298.15	0.2166	0.2238	0.2199	0.2165	0.2209
303.15	0.2609	0.2581	0.2512	0.2609	0.2584
308.15	0.3004	0.2984	0.2869	0.3004	0.2979
313.15	0.3442	0.3458	0.3277	0.3443	0.3435
318.15	0.4029	0.4015	0.3741	0.4028	0.4017
323.15	0.4661	0.4670	0.4270	0.4662	0.4687
benzene + *n*-propanol ($w_1 = 0.56/x_2 = 0.4948$)					
283.15	0.1712	0.1680	0.1790	0.1712	0.1748
288.15	0.1943	0.1950	0.2047	0.1942	0.1978
293.15	0.2223	0.2254	0.2341	0.2223	0.2246
298.15	0.2573	0.2596	0.2676	0.2574	0.2566
303.15	0.2930	0.2978	0.3059	0.2930	0.2920
308.15	0.3517	0.3406	0.3496	0.3517	0.3410
313.15	0.3928	0.3881	0.3995	0.3928	0.3869
318.15	0.4289	0.4409	0.4563	0.4289	0.4345
323.15	0.5034	0.4993	0.5211	0.5034	0.5076
benzene + *n*-propanol ($w_1 = 0.46/x_2 = 0.3959$)					
283.15	0.2015	0.1990	0.2026	0.2015	0.2055
288.15	0.2317	0.2302	0.2321	0.2318	0.2338
293.15	0.2623	0.2660	0.2659	0.2623	0.2651
298.15	0.3033	0.3067	0.3045	0.3033	0.3033
303.15	0.3487	0.3531	0.3487	0.3487	0.3474
308.15	0.4136	0.4058	0.3992	0.4136	0.4047
313.15	0.4715	0.4656	0.4568	0.4714	0.4648
318.15	0.5256	0.5334	0.5226	0.5257	0.5288
323.15	0.6118	0.6102	0.5976	0.6118	0.6176
benzene + *n*-propanol ($w_1 = 0.36/x_2 = 0.3021$)					
283.15	0.2282	0.2301	0.2184	0.2281	0.2278
288.15	0.2592	0.2558	0.2508	0.2593	0.2571
293.15	0.2824	0.2869	0.2881	0.2824	0.2862
298.15	0.3292	0.3245	0.3307	0.3292	0.3276
303.15	0.3694	0.3697	0.3796	0.3695	0.3702
308.15	0.4235	0.4243	0.4356	0.4236	0.4237
313.15	0.4901	0.4900	0.4997	0.4900	0.4891
318.15	0.5674	0.5693	0.5729	0.5674	0.5672
323.15	0.6662	0.6651	0.6565	0.6662	0.6666
benzene + *n*-propanol ($w_1 = 0.26/x_2 = 0.2128$)					
283.15	0.2405	0.2385	0.2285	0.2405	0.2404
288.15	0.2767	0.2704	0.2633	0.2768	0.2737
293.15	0.3025	0.3076	0.3033	0.3025	0.3065
298.15	0.3452	0.3510	0.3493	0.3452	0.3486
303.15	0.3951	0.4015	0.4021	0.3951	0.3976
308.15	0.4673	0.4604	0.4627	0.4673	0.4617
313.15	0.5383	0.5291	0.5322	0.5383	0.5317
318.15	0.6041	0.6093	0.6117	0.6042	0.6059
323.15	0.7016	0.7028	0.7028	0.7015	0.7052

Table 3 (*continued*)

T/K	x_1^{exp}	x_1^{AP}	x_1^{IA}	x_1^{NRTL}	x_1^{Wilson}
benzene + *n*-butanol ($w_1 = 0.90/x_2 = 0.8952$)					
283.15	0.04476	0.04450	0.03667	0.04477	0.04465
288.15	0.04907	0.04956	0.04203	0.04907	0.04955
293.15	0.05437	0.05544	0.04833	0.05436	0.05519
298.15	0.06440	0.06226	0.05576	0.06439	0.06308
303.15	0.07089	0.07018	0.06453	0.07089	0.07035
308.15	0.07798	0.07937	0.07487	0.07797	0.07850
313.15	0.08833	0.09004	0.08707	0.08834	0.08893
318.15	0.1048	0.1024	0.1015	0.1048	0.1036
323.15	0.1161	0.1168	0.1185	0.1161	0.1168
benzene + *n*-butanol ($w_1 = 0.80/x_2 = 0.7915$)					
283.15	0.08034	0.07975	0.07057	0.08033	0.07773
288.15	0.08822	0.08817	0.08010	0.08823	0.08628
293.15	0.09738	0.09766	0.09125	0.09738	0.09592
298.15	0.1067	0.1083	0.1043	0.1067	0.1064
303.15	0.1188	0.1204	0.1196	0.1188	0.1188
308.15	0.1390	0.1339	0.1375	0.1390	0.1357
313.15	0.1477	0.1491	0.1585	0.1477	0.1491
318.15	0.1648	0.1663	0.1832	0.1648	0.1675
323.15	0.1861	0.1855	0.2121	0.1861	0.1898
benzene + *n*-butanol ($w_1 = 0.70/x_2 = 0.6889$)					
283.15	0.1133	0.1190	0.1133	0.1133	0.1160
288.15	0.1341	0.1319	0.1278	0.1341	0.1325
293.15	0.1530	0.1476	0.1447	0.1530	0.1501
298.15	0.1687	0.1664	0.1643	0.1687	0.1681
303.15	0.1881	0.1892	0.1872	0.1881	0.1893
308.15	0.2162	0.2165	0.2139	0.2161	0.2165
313.15	0.2461	0.2494	0.2451	0.2461	0.2474
318.15	0.2871	0.2891	0.2814	0.2871	0.2875
323.15	0.3396	0.3370	0.3239	0.3396	0.3387
benzene + *n*-butanol ($w_1 = 0.60/x_2 = 0.5874$)					
283.15	0.1476	0.1511	0.1567	0.1476	0.1506
288.15	0.1706	0.1709	0.1760	0.1706	0.1714
293.15	0.2004	0.1938	0.1985	0.2004	0.1964
298.15	0.2209	0.2204	0.2246	0.2208	0.2206
303.15	0.2497	0.2511	0.2548	0.2497	0.2502
308.15	0.2852	0.2867	0.2900	0.2852	0.2852
313.15	0.3249	0.3280	0.3309	0.3251	0.3256
318.15	0.3783	0.3758	0.3785	0.3782	0.3766
323.15	0.4314	0.4312	0.4338	0.4314	0.4327
benzene + *n*-butanol ($w_1 = 0.50/x_2 = 0.4869$)					
283.15	0.1809	0.1825	0.1921	0.1809	0.1835
288.15	0.2081	0.2074	0.2154	0.2081	0.2088
293.15	0.2357	0.2363	0.2424	0.2356	0.2367
298.15	0.2730	0.2699	0.2737	0.2730	0.2708
303.15	0.3083	0.3089	0.3099	0.3083	0.3076
308.15	0.3543	0.3542	0.3520	0.3544	0.3526
313.15	0.4038	0.4069	0.4007	0.4039	0.4037
318.15	0.4694	0.4683	0.4572	0.4693	0.4683
323.15	0.5402	0.5396	0.5227	0.5402	0.5424
benzene + *n*-butanol ($w_1 = 0.40/x_2 = 0.3875$)					
283.15	0.2161	0.2205	0.2145	0.2161	0.2159
288.15	0.2406	0.2416	0.2405	0.2406	0.2407
293.15	0.2710	0.2675	0.2706	0.2711	0.2699
298.15	0.3052	0.2990	0.3054	0.3052	0.3032
303.15	0.3389	0.3371	0.3457	0.3389	0.3395
308.15	0.3834	0.3832	0.3922	0.3833	0.3841
313.15	0.4327	0.4388	0.4461	0.4327	0.4356
318.15	0.5006	0.5061	0.5085	0.5006	0.5021
323.15	0.5929	0.5875	0.5807	0.5929	0.5903
benzene + *n*-butanol ($w_1 = 0.30/x_2 = 0.2891$)					
283.15	0.2304	0.2265	0.2241	0.2304	0.2325
288.15	0.2632	0.2534	0.2516	0.2632	0.2613
293.15	0.2904	0.2845	0.2833	0.2903	0.2909
298.15	0.3293	0.3207	0.3199	0.3293	0.3270
303.15	0.3625	0.3626	0.3622	0.3625	0.3643
308.15	0.4125	0.4112	0.4111	0.4125	0.4117
313.15	0.4616	0.4676	0.4676	0.4617	0.4631
318.15	0.5319	0.5331	0.5329	0.5318	0.5296
323.15	0.6007	0.6092	0.6085	0.6007	0.6019

