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Solubility determination and correlation for 3-nitropyrazole in four binary solvents (water + methanol, ethanol, 1-propanol and acetone) from 283.15 K to 323.15 K

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ABSTRACT

The solubility of 3-nitropyrazole in four binary solvents (water + methanol, ethanol, 1-propanol and acetone) was measured by a dynamic laser monitoring over the temperature range of 283.15 K, 288.15 K, 293.15 K, 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15 K at pressure of 0.1 MPa. The solubility of 3-nitropyrazole increased positively with increasing temperature, while increased with decreasing mass-fraction of water in each binary system. Moreover, the experimental solubility values of 3-nitropyrazole in this work were correlated well with four thermodynamic models namely "the modified Apelblat equation, λh equation, Jouyban-Acree model and CNIBS/R-K model" obtaining average relative deviations (10^4RMSD) lower than 4.79 for correlative studies, which shows that all the four models have a good correlation. Through the comparison of R^2 and 10^4RMSD, it was found that the modified Apelblat equation can get more satisfactory results. In addition, Hansen solubility parameters were used to explain and predict the solubility behavior. Solute-solvent interaction was calculated by molecular simulation to investigate the solubility behavior deeply. Finally, the thermodynamic parameters ($\Delta_{dis}G^o$, $\Delta_{dis}H^o$, $\Delta_{dis}S^o$) of 3-nitropyrazole dissolution processes in investigated four binary solvents were evaluated utilizing the van't Hoff equation. The positive $\Delta_{dis}H^o$ and $\Delta_{dis}S^o$, indicate that the dissolution processes of 3-nitropyrazole are endothermic and entropy-driven in all chosen binary solvents. And the main contributor of $\Delta_{dis}G^o$ is positive enthalpy. The solubility of 3-nitropyrazole in mixed solvents (water + methanol, water + ethanol, water + 1-propanol and water + acetone) will provide essential support for the further researches of crystallization and spheroidization of 3-nitropyrazole.

1. Introduction

Due to the large number of N-N, C-N bonds and large ring tension in the azacyclic compound, the enthalpy of formation is very high. And this type of compound has the characteristics of high nitrogen and low carbon hydrogen, so it has a higher density. In addition, the electronegativity of nitrogen and oxygen atoms in nitrogen heterocyclic molecules are high, especially the nitrogen heteroaromatic ring system can also form a large benzene-like structure of the bond, which has the characteristics of insensitivity and good thermal stability. It is highly valued in the research of energetic materials [1,2]. 3-Nitropyrazole ($C_3H_3N_3O_2$, Fig. 1, CAS No. 26621–44-3, molar mass 113.07 g·mol^{-1}) is a light yellow crystal. The melting point, density, getonation velocity and detonation pressure of 3-nitropyrazole is 174–175 ℃, 1.57 g·cm^{-3}, 7.02 km·s^{-1} and 20.08 GPa, respectively [3]. As a typical nitrogen heterocyclic compound, it is an important intermediate for the synthesis of new explosives such as 3,4-dinitropyrazole (DNP). It can also be used directly as an energetic material or as an intermediate to further prepare other energetic compounds.

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 [4]. Moreover, many studies have focused on the synthesis of 3-nitropyrazole (e.g., Janssen [5], Klebe [6], Cuiping Li [7], Hongli Li [8] and Xin Tian [9] et al.), but only a few have attempted to establish purification methods to obtain products with high purity

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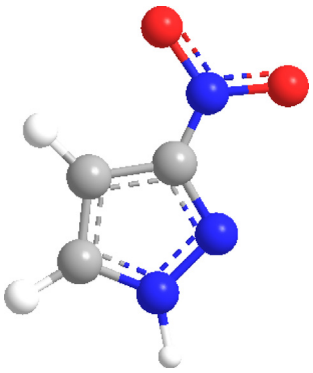

Fig. 1. The molecular structure of 3-nitropyrazole.

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 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 3-nitropyrazole has important research significance for the crystallization process of 3-nitropyrazole.