(*continued on next page*)

Table 3 (*continued*)

T/K	x_1^{exp}	x_1^{AP}	x_1^{JA}	x_1^{NRTL}	x_1^{Wilson}
benzene + isoamyl alcohol ($w_1 = 0.75/x_2 = 0.7720$)					
283.15	0.1345	0.1349	0.1247	0.1345	0.1185
288.15	0.1457	0.1452	0.1355	0.1457	0.1314
293.15	0.1559	0.1562	0.1475	0.1559	0.1449
298.15	0.1690	0.1680	0.1606	0.1690	0.1606
303.15	0.1801	0.1807	0.1752	0.1801	0.1766
308.15	0.1945	0.1942	0.1912	0.1945	0.1952
313.15	0.2078	0.2087	0.2088	0.2078	0.2148
318.15	0.2247	0.2242	0.2283	0.2247	0.2374
323.15	0.2408	0.2407	0.2497	0.2408	0.2614
benzene + isoamyl alcohol ($w_1 = 0.65/x_2 = 0.6770$)					
283.15	0.1502	0.1532	0.1543	0.1502	0.1346
288.15	0.1653	0.1641	0.1675	0.1653	0.1503
293.15	0.1795	0.1766	0.1820	0.1795	0.1670
298.15	0.1920	0.1907	0.1981	0.1920	0.1844
303.15	0.2076	0.2066	0.2158	0.2076	0.2043
308.15	0.2234	0.2247	0.2353	0.2234	0.2259
313.15	0.2405	0.2451	0.2567	0.2405	0.2497
318.15	0.2693	0.2681	0.2803	0.2693	0.2810
323.15	0.2955	0.2941	0.3063	0.2955	0.3136
benzene + isoamyl alcohol ($w_1 = 0.55/x_2 = 0.5797$)					
283.15	0.1806	0.1830	0.1785	0.1806	0.1660
288.15	0.1993	0.1978	0.1939	0.1993	0.1854
293.15	0.2170	0.2148	0.2108	0.2170	0.2061
298.15	0.2336	0.2343	0.2294	0.2336	0.2281
303.15	0.2562	0.2566	0.2499	0.2561	0.2541
308.15	0.2849	0.2820	0.2724	0.2850	0.2847
313.15	0.3076	0.3109	0.2972	0.3076	0.3153
318.15	0.3420	0.3439	0.3245	0.3421	0.3540
323.15	0.3837	0.3816	0.3545	0.3836	0.3999
benzene + isoamyl alcohol ($w_1 = 0.45/x_2 = 0.4801$)					
283.15	0.1810	0.1832	0.1967	0.1810	0.1727
288.15	0.2033	0.2013	0.2138	0.2034	0.1931
293.15	0.2193	0.2213	0.2327	0.2192	0.2133
298.15	0.2443	0.2435	0.2535	0.2443	0.2381
303.15	0.2734	0.2680	0.2764	0.2734	0.2667
308.15	0.2965	0.2952	0.3015	0.2965	0.2953
313.15	0.3190	0.3252	0.3292	0.3191	0.3259
318.15	0.3554	0.3583	0.3596	0.3555	0.3656
323.15	0.3985	0.3949	0.3929	0.3985	0.4124
benzene + isoamyl alcohol ($w_1 = 0.34/x_2 = 0.3676$)					
283.15	0.2143	0.2173	0.2110	0.2144	0.2008
288.15	0.2389	0.2339	0.2298	0.2387	0.2230
293.15	0.2503	0.2528	0.2506	0.2503	0.2428
298.15	0.2746	0.2742	0.2734	0.2745	0.2685
303.15	0.3024	0.2984	0.2984	0.3025	0.2976
308.15	0.3205	0.3258	0.3260	0.3203	0.3250
313.15	0.3588	0.3566	0.3564	0.3589	0.3635
318.15	0.3895	0.3913	0.3897	0.3895	0.4017
323.15	0.4316	0.4304	0.4263	0.4315	0.4490
benzene + isoamyl alcohol ($w_1 = 0.23/x_2 = 0.2521$)					
283.15	0.2298	0.2298	0.2227	0.2298	0.2180
288.15	0.2451	0.2472	0.2431	0.2451	0.2373
293.15	0.2709	0.2669	0.2655	0.2709	0.2614
298.15	0.2882	0.2892	0.2902	0.2882	0.2845
303.15	0.3163	0.3144	0.3174	0.3163	0.3133
308.15	0.3347	0.3428	0.3473	0.3347	0.3404
313.15	0.3807	0.3748	0.3801	0.3807	0.3820
318.15	0.4111	0.4108	0.4163	0.4111	0.4197
323.15	0.4505	0.4513	0.4560	0.4505	0.4653
benzene + isoamyl alcohol ($w_1 = 0.12/x_2 = 0.1334$)					
283.15	0.2339	0.2352	0.2364	0.2339	0.2398
288.15	0.2573	0.2587	0.2585	0.2574	0.2605
293.15	0.2780	0.2843	0.2829	0.2779	0.2819
298.15	0.3237	0.3120	0.3097	0.3238	0.3138
303.15	0.3500	0.3420	0.3392	0.3499	0.3415
308.15	0.3682	0.3744	0.3717	0.3681	0.3680
313.15	0.4039	0.4095	0.4075	0.4039	0.4044
318.15	0.4426	0.4474	0.4468	0.4427	0.4453
323.15	0.4941	0.4883	0.4900	0.4941	0.4968

[a] The standard uncertainty u are $u(T) = 0.05$ K and $u(P) = 0.2$ kPa; Relative standard uncertainty u_r is $u_r(x_1) = 0.05$.

[b] x_1^{exp} is the experimental solubility; x_1^{AP}, x_1^{JA} x_1^{NRTL} and x_1^{Wilson} represent the calculated mole fraction solubility correlated by the modified Apelblat equation, Jouyban-Acree model, NRTL model and Wilson model, respectively.

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{\Delta g_{ji}}{RT} \tag{20}$$

The expressions of G_{ij} and G_{ji} can be given by:

$$G_{ij} = \exp\left(-\alpha_{ij} \cdot \tau_{ij}\right) \tag{21}$$

$$G_{ji} = \exp\left(-\alpha_{ji} \cdot \tau_{ji}\right)(\alpha_{ij} = \alpha_{ji}) \tag{22}$$

For a solute in binary solvent, the $\ln\gamma_1$ can be expressed as:

$$\begin{aligned}\ln\gamma_1 = &\frac{(\tau_{21}x_2G_{21} + \tau_{31}x_3G_{31})(x_2G_{21} + x_3G_{31})}{(x_1 + x_2G_{21} + x_3G_{31})^2} \\ &+ \frac{x_2G_{12}(\tau_{12}x_2 + \tau_{12}x_3G_{32} - \tau_{32}x_3G_{32})}{(x_1G_{12} + x_2 + x_3G_{32})^2} \\ &+ \frac{x_3G_{13}(\tau_{13}x_3 + \tau_{13}x_2G_{23} - \tau_{23}x_2G_{23})}{(x_1G_{13} + x_2G_{23} + x_3)^2}\end{aligned} \tag{23}$$

Where x_1 represents the mole fraction of DNP; x_2 and x_3 stand for the mole fraction of benzene and (ethanol, *n*-propanol, *n*-butanol and isoamyl alcohol) in ternary mixture solution.

3.1.4. Wilson model

The Wilson model based on the Flory-Huggins non-thermal mixture expression has been widely used for correlating solubility data. The expression of Wilson model for ternary mixtures could be expressed as: [27,28].

$$\frac{g^E}{RT} = -\sum_{i=1}^{3} x_i \ln\left(\sum_{j=1}^{3} x_j\Lambda_{ij}\right) \tag{24}$$

Where g^E stands for the excess Gibbs energy; Λ_{ij} and Λ_{ij} are adjustable parameters of Wilson model, which can be estimated by corresponding molar volumes of pure-component (ν_i and ν_j) and characteristic energy differences ($\Delta\lambda_{ij}$ and $\Delta\lambda_{ji}$):

$$\Lambda_{ij} = \frac{v_j}{v_i}\exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) = \frac{v_j}{v_i}\exp\left(-\frac{\Delta\lambda_{ij}}{RT}\right) \tag{25}$$

$$\Lambda_{ji} = \frac{v_i}{v_j}\exp\left(-\frac{\lambda_{ji} - \lambda_{jj}}{RT}\right) = \frac{v_i}{v_j}\exp\left(-\frac{\Delta\lambda_{ji}}{RT}\right) \tag{26}$$

For ternary mixture system, activity coefficient of $\ln\gamma_1$ could be expressed as:

$$\begin{aligned}\ln\gamma_1 = &1 - \ln(x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}) \\ &- \frac{x_1}{x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}} - \frac{x_2}{x_1\Lambda_{21} + x_2 + x_3\Lambda_{23}} - \frac{x_3}{x_1\Lambda_{31} + x_2\Lambda_{32} + x_3}\end{aligned} \tag{27}$$

Where x_1 represents the mole fraction of DNP; x_2 and x_3 stand for the mole fraction of benzene and (ethanol, *n*-propanol, *n*-butanol and isoamyl alcohol) in ternary mixture solution.

3.2. Solubility data

The Hansen solubility parameters (δ_d, δ_p, δ_h, δ_t and $\Delta\delta_t$) of four binary systems and DNP are listed in Table 2. As can be seen from Table 2, values of δ_t for ethanol and *n*-propanol are mainly contributed by δ_H. However, values of δ_t for benzene, *n*-butanol and isoamyl alcohol are mainly contributed by δ_d. It indicates that the major forces of ethanol and *n*-propanol differ from theses of benzene, *n*-butanol and isoamyl alcohol. Therefore, solubility of DNP in ethanol and *n*-propanol is higher than that in benzene, *n*-butanol and isoamyl alcohol. In addition, values of $\Delta\delta_t$ between DNP and binary solvents (benzene + ethanol, *n*-propanol, *n*-butanol and isoamyl alcohol) decrease as the mass fraction of benzene decreases. For four binary solvents, the difference of δ_d between mixed solvent and DNP reduces as mass fraction of benzene decreases. So the solubility of DNP increases with the decrease of mass fraction of benzene. Moreover, the values of the Hildebrand solubility parameter δ increases with decreasing the content of benzene, and the solubility of DNP also increases.

The solubility data is fitted by the modified Apelblat equation, Jouyban-Acree model, NRTL model and Wilson model, the results were listed in Table 3. And the experimental values correlated by NRTL model are given in Figs. 5-8. The results showed that solubility data increases with increasing temperature in all selected solvents, and as the benzene content in the mixed solvents decreases, the solubility data also increases, which suggests that cooling crystallization using the above solvents is appropriate for crystallization of DNP. At a given temperature and mass fraction of benzene, the solubility order of DNP

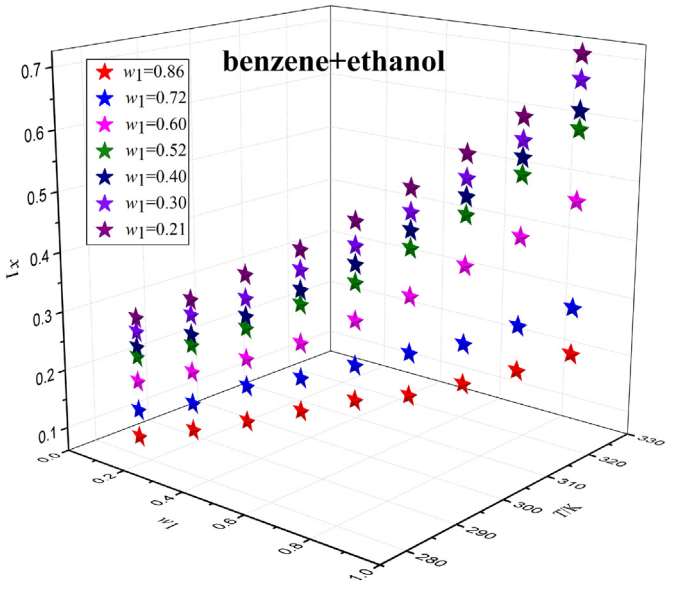

Fig. 5. Experimental data correlated by the NRTL model for DNP in (benzene + ethanol) binary solvent mixtures.

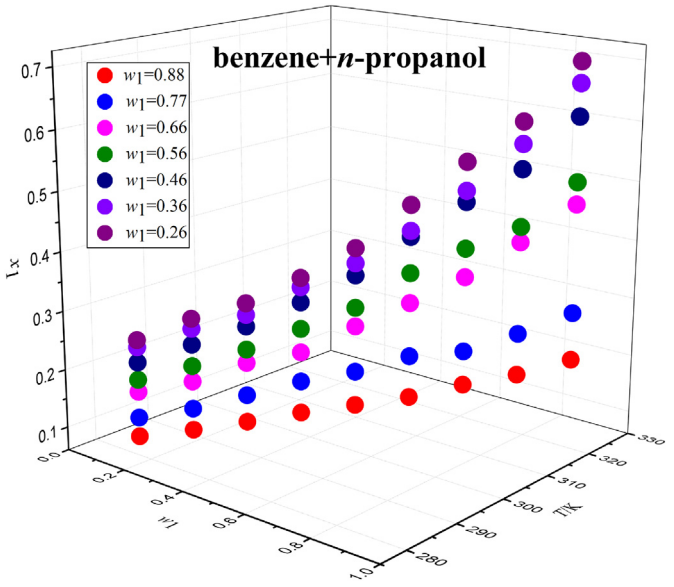

Fig. 6. Experimental data correlated by the NRTL model for DNP in (benzene + *n*-propanol) binary solvents.