In this work, to optimize the crystallization process of 3-nitropyrazole (e.g., yield, stability, whiteness, fluidity and so on). The solid–liquid equilibrium solubility of 3-nitropyrazole in four kinds of binary solvent mixtures (including water + methanol, water + ethanol, water + 1-propanol and water + acetone) was determined with a temperature ranging from 283.15 K to 323.15 K under approximately 0.1 MPa. The Hansen solubility parameter for 3-nitropyrazole and the selected solvents was employed to analyze the probabilities of miscibility between solute and solvents. The solubility behavior was studied by molecular simulation. In addition, four thermodynamic models (i.e., the modified Apelblat equation, λh equation, Jouyban-Acree model and CNIBS/R-K model) were selected to correlate the experimental data. The solubility data are of guiding significance to the crystallization process of 3-nitropyrazole. Furthermore, the thermodynamic properties of the solution process, including the standard molar Gibbs energy, standard molar enthalpy and standard molar entropy, were calculated by the van't Hoff analysis.

2. Experimental

2.1. Chemical materials

3-Nitropyrazole was synthesized from pyrazole by a two-step reaction of nitration and rearrangement [7], and the synthetic route is showed in Fig. 2. It was purified by crystallization in methanol and its mass fraction purity, measured by High Performance Liquid Chromatography (HPLC), was 0.990. All solvents used in this experiment, such as methanol, ethanol, 1-propanol and acetone, were purchased from local reagent factories without further purification, and their mass fraction purity was not<0.990. The distilled water received the production in a pure water machine (IQ-7005, Milli-Q). More information of all the materials used in this experiment is presented in Table 1.

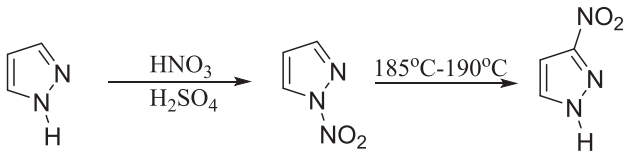

Fig. 2. Synthesis route of 3-nitropyrazole.

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 3-nitropyrazole. The standard uncertainties of the measurement were a temperature of 0.5 K and a fusion enthalpy of 400 J·mol^{-1}. Fig. 3 indicates that the fusion enthalpy is 16.72 kJ·mol^{-1} and the melting temperature is 447.05 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 3-nitropyrazole 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 °·min^{-1}. The XRD curves of 3-nitropyrazole in four binary solvents were showed in Fig. 4. The results showed that no polymorph transformation of 3-nitropyrazole was identified.

2.4. Hansen solubility parameter

The concept of Hansen solubility parameter (HSP) has been widely used for selecting suitable solvents for solute [10]. 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):

$$E_t = E_d + E_p + E_h \quad (1)$$

Dividing each contribution by the molar volume:

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

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

$$\delta_t = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (3)$$

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 [10]. The solubility parameter for binary solvents (δ_{mix}) can be expressed as: [11]

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

Where α stands for the volume fraction of water; δ_1 and δ_2 are the Hansen solubility parameters of water and methanol, ethanol, 1-propanol and acetone.

The group contribution (Hoftyzer-Van Krevelen) method was used to calculate the values of δ_d, δ_p and δ_h of 3-nitropyrazole [12]. The molar volume of 3-nitropyrazole, V_s = 61.5 cm^3·mol^{-1}, was taken from the SciFinder database [13].

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

Material	Molar mass/(g·mol^{-1})	Source	Purity	Purification method	Analysis method
3-nitropyrazole	113.07	Synthesized by us	0.990	crystallization	HPLC[a]
Methanol	32.04	Sinopharm Chemical Reagent Co., Ltd	0.995	none	GC[b]
Ethanol	46.07	Sinopharm Chemical Reagent Co., Ltd	0.995	none	GC[b]
1-propanol	60.10	Sinopharm Chemical Reagent Co., Ltd	0.990	none	GC[b]
Acetone	58.08	Sinopharm Chemical Reagent Co., Ltd	0.990	none	GC[b]
Water	18.02	prepared by the laboratory	/	/	/

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

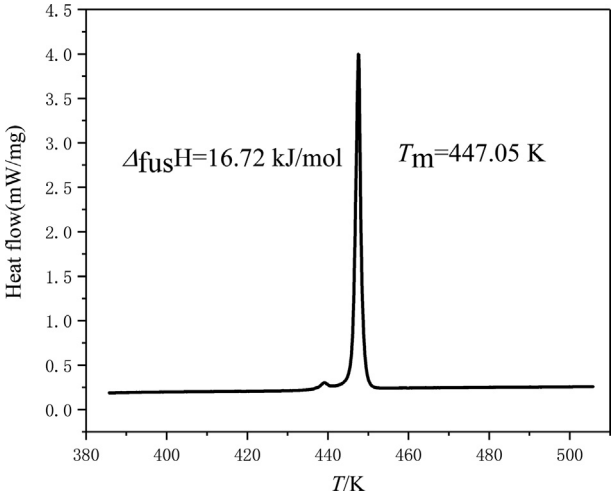

Fig. 3. DSC plot of 3-nitropyrazole.