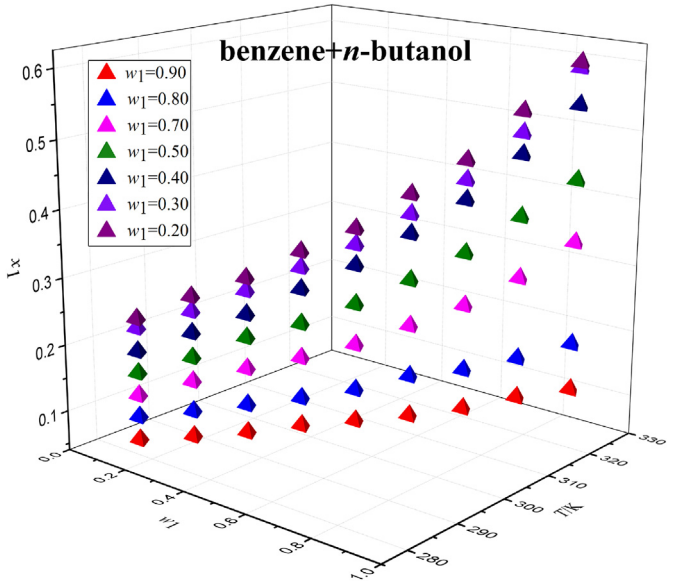

Fig. 7. Experimental data correlated by the NRTL model for DNP in (benzene + *n*-butanol) binary solvent systems.

in four binary solvents is benzene + ethanol ($w_1 = 0.30$) > benzene + *n*-propanol ($w_1 = 0.26$) > benzene + *n*-butanol ($w_1 = 0.30$) > benzene + isoamyl alcohol ($w_1 = 0.23$) in general. It can be inferred that the solubility order of DNP is ethanol > *n*-propanol > *n*-butanol > isoamyl alcohol > benzene. In addition, the polarity order of pure solvents is ethanol (65.4) > *n*-propanol (61.7) > *n*-butanol (60.2) > isoamyl alcohol (56.5) > benzene (11.1) [29], which is strictly consistent with the solubility sequence of DNP. The phenomenon can be explained by the "like dissolves like" rule [30] that the solubility of materials highly corresponds to the similarities between the solutes and the solvents. As displayed in Fig. 1, DNP is a five-membered ring structure. Because $-NO_2$ is an electron-withdrawing group, the electron cloud density of the H atoms on N is reduced, and DNP molecule exhibits N–H hydrogen bonding donor group, meaning that a hydrogen bond can be formed between the DNP and solvent molecules, so the solubility increases with

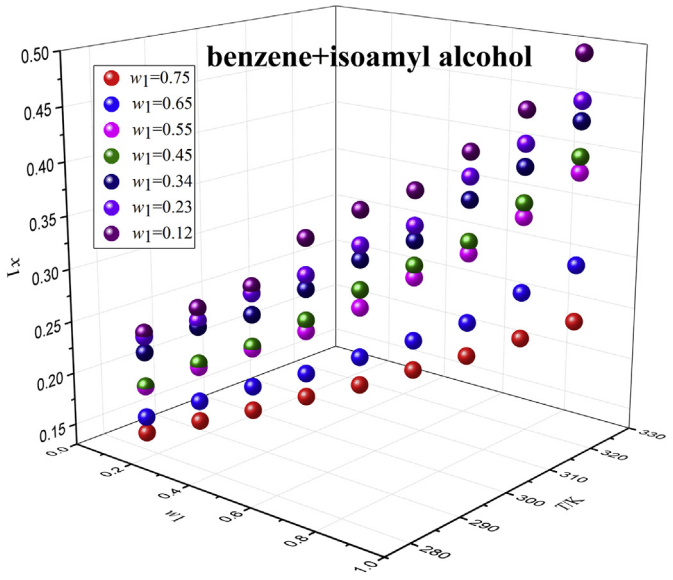

Fig. 8. Experimental data correlated by the NRTL model for DNP in (benzene + isoamyl alcohol) mixed solvents.

the increasing mole fraction of alcohols. Moreover, when the increasing mole fraction of benzene, the interaction of benzene and organic solvent will be weakened. Therefore, the solubility of DNP decreases with the increasing mole fraction of benzene in the determined temperature. When the temperature is changed from 283.15 K to 323.15 K, the maximum increased solubility of DNP in each mixed solvents (benzene + ethanol, benzene + *n*-propanol, benzene + *n*-butanol and benzene + isoamyl alcohol) with different mole fractions of benzene are 191.15% ($w_1 = 0.86$), 179.92% ($w_1 = 0.88$), 159.36% ($w_1 = 0.90$) and 79.05% ($w_1 = 0.75$), respectively.

The calculated solubility data by these models, along with the values of 10^4RMSD, were presented in Tables 4-7. It can be easily observed that for the studied binary solvent mixtures, the maximum values of 10^4RMSD of selected four models: the modified Apelblat equation, Jouyban-Acree model, NRTL model and Wilson model are 64.38, 128.41, 2.17 and 120.21, respectively. In addition, the average 10^4RMSD within the experimental temperature range of these models are 36.07 (the modified Apelblat equation), 98.93 (Jouyban-Acree model), 0.52 (NRTL model) and 43.80 (Wilson model). Because the average 10^4RMSD and the maximum 10^4RMSD of NRTL model are the smallest in four binary mixtures of (benzene + ethanol), (benzene + *n*-propanol), (benzene + *n*-butanol) and (benzene + isoamyl alcohol) at all initial composition ranges, and R^2 is close to 1, the NRTL model can better correlate the solubility data than other three models. The accuracy of the correlation is acceptable for industrial design and operation purpose. From the result, it can be concluded that, the solubility as a function of temperature is correlated well with the NRTL model as a function of solvent composition in binary solvent mixtures. The experimental solubility and correlation models in this paper can be used as basic data and applicable simulation equations in the industrial separation and purification process of DNP. The results mentioned above

Table 4
Model parameters, 10^4RMSD and R^2 of the modified Apelblat equation for solubility of DNP in different binary solvents.

w_1	*A*	*B*	*C*	10^4RMSD	R^2
benzene + ethanol					
0.86	−30.03	−758.66	5.33	31.93	0.9946
0.72	12.39	−2341.11	−1.11	38.81	0.9949
0.60	−181.05	6028.98	27.98	36.07	0.9987
0.52	−182.58	6129.90	28.23	34.12	0.9992
0.40	−123.90	3540.35	19.47	34.27	0.9993
0.30	−196.82	6960.20	30.27	45.25	0.9988
0.21	−136.42	4318.70	21.24	54.32	0.9984
benzene + *n*-propanol					
0.88	−22.26	−1056.35	4.14	16.37	0.9984
0.77	78.71	−5386.07	−10.62	50.45	0.9916
0.66	−170.24	5373.85	26.45	32.99	0.9990
0.56	−17.76	−1376.08	3.69	62.77	0.9966
0.46	−65.64	726.82	10.88	48.32	0.9987
0.36	−274.45	10,248.82	41.94	26.59	0.9996
0.26	−162.90	5190.89	25.35	58.22	0.9985
benzene + *n*-butanol					
0.90	−176.52	5950.46	26.99	13.90	0.9965
0.80	−114.04	3396.55	17.63	20.06	0.9966
0.70	−272.10	10,287.59	41.91	32.56	0.9979
0.60	−150.39	4668.45	23.38	28.85	0.9990
0.50	−152.49	4703.91	23.76	16.76	0.9998
0.40	−295.07	11,331.78	44.91	43.60	0.9986
0.30	−168.63	5622.11	26.09	60.62	0.9994
benzene + isoamyl alcohol					
0.75	−48.43	976.56	7.61	5.55	0.9997
0.65	−146.36	5251.13	22.31	23.14	0.9974
0.55	−161.76	5793.26	24.73	21.37	0.9989
0.45	−84.59	2254.57	13.27	38.87	0.9975
0.34	−140.56	4944.64	21.53	32.24	0.9978
0.23	−138.38	4865.29	21.21	37.46	0.9973
0.12	−41.73	408.24	6.88	64.38	0.9938

Table 5
Model parameters, 10^4RMSD and R^2 of Jouyban-Acree model for solubility of DNP in binary solvent systems.

benzene + ethanol		benzene + *n*-propanol		benzene + *n*-butanol		benzene + isoamyl alcohol	
A_1	−158.69	A_1	−94.96	A_1	−143.01	A_1	−77.39
A_2	5382.06	A_2	1932.39	A_2	4392.65	A_2	2002.53
A_3	24.60	A_3	15.37	A_3	22.31	A_3	12.22
A_4	−68.30	A_4	−3.66	A_4	−40.31	A_4	−16.74
A_5	1643.83	A_5	559.51	A_5	2004.64	A_5	816.37
A_6	5374.14	A_6	329.14	A_6	286.23	A_6	581.45
A_7	−8576.01	A_7	−504.15	A_7	−865.39	A_7	−733.98
A_8	4078.43	A_8	−256.73	A_8	−199.94	A_8	−35.63
A_9	10.14	A_9	0.20	A_9	5.90	A_9	2.28
10^4RMSD	128.41	10^4RMSD	111.95	10^4RMSD	75.41	10^4RMSD	79.97
R^2	0.9917	R^2	0.9938	R^2	0.9970	R^2	0.9900

suggest that the experimental data provide a certain foundation for crystallization process of DNP in the future.

4. Thermodynamic properties

For a non-ideal solution, it is necessary to study the mixing thermodynamic properties of the solute in different binary solvent mixtures, such as the mixing enthalpy, the mixing Gibbs energy and the mixing entropy.

The mixing properties can be calculated by the following equations [31].

$$\Delta_{mix}G = G^E + \Delta_{mix}G^{id} \tag{28}$$

$$\Delta_{mix}H = H^E + \Delta_{mix}H^{id} \tag{29}$$

$$\Delta_{mix}S = S^E + \Delta_{mix}S^{id} \tag{30}$$

Where G^E and $\Delta_{mix}G^{id}$, S^E and $\Delta_{mix}S^{id}$, H^E and $\Delta_{mix}H^{id}$ stand for the excess properties and mixing properties of ideal systems.

The mixing thermodynamic properties of the ideal solution can be calculated by the following equations [32].

$$\Delta_{mix}G^{id} = RT\sum_{i}^{n} x_i \ln x_i \tag{31}$$

$$\Delta_{mix}H^{id} = 0 \tag{32}$$

Table 6
Model parameters, 10^4RMSD and R^2 of NRTL model for solubility of DNP in binary solvent mixtures.

w_1	α	Δg_{12}/(J·mol^{-1})	Δg_{13}/(J·mol^{-1})	Δg_{21}/(J·mol^{-1})	Δg_{23}/(J·mol^{-1})	Δg_{31}/(J·mol^{-1})	Δg_{32}/(J·mol^{-1})	10^4RMSD	R^2
benzene + ethanol									
0.86	0.15	6450.91	−36,861.79	463.29	−5175.26	94,504.11	−9386.71	0.57	0.9999
0.72	1.20	4513.78	−2375.47	618.79	−9713.64	19,818.08	−1194.30	0.24	0.9998
0.60	1.06	7603.23	−1367.72	1390.87	−11,894.43	25,781.57	−11,964.42	0.43	0.9998
0.52	0.49	8502.85	−10,011.11	157.61	6073.04	3200.37	−15,171.84	0.65	0.9999
0.40	0.99	−1096.34	7772.37	26,936.80	−12,273.08	1445.45	0.98	0.27	0.9994
0.30	1.02	−1908.88	7004.92	24,903.40	−12,124.42	714.35	4.58	1.09	0.9995
0.21	0.24	−98,564.04	−53,735.52	120,333.75	44,446.46	−71,412.23	48,612.40	2.17	0.9995
benzene + *n*-propanol									
0.88	0.31	−18,955.20	6293.38	694.07	−8757.05	−4032.22	−9549.20	0.40	0.9994
0.77	0.51	171,153.24	−19,484.45	−119,877.24	−108,020.58	−45.94	−64,281.02	0.50	0.9998
0.66	0.74	6628.61	−4090.50	1181.53	2047.75	38,401.32	−10,574.48	0.52	0.9999
0.56	0.45	−12,109.09	8401.54	2801.76	−16,329.02	−134.07	9828.95	0.27	0.9999
0.46	0.41	11,756.23	−11,072.58	−951.74	−18,704.59	3815.82	8964.30	0.47	0.9994
0.36	0.91	−4626.12	4931.02	1081.89	0.72	9.09	−11,526.65	0.38	0.9997
0.26	0.20	32,286.37	−22,093.15	−11,246.40	−36,611.34	8011.65	14,189.66	0.24	0.9996
benzene + *n*-butanol									
0.90	1.40	555.24	−3840.45	207.44	−5407.40	12,312.99	2678.89	0.10	0.9991
0.80	0.05	55,314.40	−17,926.63	19,318.72	19.47	−10,498.33	−13,928.83	0.13	0.9997
0.70	1.56	3721.18	−2384.07	475.97	−3057.87	18,168.45	−9825.85	0.28	0.9991
0.60	0.51	6905.07	−9731.67	−368.58	7850.77	2777.98	−12,836.31	0.54	0.9996
0.50	0.65	−3212.95	12,156.23	11,634.80	−16,284.89	3298.33	−12,493.82	0.80	0.9995
0.40	0.98	−3891.79	6743.22	1358.85	−1392.96	33.88	−3397.21	0.43	0.9999
0.30	1.08	−1532.49	6935.99	24,786.69	−12,036.54	683.02	−4491.53	0.62	0.9998
benzene + isoamyl alcohol									
0.75	1.35	1480.07	−2288.62	−148.63	1941.37	−2790.81	−3837.58	0.01	0.9998
0.65	0.25	−81,080.49	0.82	143,944.30	−23,224.87	−38,899.72	−19,530.79	0.16	0.9994
0.55	0.41	389,562.89	361,276.59	24,580.38	62,727.08	32,889.51	−11,205.98	0.60	0.9995
0.45	0.54	−8095.70	9197.81	3213.40	−15,023.97	56.71	5063.34	0.68	0.9998
0.34	0.21	23,339.98	−6556.66	−70,578.84	−25,842.99	23,983.54	−26,466.78	0.88	0.9992
0.23	0.77	5424.01	−6149.87	383.54	53.99	955.53	−13,387.85	0.07	0.9997
0.12	1.31	−2662.24	4753.31	244.01	−10,248.49	42.47	−3490.19	0.94	0.9999