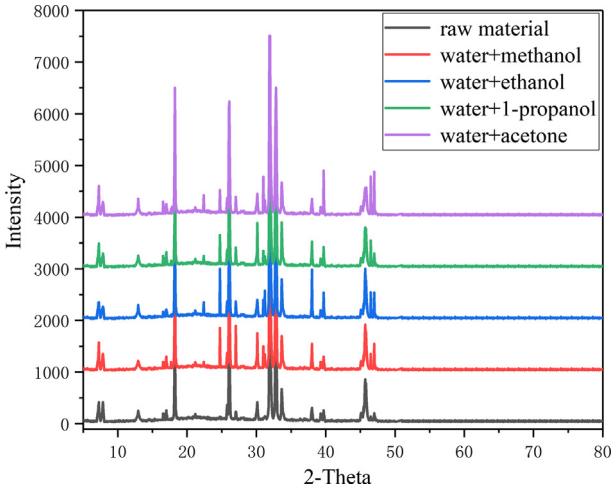

Fig. 4. XRD pattern of 3-nitropyrazole.

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: [14]

$$\Delta\delta_t = |\delta_{t2} - \delta_{t1}| \quad (5)$$

Where δ_{t1} and δ_{t2} are total Hansen solubility parameters of solute and binary solvents, respectively. Values of δ_d, δ_p, δ_h, δ_t and $\Delta\delta_t$ of four binary solvents and solute are listed in Table 2.

2.5. Simulation methods

The calculations based on density functional theory (DFT) were conducted with the Dmol^3 module implemented in Materials Studio [15] to determine the solubility sequence of 3-nitropyrazole. In the present study, molecules of 3-nitropyrazole and solvents were optimized with adopting the DFT method in the generalized gradient approximation (GGA) and with the Perdew-Burke-Ernzerhof (PBE) functional form [16]. The double numerical polarized (DNP) basis sets were applied [17], equivalent to 6-31G* basis sets. The self-consistent-field calculation complied with the convergence criteria of 10^{-6} Hartree, and the tolerances of energy, maximal force, and maximal displacement for the geometry optimization were set to 1.0×10^{-5} au, 0.002 au and 0.005 au, respectively. After the geometries of all involving molecules were optimized at this level, the interaction energy E_{inter} was obtained as:

$$-E_{inter} = \Delta E = E_{total} - E_{solute} - E_{solvent} \quad (6)$$

Herein, parameters E_{total} and E_{solute} represent the energies of 3-nitropyrazole + binary solvent and 3-nitropyrazole, respectively; $E_{solvent}$ stands for energy of selected solvent. Values of solvent polarity and interaction energy E_{inter} calculated by Dmol^3 are presented in Table 3.

2.6. Experimental procedures

In this research work, the solubility of 3-nitropyrazole in four selected binary solvents including "water + methanol, ethanol, 1-propanol and acetone" at 283.15–323.15 K was investigated by a laser monitoring method. The experimental approach and apparatus were similar to our previous published paper and briefly

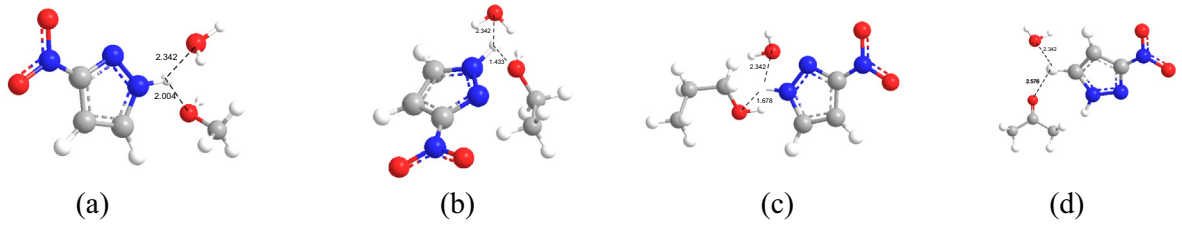

Fig. 5. Optimized structures between 3-nitropyrazole and methanol + water (a), ethanol + water (b), 1-propanol + water (c) and acetone + water (d), respectively. The dashed lines indicate hydrogen bonds with a distance (Unit: Å, 1 Ã. . . = 0.1 nm).