Table 7
Model parameters, 10^4RMSD and R^2 of Wilson model for solubility of DNP in mixed solvents.

w_1	$\Delta\lambda_{12}$/(J·mol^{-1})	$\Delta\lambda_{13}$/(J·mol^{-1})	$\Delta\lambda_{21}$/(J·mol^{-1})	$\Delta\lambda_{23}$/(J·mol^{-1})	$\Delta\lambda_{31}$/(J·mol^{-1})	$\Delta\lambda_{32}$/(J·mol^{-1})	10^4RMSD	R^2
benzene + ethanol								
0.86	46,426.60	−1999.58	37,579.67	−6959.46	−14,387.52	−194,520.12	24.23	0.9969
0.72	51,145.33	−2244.79	65,185.98	0.86	31,746.26	−37,593.34	38.36	0.9957
0.60	1575.62	−1030.60	41,898.71	11.75	5857.20	−7.74	26.28	0.9993
0.52	−369.89	−363.57	41,807.55	−37.13	6292.39	−12.68	26.45	0.9995
0.40	−632.68	−624.61	7370.67	44.74	38,563.73	−323,267.64	31.23	0.9994
0.30	32,347.06	−1750.69	6095.27	−1.41	40,585.40	−10,884.87	23.43	0.9997
0.21	98,325.89	−1777.75	93,178.56	48,175.32	75,367.42	1.07	29.88	0.9995
benzene + *n*-propanol								
0.88	4922.39	−2728.70	2.34	−723,220.03	14,827.61	−34,009.64	17.82	0.9981
0.77	6257.11	−2655.27	56,366.86	−1447.16	36,598.87	−10,772.38	45.34	0.9932
0.66	503.59	496.96	34,578.93	−39,459.71	3126.33	22.90	24.07	0.9994
0.56	−114.57	−112.93	38,530.17	−42,885.30	6239.80	−0.16	50.69	0.9978
0.46	−371.70	−365.68	4147.74	−7.92	39,871.99	−32,618.75	46.68	0.9988
0.36	−1710.12	29,776.56	−598.03	17.74	33,774.31	0.71	16.18	0.9999
0.26	6285.52	−1016.80	2662.53	11,628.13	46,998.11	−10.32	38.68	0.9993
benzene + *n*-butanol								
0.90	31,912.93	−1979.07	29,860.19	−3463.81	1233.07	29.62	7.88	0.9989
0.80	67,793.74	−1811.85	132,113.16	−25,490.16	94,003.37	0.59	22.71	0.9985
0.70	36,979.40	−1492.08	8889.54	−14,384.52	1997.55	−315.09	15.98	0.9995
0.60	349.61	345.51	31,898.63	−10,779.47	10,506.96	−233.31	18.42	0.9996
0.50	4.05	5.21	67,278.09	−14,220.33	5906.22	6.84	16.07	0.9998
0.40	−2550.75	33,706.76	9371.51	12,757.25	−161,640.63	−170,719.49	16.37	0.9998
0.30	8567.87	−1464.95	33,993.47	0.10	147,103.37	2.80	16.91	0.9998
benzene + isoamyl alcohol								
0.75	76,592.08	−1776.45	37,095.63	−527,655.51	70,291.52	−8603.84	120.21	0.9991
0.65	437,427.78	−1301.65	588,689.36	3737.30	1,082,028.37	420,496.47	117.75	0.9990
0.55	−1252.39	71,809.87	133,156.26	25,494.07	103,346.01	−2236.69	106.62	0.9996
0.45	−1861.10	236,353.47	147,151.38	0.54	89,928.84	3.49	84.06	0.9987
0.34	−2869.97	80,685.63	102,190.83	−2518.64	96,272.60	−2438.61	107.52	0.9990
0.23	−4008.89	67,857.63	100,914.26	5555.15	69,082.45	−3351.98	84.36	0.9989
0.12	−5846.77	12,424.88	36,658.47	−6710.01	43,025.12	−11,362.82	52.17	0.9960

Table 8
$\Delta_{mix}H$, $\Delta_{mix}S$ and $\Delta_{mix}G$ of DNP in different binary solvents from $T = (283.15\ \text{K to } 323.15\ \text{K})$ and $P = 0.1$ MPa.

T/K	$\Delta_{mix}G$/(kJ·mol^{-1})	$\Delta_{mix}H$/(kJ·mol^{-1})	$\Delta_{mix}S$/(J·K^{-1}·mol^{-1})	T/K	$\Delta_{mix}G$/(kJ·mol^{-1})	$\Delta_{mix}H$/(kJ·mol^{-1})	$\Delta_{mix}S$/(J·K^{-1}·mol^{-1})
	benzene + ethanol ($w_1 = 0.86$)				benzene + *n*-propanol ($w_1 = 0.88$)		
283.15	−2.510	−2.356	0.544	283.15	−2.416	−2.273	0.508
288.15	−2.573	−2.412	0.559	288.15	−2.480	−2.329	0.523
293.15	−2.649	−2.480	0.577	293.15	−2.549	−2.391	0.540
298.15	−2.728	−2.550	0.597	298.15	−2.623	−2.456	0.558
303.15	−2.804	−2.618	0.615	303.15	−2.684	−2.511	0.571
308.15	−2.851	−2.660	0.622	308.15	−2.745	−2.565	0.584
313.15	−2.926	−2.726	0.638	313.15	−2.822	−2.634	0.601
318.15	−3.000	−2.792	0.654	318.15	−2.885	−2.690	0.614
323.15	−3.078	−2.862	0.670	323.15	−2.959	−2.756	0.629
	benzene + ethanol ($w_1 = 0.72$)				benzene + *n*-propanol ($w_1 = 0.77$)		
283.15	−3.102	−2.883	0.774	283.15	−2.935	−2.734	0.709
288.15	−3.165	−2.939	0.785	288.15	−3.010	−2.801	0.725
293.15	−3.267	−3.030	0.810	293.15	−3.100	−2.881	0.747
298.15	−3.331	−3.086	0.819	298.15	−3.185	−2.956	0.765
303.15	−3.406	−3.153	0.833	303.15	−3.250	−3.015	0.777
308.15	−3.474	−3.214	0.844	308.15	−3.328	−3.084	0.792
313.15	−3.533	−3.266	0.851	313.15	−3.375	−3.126	0.796
318.15	−3.605	−3.330	0.863	318.15	−3.448	−3.191	0.809
323.15	−3.668	−3.386	0.871	323.15	−3.517	−3.252	0.819
	benzene + ethanol ($w_1 = 0.60$)				benzene + *n*-propanol ($w_1 = 0.66$)		
283.15	−3.402	−3.150	0.891	283.15	−3.289	−3.049	0.847
288.15	−3.470	−3.211	0.901	288.15	−3.362	−3.114	0.860
293.15	−3.545	−3.277	0.914	293.15	−3.455	−3.197	0.880
298.15	−3.620	−3.344	0.926	298.15	−3.520	−3.255	0.889
303.15	−3.699	−3.414	0.939	303.15	−3.609	−3.334	0.907
308.15	−3.766	−3.473	0.948	308.15	−3.678	−3.396	0.917
313.15	−3.820	−3.522	0.952	313.15	−3.735	−3.446	0.922
318.15	−3.857	−3.551	0.959	318.15	−3.775	−3.477	0.935
323.15	−3.870	−3.558	0.968	323.15	−3.788	−3.482	0.948