Table 2
Hansen solubility parameter of selected binary solvents and 3-nitropyrazole.

w_1	δ_d $(MPa)^{0.5}$	δ_p $(MPa)^{0.5}$	δ_h $(MPa)^{0.5}$	δ_t $(MPa)^{0.5}$	$\Delta\delta_t$ $(MPa)^{0.5}$
Water + methanol					
0.1000	13.9	13.8	23.3	30.4	0.17
0.2000	25.8	15.4	24.3	38.6	8.38
0.3000	35.4	17.1	25.3	46.8	16.5
0.4000	42.3	18.9	26.4	53.3	23.1
0.5000	46.1	20.7	27.6	57.6	27.3
0.6000	46.4	22.6	28.8	59.1	28.9
0.7000	42.6	24.6	30.1	57.7	27.4
0.8000	34.1	26.7	31.4	53.5	23.3
0.9000	20.2	29.0	32.8	48.2	17.9
Water + ethanol					
0.1000	14.4	10.6	20.7	27.4	2.91
0.2000	26.7	12.5	21.9	36.8	6.52
0.3000	36.7	14.5	23.2	45.8	15.5
0.4000	43.9	16.6	24.6	53.0	22.7
0.5000	47.9	18.7	26.0	57.6	27.4
0.6000	48.2	21.0	27.5	59.4	29.1
0.7000	44.3	23.4	29.1	57.9	27.7
0.8000	35.5	25.9	30.7	53.6	23.4
0.9000	21.0	28.5	32.5	48.1	17.8
Water + 1-propanol					
0.1000	14.7	8.80	18.8	25.4	4.86
0.2000	27.2	10.9	20.2	35.6	5.30
0.3000	37.2	13.1	21.7	45.0	14.7
0.4000	44.4	15.3	23.3	52.4	22.1
0.5000	48.3	17.7	24.9	57.1	26.9
0.6000	48.5	20.2	26.6	58.9	28.6
0.7000	44.4	22.8	28.4	57.4	27.2
0.8000	35.5	25.5	30.3	53.1	22.9
0.9000	20.9	28.3	32.2	47.7	17.5
Water + acetone					
0.1000	14.1	12.1	9.22	20.7	9.58
0.2000	26.1	13.8	11.5	31.7	1.45
0.3000	35.9	15.7	13.9	41.5	11.3
0.4000	43.0	17.6	16.4	49.2	19.0
0.5000	47.0	19.6	19.0	54.3	24.1
0.6000	47.3	21.7	21.8	56.4	26.2
0.7000	43.6	23.9	24.7	55.5	25.2
0.8000	34.9	26.2	27.7	51.7	21.5
0.9000	20.7	28.7	30.9	47.0	16.7
3-nitropyrazole	16.6	22.0	12.5	30.3	0.00

Table 3
Values of interaction energy E_{inter} calculated by Dmol^3.[a]

Solvents	E_{total}/ (Hartree)	$E_{solvent}/E_{solute}$/ (Hartree)	E_{inter}/ (kJ·mol^{-1})
Methanol	−970.00	−115.65	48.44
Ethanol	−1009.28	−154.94	62.17
1-propanol	−1041.71	−187.36	52.25
Acetone	−1067.55	−213.21	17.18
Water	−958.65	−104.32	4.18
Water + methanol	−1074.31	−219.97	26.26
Water + ethanol	−1113.61	−259.26	57.76
Water + 1-propanol	−1146.02	−291.68	34.13
Water + acetone	−1171.87	−317.53	21.00
3-nitropyrazole		−854.33	

[a] 1 Hartree = 2625.5 kJ·mol^{-1}.

described here [18–20]. 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 3-nitropyrazole in selected binary solvents. The mixture solution was stirred for>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 3-nitropyrazole 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 (x_1) of 3-nitropyrazole in binary solvents can be expressed as:

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \tag{7}$$

$$x_2 = \frac{m_2/M_2}{m_2/M_2 + m_3/M_3} \tag{8}$$

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

Table 4
Mole fraction solubility (x_1) of 3-nitropyrazole in binary solvent mixtures at different temperatures from 283.15 K to 323.15 K and P = 0.1 MPa[a,b].

T/K	$10^3 \cdot x_1^{exp}$	$10^3 \cdot x_1^{AP}$	$10^3 \cdot x_1^{\lambda h}$	$10^3 \cdot x_1^{JA}$	$10^3 \cdot x_1^{RK}$
Water + methanol (w_1 = 0.1000)					
283.15	3.83	3.49	3.52	3.72	3.85
288.15	4.85	4.64	4.67	4.80	4.87
293.15	6.02	6.12	6.13	6.16	6.04
298.15	7.49	7.98	7.98	7.88	7.50
303.15	9.88	10.31	10.30	10.03	9.90
308.15	13.62	13.19	13.17	12.73	13.61
313.15	16.79	16.73	16.70	16.09	16.77
318.15	21.30	21.04	21.03	20.26	21.31
323.15	26.03	26.24	26.27	25.41	26.07
Water + methanol (w_1 = 0.2000)					
283.15	3.73	3.93	3.17	3.37	3.69
288.15	4.58	4.66	4.14	4.35	4.54
293.15	5.62	5.61	5.37	5.60	5.55
298.15	6.87	6.85	6.90	7.17	6.83
303.15	8.57	8.47	8.79	9.15	8.51
308.15	10.62	10.60	11.11	11.62	10.72
313.15	13.49	13.41	13.94	14.71	13.60
318.15	17.30	17.15	17.37	18.54	17.30
323.15	21.97	22.14	21.50	23.30	21.89
Water + methanol (w_1 = 0.3000)					
283.15	3.52	3.54	2.98	3.06	3.52
288.15	4.31	4.30	3.91	3.96	4.34
293.15	5.31	5.29	5.09	5.10	5.36
298.15	6.57	6.55	6.57	6.54	6.58
303.15	8.14	8.18	8.40	8.36	8.15
308.15	10.29	10.30	10.67	10.63	10.10
313.15	13.10	13.05	13.44	13.47	12.85
318.15	16.61	16.64	16.81	17.01	16.50
323.15	21.36	21.35	20.88	21.39	21.32
Water + methanol (w_1 = 0.4000)					
283.15	3.16	3.25	2.67	2.75	3.24
288.15	4.01	3.96	3.55	3.56	4.02
293.15	5.01	4.88	4.66	4.59	5.03
298.15	6.13	6.07	6.07	5.90	6.17
303.15	7.69	7.62	7.84	7.54	7.73
308.15	9.61	9.67	10.04	9.61	9.69
313.15	12.17	12.35	12.76	12.19	12.28
318.15	15.86	15.91	16.09	15.42	15.90
323.15	20.73	20.62	20.14	19.42	20.77
Water + methanol (w_1 = 0.5000)					
283.15	2.87	3.08	2.35	2.39	2.80
288.15	3.50	3.62	3.11	3.10	3.49
293.15	4.39	4.34	4.09	4.00	4.37
298.15	5.36	5.30	5.32	5.15	5.36
303.15	6.74	6.58	6.87	6.61	6.76
308.15	8.45	8.31	8.80	8.43	8.57
313.15	10.62	10.66	11.17	10.72	10.89
318.15	13.80	13.85	14.08	13.58	14.11
323.15	18.21	18.24	17.63	17.15	18.52
Water + methanol (w_1 = 0.6000)					
283.15	2.24	2.24	1.83	1.96	2.24
288.15	2.78	2.75	2.45	2.56	2.79
293.15	3.46	3.41	3.24	3.31	3.45
298.15	4.23	4.27	4.26	4.28	4.22
303.15	5.39	5.41	5.55	5.50	5.32
308.15	6.79	6.90	7.17	7.04	6.72
313.15	8.98	8.89	9.18	8.98	8.67
318.15	11.54	11.53	11.67	11.40	11.17
323.15	15.05	15.06	14.72	14.43	14.65
Water + methanol (w_1 = 0.7000)					
283.15	1.71	1.76	1.41	1.49	1.65
288.15	2.16	2.12	1.87	1.95	2.05
293.15	2.61	2.58	2.46	2.54	2.50
298.15	3.21	3.19	3.20	3.29	3.06
303.15	3.97	3.99	4.13	4.25	3.84
308.15	5.02	5.05	5.28	5.46	4.79
313.15	6.53	6.46	6.70	6.99	6.33
318.15	8.29	8.35	8.45	8.92	8.08
323.15	10.89	10.87	10.59	11.33	10.58
Water + methanol (w_1 = 0.8000)					
283.15	0.99	1.00	0.81	1.02	1.12
288.15	1.25	1.23	1.09	1.34	1.41
293.15	1.54	1.53	1.45	1.75	1.73