Table 8 (*continued*)

T/K	$\Delta_{mix}G$/(kJ·mol^{-1})	$\Delta_{mix}H$/(kJ·mol^{-1})	$\Delta_{mix}S$/(J·K^{-1}·mol^{-1})	T/K	$\Delta_{mix}G$/(kJ·mol^{-1})	$\Delta_{mix}H$/(kJ·mol^{-1})	$\Delta_{mix}S$/(J·K^{-1}·mol^{-1})
	benzene + ethanol (w_1 = 0.52)				benzene + *n*-propanol (w_1 = 0.56)		
283.15	−3.515	−3.250	0.934	283.15	−3.436	−3.180	0.904
288.15	−3.581	−3.309	0.943	288.15	−3.516	−3.251	0.918
293.15	−3.651	−3.372	0.954	293.15	−3.597	−3.323	0.933
298.15	−3.722	−3.435	0.964	298.15	−3.676	−3.394	0.947
303.15	−3.779	−3.485	0.968	303.15	−3.746	−3.456	0.956
308.15	−3.824	−3.525	0.969	308.15	−3.809	−3.512	0.963
313.15	−3.848	−3.543	0.974	313.15	−3.852	−3.545	0.978
318.15	−3.853	−3.540	0.985	318.15	−3.885	−3.570	0.989
323.15	−3.864	−3.542	0.995	323.15	−3.908	−3.585	0.999
	benzene + ethanol (w_1 = 0.40)				benzene + *n*-propanol (w_1 = 0.46)		
283.15	−3.490	−3.228	0.924	283.15	−3.494	−3.232	0.926
288.15	−3.553	−3.284	0.933	288.15	−3.575	−3.304	0.941
293.15	−3.620	−3.344	0.942	293.15	−3.647	−3.368	0.952
298.15	−3.684	−3.401	0.950	298.15	−3.717	−3.431	0.962
303.15	−3.734	−3.445	0.952	303.15	−3.775	−3.482	0.967
308.15	−3.766	−3.470	0.959	308.15	−3.813	−3.513	0.975
313.15	−3.779	−3.476	0.967	313.15	−3.829	−3.521	0.985
318.15	−3.785	−3.473	0.980	318.15	−3.835	−3.517	0.998
323.15	−3.790	−3.468	0.997	323.15	−3.839	−3.508	1.025
	benzene + ethanol (w_1 = 0.30)				benzene + *n*-propanol (w_1 = 0.36)		
283.15	−3.369	−3.121	0.878	283.15	−3.442	−3.186	0.906
288.15	−3.430	−3.175	0.886	288.15	−3.514	−3.250	0.918
293.15	−3.484	−3.223	0.891	293.15	−3.573	−3.302	0.924
298.15	−3.536	−3.269	0.895	298.15	−3.637	−3.359	0.932
303.15	−3.574	−3.300	0.901	303.15	−3.684	−3.401	0.934
308.15	−3.593	−3.311	0.915	308.15	−3.716	−3.430	0.930
313.15	−3.601	−3.311	0.926	313.15	−3.721	−3.425	0.945
318.15	−3.605	−3.307	0.938	318.15	−3.742	−3.437	0.958
323.15	−3.615	−3.305	0.958	323.15	−3.759	−3.443	0.978
	benzene + ethanol (w_1 = 0.21)				benzene + *n*-propanol (w_1 = 0.26)		
283.15	−3.159	−2.934	0.796	283.15	−3.266	−3.029	0.838
288.15	−3.211	−2.980	0.802	288.15	−3.335	−3.090	0.849
293.15	−3.259	−3.022	0.806	293.15	−3.388	−3.138	0.855
298.15	−3.294	−3.052	0.812	298.15	−3.441	−3.184	0.860
303.15	−3.315	−3.064	0.829	303.15	−3.479	−3.217	0.865
308.15	−3.318	−3.057	0.845	308.15	−3.489	−3.218	0.879
313.15	−3.302	−3.030	0.869	313.15	−3.498	−3.221	0.885
318.15	−3.125	−2.842	0.888	318.15	−3.504	−3.219	0.897
323.15	−3.136	−2.845	0.902	323.15	−3.516	−3.225	0.902
	benzene + *n*-butanol (w_1 = 0.90)				benzene + isoamyl alcohol (w_1 = 0.75)		
283.15	−2.203	−2.082	0.424	283.15	−3.069	−2.854	0.761
288.15	−2.243	−2.119	0.433	288.15	−3.130	−2.908	0.771
293.15	−2.288	−2.159	0.442	293.15	−3.187	−2.958	0.779
298.15	−2.354	−2.217	0.459	298.15	−3.249	−3.013	0.789
303.15	−2.402	−2.260	0.469	303.15	−3.306	−3.064	0.797
308.15	−2.453	−2.305	0.479	308.15	−3.367	−3.118	0.806
313.15	−2.515	−2.360	0.493	313.15	−3.424	−3.170	0.813
318.15	−2.595	−2.432	0.513	318.15	−3.485	−3.224	0.821
323.15	−2.655	−2.485	0.526	323.15	−3.542	−3.275	0.828
	benzene + *n*-butanol (w_1 = 0.80)				benzene + isoamyl alcohol (w_1 = 0.65)		
283.15	−2.765	−2.583	0.643	283.15	−3.305	−3.063	0.853
288.15	−2.822	−2.634	0.654	288.15	−3.374	−3.125	0.864
293.15	−2.882	−2.688	0.665	293.15	−3.439	−3.183	0.874
298.15	−2.942	−2.741	0.676	298.15	−3.500	−3.237	0.882
303.15	−3.009	−2.800	0.689	303.15	−3.565	−3.295	0.891
308.15	−3.095	−2.877	0.709	308.15	−3.627	−3.350	0.898
313.15	−3.148	−2.924	0.716	313.15	−3.688	−3.405	0.906
318.15	−3.220	−2.988	0.729	318.15	−3.757	−3.466	0.915
323.15	−3.295	−3.055	0.744	323.15	−3.817	−3.520	0.922
	benzene + *n*-butanol (w_1 = 0.70)				benzene + isoamyl alcohol (w_1 = 0.55)		
283.15	−3.129	−2.907	0.784	283.15	−3.458	−3.200	0.912
288.15	−3.219	−2.987	0.805	288.15	−3.529	−3.263	0.923
293.15	−3.299	−3.058	0.821	293.15	−3.595	−3.322	0.933
298.15	−3.369	−3.120	0.833	298.15	−3.658	−3.378	0.940
303.15	−3.442	−3.185	0.846	303.15	−3.724	−3.436	0.948
308.15	−3.523	−3.258	0.862	308.15	−3.790	−3.495	0.957
313.15	−3.599	−3.325	0.874	313.15	−3.846	−3.545	0.961
318.15	−3.674	−3.392	0.886	318.15	−3.901	−3.594	0.965
323.15	−3.737	−3.448	0.894	323.15	−3.946	−3.634	0.966

(*continued on next page*)

Table 8 (*continued*)