(*continued on next page*)

Table 4 (*continued*)

T/K	$10^3 \cdot x_1^{exp}$	$10^3 \cdot x_1^{AP}$	$10^3 \cdot x_1^{\lambda h}$	$10^3 \cdot x_1^{lA}$	$10^3 \cdot x_1^{RK}$
298.15	1.90	1.92	1.91	2.28	2.15
303.15	2.43	2.43	2.50	2.97	2.72
308.15	3.07	3.11	3.23	3.83	3.39
313.15	4.07	4.02	4.15	4.94	4.55
318.15	5.23	5.23	5.29	6.33	5.81
323.15	6.84	6.85	6.70	8.08	7.62
Water + methanol (w_1 = 0.9000)					
283.15	0.78	0.79	0.67	0.60	0.71
288.15	1.02	1.02	0.93	0.80	0.94
293.15	1.33	1.32	1.26	1.05	1.23
298.15	1.70	1.71	1.70	1.39	1.59
303.15	2.25	2.23	2.26	1.81	2.13
308.15	2.85	2.91	2.99	2.36	2.75
313.15	3.86	3.82	3.91	3.07	3.68
318.15	5.02	5.03	5.07	3.96	4.79
323.15	6.63	6.63	6.54	5.09	6.32
Water + ethanol (w_1 = 0.1000)					
283.15	14.42	14.40	13.00	13.19	14.41
288.15	16.36	16.26	15.51	15.59	16.34
293.15	18.56	18.54	18.39	18.39	18.54
298.15	21.24	21.31	21.70	21.63	21.22
303.15	24.23	24.69	25.48	25.38	24.20
308.15	28.92	28.82	29.78	29.70	28.89
313.15	34.12	33.86	34.66	34.67	34.07
318.15	40.34	40.04	40.17	40.38	40.28
323.15	47.36	47.63	46.38	46.93	47.27
Water + ethanol (w_1 = 0.2000)					
283.15	8.47	8.53	7.44	7.60	8.53
288.15	9.72	9.71	9.09	9.15	9.80
293.15	11.20	11.20	11.03	10.98	11.30
298.15	13.07	13.05	13.30	13.14	13.20
303.15	15.51	15.37	15.94	15.68	15.65
308.15	18.25	18.27	19.01	18.66	18.44
313.15	21.69	21.91	22.56	22.15	21.97
318.15	26.67	26.49	26.64	26.22	27.03
323.15	32.23	32.28	31.32	30.96	32.67
Water + ethanol (w_1 = 0.3000)					
283.15	4.75	4.86	4.10	4.25	4.63
288.15	5.58	5.58	5.12	5.21	5.43
293.15	6.56	6.51	6.35	6.37	6.36
298.15	7.71	7.68	7.81	7.76	7.46
303.15	9.27	9.18	9.56	9.42	9.00
308.15	11.07	11.10	11.62	11.41	10.70
313.15	13.45	13.57	14.05	13.77	12.93
318.15	16.91	16.75	16.89	16.58	16.26
323.15	20.78	20.86	20.20	19.90	20.03
Water + ethanol (w_1 = 0.4000)					
283.15	2.54	2.61	2.18	2.36	2.52
288.15	3.05	3.05	2.77	2.95	3.02
293.15	3.67	3.60	3.49	3.67	3.61
298.15	4.34	4.32	4.37	4.55	4.30
303.15	5.31	5.23	5.43	5.63	5.22
308.15	6.40	6.42	6.71	6.93	6.33
313.15	7.83	7.95	8.23	8.51	7.78
318.15	9.99	9.95	10.05	10.42	9.86
323.15	12.58	12.56	12.19	12.71	12.32
Water + ethanol (w_1 = 0.5000)					
283.15	1.22	1.22	1.07	1.34	1.46
288.15	1.47	1.47	1.37	1.70	1.79
293.15	1.79	1.79	1.75	2.16	2.20
298.15	2.22	2.20	2.21	2.73	2.71
303.15	2.69	2.71	2.78	3.43	3.30
308.15	3.38	3.36	3.46	4.30	4.10
313.15	4.19	4.19	4.29	5.37	5.11
318.15	5.23	5.25	5.29	6.68	6.48
323.15	6.61	6.60	6.48	8.28	8.20
Water + ethanol (w_1 = 0.6000)					
283.15	1.02	1.02	0.91	0.81	0.94
288.15	1.27	1.27	1.20	1.05	1.17
293.15	1.59	1.59	1.55	1.35	1.48
298.15	2.03	1.99	2.00	1.73	1.92
303.15	2.50	2.50	2.55	2.21	2.35
308.15	3.15	3.15	3.23	2.82	2.98
313.15	3.99	3.98	4.06	3.57	3.76
318.15	5.02	5.04	5.07	4.51	4.76

Table 4 (*continued*)

T/K	$10^3 \cdot x_1^{exp}$	$10^3 \cdot x_1^{AP}$	$10^3 \cdot x_1^{\lambda h}$	$10^3 \cdot x_1^{lA}$	$10^3 \cdot x_1^{RK}$
323.15	6.40	6.39	6.30	5.68	6.08
Water + ethanol (w_1 = 0.7000)					
283.15	0.80	0.81	0.76	0.54	0.69
288.15	1.02	1.05	1.02	0.71	0.86
293.15	1.35	1.37	1.35	0.93	1.12
298.15	1.85	1.77	1.77	1.21	1.50
303.15	2.28	2.29	2.30	1.57	1.86
308.15	2.93	2.94	2.97	2.03	2.37
313.15	3.75	3.77	3.81	2.61	3.04
318.15	4.80	4.82	4.84	3.35	3.84
323.15	6.16	6.14	6.10	4.27	4.94
Water + ethanol (w_1 = 0.8000)					
283.15	0.58	0.57	0.49	0.42	0.56
288.15	0.70	0.69	0.64	0.56	0.71
293.15	0.87	0.85	0.82	0.74	0.92
298.15	1.06	1.05	1.06	0.98	1.22
303.15	1.31	1.31	1.35	1.29	1.54
308.15	1.59	1.65	1.70	1.69	1.93
313.15	2.10	2.08	2.14	2.20	2.53
318.15	2.65	2.64	2.67	2.85	3.21
323.15	3.37	3.37	3.31	3.68	4.12
Water + ethanol (w_1 = 0.9000)					
283.15	0.45	0.45	0.40	0.41	0.49
288.15	0.59	0.57	0.53	0.55	0.63
293.15	0.75	0.73	0.70	0.73	0.79
298.15	0.90	0.93	0.93	0.98	0.91
303.15	1.21	1.19	1.21	1.29	1.20
308.15	1.46	1.52	1.56	1.71	1.42
313.15	1.98	1.96	2.00	2.24	1.94
318.15	2.56	2.53	2.55	2.93	2.51
323.15	3.25	3.27	3.22	3.82	3.16
Water + 1-propanol (w_1 = 0.1000)					
283.15	11.78	12.11	10.88	10.91	11.80
288.15	13.63	13.52	12.88	12.84	13.64
293.15	15.53	15.27	15.18	15.07	15.55
298.15	17.63	17.42	17.80	17.64	17.65
303.15	20.06	20.05	20.77	20.59	20.10
308.15	23.22	23.29	24.15	23.98	23.26
313.15	26.92	27.27	27.96	27.86	26.97
318.15	32.30	32.17	32.25	32.29	32.45
323.15	38.26	38.21	37.09	37.33	38.35
Water + 1-propanol (w_1 = 0.2000)					
283.15	9.18	9.19	8.17	8.31	9.10
288.15	10.51	10.45	9.87	9.95	10.44
293.15	12.01	12.00	11.86	11.86	11.91
298.15	13.95	13.92	14.18	14.11	13.83
303.15	16.21	16.29	16.85	16.73	16.01
308.15	19.02	19.23	19.93	19.78	18.88
313.15	22.85	22.86	23.46	23.33	22.67
318.15	27.77	27.37	27.49	27.45	27.09
323.15	32.79	32.99	32.09	32.20	32.46
Water + 1-propanol (w_1 = 0.3000)					
283.15	6.59	6.69	5.79	6.11	6.71
288.15	7.74	7.69	7.16	7.44	7.81
293.15	9.00	8.95	8.78	9.02	9.12
298.15	10.62	10.53	10.71	10.90	10.76
303.15	12.42	12.51	12.97	13.14	12.69
308.15	15.14	15.01	15.63	15.79	15.24
313.15	18.35	18.17	18.73	18.92	18.47
318.15	21.63	22.18	22.33	22.60	22.57
323.15	27.55	27.28	26.49	26.92	27.82
Water + 1-propanol (w_1 = 0.4000)					
283.15	4.82	4.89	4.08	4.30	4.78
288.15	5.65	5.67	5.16	5.32	5.68
293.15	6.74	6.67	6.47	6.57	6.77
298.15	8.04	7.94	8.06	8.08	8.08
303.15	9.70	9.59	9.96	9.91	9.70
308.15	11.59	11.70	12.24	12.10	11.78
313.15	14.12	14.42	14.94	14.74	14.33
318.15	18.26	17.96	18.13	17.89	18.01
323.15	22.51	22.57	21.88	21.65	22.75
Water + 1-propanol (w_1 = 0.5000)					
283.15	3.35	3.45	2.87	2.86	3.29
288.15	4.05	4.05	3.67	3.61	3.96
293.15	4.90	4.83	4.67	4.55	4.78