T/K	$\Delta_{mix}G$/(kJ·mol^{-1})	$\Delta_{mix}H$/(kJ·mol^{-1})	$\Delta_{mix}S$/(J·K^{-1}·mol^{-1})	T/K	$\Delta_{mix}G$/(kJ·mol^{-1})	$\Delta_{mix}H$/(kJ·mol^{-1})	$\Delta_{mix}S$/(J·K^{-1}·mol^{-1})
	benzene + *n*-butanol (w_1 = 0.60)				benzene + isoamyl alcohol (w_1 = 0.45)		
283.15	−3.359	−3.112	0.874	283.15	−3.458	−3.200	0.912
288.15	−3.445	−3.188	0.891	288.15	−3.535	−3.268	0.926
293.15	−3.536	−3.269	0.910	293.15	−3.598	−3.325	0.934
298.15	−3.605	−3.331	0.921	298.15	−3.669	−3.388	0.944
303.15	−3.680	−3.397	0.932	303.15	−3.738	−3.449	0.954
308.15	−3.751	−3.461	0.943	308.15	−3.797	−3.501	0.959
313.15	−3.813	−3.516	0.950	313.15	−3.851	−3.549	0.963
318.15	−3.863	−3.560	0.952	318.15	−3.903	−3.596	0.966
323.15	−3.893	−3.581	0.965	323.15	−3.944	−3.628	0.978
	benzene + *n*-butanol (w_1 = 0.50)				benzene + isoamyl alcohol (w_1 = 0.34)		
283.15	−3.470	−3.210	0.917	283.15	−3.396	−3.145	0.888
288.15	−3.553	−3.285	0.933	288.15	−3.465	−3.206	0.899
293.15	−3.630	−3.353	0.945	293.15	−3.517	−3.253	0.903
298.15	−3.707	−3.421	0.958	298.15	−3.579	−3.307	0.911
303.15	−3.771	−3.479	0.966	303.15	−3.637	−3.359	0.917
308.15	−3.828	−3.529	0.970	308.15	−3.687	−3.403	0.920
313.15	−3.868	−3.562	0.979	313.15	−3.737	−3.448	0.923
318.15	−3.883	−3.568	0.989	318.15	−3.777	−3.482	0.928
323.15	−3.897	−3.864	0.103	323.15	−3.807	−3.504	0.936
	benzene + *n*-butanol (w_1 = 0.40)				benzene + isoamyl alcohol (w_1 = 0.23)		
283.15	−3.474	−3.214	0.918	283.15	−3.175	−2.948	0.802
288.15	−3.544	−3.276	0.929	288.15	−3.228	−2.995	0.808
293.15	−3.613	−3.338	0.939	293.15	−3.287	−3.047	0.817
298.15	−3.676	−3.394	0.947	298.15	−3.336	−3.091	0.821
303.15	−3.731	−3.442	0.951	303.15	−3.387	−3.137	0.826
308.15	−3.776	−3.483	0.952	308.15	−3.430	−3.175	0.828
313.15	−3.806	−3.504	0.965	313.15	−3.471	−3.210	0.836
318.15	−3.807	−3.495	0.978	318.15	−3.503	−3.234	0.845
323.15	−3.814	−3.494	0.989	323.15	−3.524	−3.246	0.860
	benzene + *n*-butanol (w_1 = 0.30)				benzene + isoamyl alcohol (w_1 = 0.12)		
283.15	−3.344	−3.099	0.868	283.15	−2.774	−2.591	0.646
288.15	−3.415	−3.162	0.880	288.15	−2.826	−2.637	0.655
293.15	−3.474	−3.214	0.887	293.15	−2.872	−2.678	0.661
298.15	−3.531	−3.265	0.893	298.15	−2.925	−2.725	0.670
303.15	−3.577	−3.306	0.895	303.15	−2.961	−2.757	0.672
308.15	−3.611	−3.334	0.900	308.15	−2.993	−2.781	0.687
313.15	−3.630	−3.344	0.912	313.15	−3.019	−2.800	0.698
318.15	−3.648	−3.354	0.925	318.15	−3.035	−2.810	0.708
323.15	−3.665	−3.362	0.938	323.15	−3.048	−2.815	0.721

$$\Delta_{mix}S^{id} = -R\sum_{i}^{n} x_i \ln x_i \tag{33}$$

$$G^E = RT\sum_{i}^{n} x_i \ln \gamma_i \tag{34}$$

Where x_i and γ_i are the mole fraction and activity coefficient of component i in real solution, respectively. $i = 2$ means a binary solution and $i = 3$ means a ternary solution.

In addition, the activity coefficient can be calculated by the given Wilson model. The excess mixing properties can be calculated by the following equations [33].

$$H^E = -RT^2\sum_{i}^{n} x_i\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,x} \tag{35}$$

$$S^E = \frac{H^E - G^E}{T} \tag{36}$$

The calculated mixing thermodynamic properties in four binary solvent mixtures are given in Table 8, in addition, these mixing thermodynamic parameters are calculated based on per mole mixture. As shown in Table 8, it can be found that the values of $\Delta_{mix}G$ are all negative and decrease with increasing temperature, which indicates that the dissolution process of DNP in all investigated solvents is a spontaneous and favorable process [34]. The negative $\Delta_{mix}H$ illustrates that the dissolution process in binary solvents is exothermic. The values of $\Delta_{mix}S$ in all tested solvents are positive and increase with increasing temperature, which indicates that the mixing process is also entropy-driven [31]. In brief, these results are helpful for the optimization of the mixing and crystallization processes of DNP.

5. Conclusions

The solubility of DNP in four binary mixed solvents like benzene + ethanol, benzene + *n*-propanol, benzene + *n*-butanol and benzene + isoamyl alcohol was investigated by laser monitoring technique in the temperature range from 283.15 K to 323.15 K under 0.1 MPa. Experimental solubility increases with increasing temperature at given solvent composition and increases with decreasing mass fraction of benzene at constant temperature. Hansen solubility parameters (HSP) were used to explain and predict the solubility behavior. If the Hildebrand solubility parameter δ of some solvent was known, the solubility of DNP in some solvent may be predicted based on solubility and selected solvents. In addition, four correlation models (i.e., the modified Apelblat equation, Jouyban-Acree model, NRTL model and Wilson model) selected in this study can all be used to fit the solubility values of DNP precisely. What's more, all of the 252 experimental values are used to correlate the parameters of NRTL model and the correlated results are superior to the other three models by comparing the average 10^4RMSD and R^2. Moreover, mixing properties of DNP in selected binary

solvents, including mixing enthalpy ($\Delta_{mix}H$), mixing entropy ($\Delta_{mix}S$) and mixing Gibbs energy ($\Delta_{mix}G$) were studied based on solubility data and Wilson model. The results show that the dissolution process of DNP in selected binary solvents is spontaneous and entropy-driven, and the mixing process in most solvents is exothermic. Furthermore, the solubility data and correlation results are worthwhile and very useful for choosing a suitable solvent for the purification process of DNP on an industrial scale and further theoretical studies.

Declaration of Competing Interest

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Conflict of interest

The authors declare no competing financial interest.

Credit authorship statement

Hao-qi Guo: Data curation, Writing-original draft, Resources **Yong-xiang Li**: Formal analysis, Writing-review & editing, Software, Supervision **Yu-lin Yang**: Investigation, Methodology, Project administration, Validation **Zi-yang Li**: Conceptualization, Funding acquisition.

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