(*continued on next page*)

Table 4 (*continued*)

T/K	$10^3 \cdot x_1^{exp}$	$10^3 \cdot x_1^{AP}$	$10^3 \cdot x_1^{\lambda h}$	$10^3 \cdot x_1^{lA}$	$10^3 \cdot x_1^{RK}$
298.15	5.88	5.82	5.88	5.69	5.76
303.15	7.20	7.10	7.36	7.10	7.01
308.15	8.76	8.75	9.15	8.83	8.54
313.15	10.72	10.91	11.29	10.94	10.50
318.15	13.73	13.72	13.86	13.50	13.46
323.15	17.44	17.40	16.90	16.61	17.19
Water + 1-propanol (w_1 = 0.6000)					
283.15	2.15	2.20	1.82	1.79	2.15
288.15	2.65	2.62	2.37	2.31	2.61
293.15	3.21	3.17	3.05	2.96	3.17
298.15	3.95	3.88	3.90	3.78	3.86
303.15	4.79	4.80	4.95	4.80	4.74
308.15	5.96	5.99	6.23	6.08	5.79
313.15	7.48	7.54	7.79	7.67	7.26
318.15	9.60	9.58	9.68	9.64	9.39
323.15	12.28	12.26	11.95	12.06	11.95
Water + 1-propanol (w_1 = 0.7000)					
283.15	1.27	1.34	1.05	1.04	1.30
288.15	1.56	1.59	1.39	1.37	1.59
293.15	1.92	1.91	1.82	1.79	1.96
298.15	2.37	2.34	2.35	2.34	2.42
303.15	2.95	2.91	3.03	3.03	3.00
308.15	3.64	3.67	3.86	3.91	3.72
313.15	4.74	4.69	4.89	5.03	4.77
318.15	6.09	6.05	6.14	6.44	6.19
323.15	7.86	7.91	7.67	8.21	7.82
Water + 1-propanol (w_1 = 0.8000)					
283.15	0.57	0.57	0.48	0.56	0.70
288.15	0.70	0.72	0.65	0.75	0.87
293.15	0.91	0.90	0.86	1.00	1.14
298.15	1.15	1.14	1.14	1.34	1.43
303.15	1.44	1.46	1.49	1.77	1.80
308.15	1.89	1.88	1.94	2.33	2.33
313.15	2.42	2.43	2.49	3.06	3.02
318.15	3.16	3.15	3.19	4.00	3.99
323.15	4.11	4.12	4.04	5.20	5.07
Water + 1-propanol (w_1 = 0.9000)					
283.15	0.47	0.47	0.40	0.27	0.32
288.15	0.60	0.61	0.56	0.37	0.42
293.15	0.82	0.80	0.76	0.51	0.62
298.15	1.06	1.04	1.04	0.70	0.81
303.15	1.35	1.37	1.39	0.94	1.05
308.15	1.80	1.80	1.84	1.27	1.48
313.15	2.30	2.38	2.42	1.71	1.89
318.15	3.24	3.14	3.16	2.28	2.64
323.15	4.11	4.14	4.09	3.02	3.53
Water + acetone (w_1 = 0.1000)					
283.15	1.26	1.29	1.22	1.11	1.15
288.15	1.47	1.46	1.42	1.33	1.42
293.15	1.67	1.66	1.65	1.56	1.65
298.15	1.94	1.89	1.91	1.88	1.95
303.15	2.17	2.16	2.21	2.15	2.06
308.15	2.43	2.49	2.54	2.45	2.40
313.15	2.86	2.87	2.91	2.94	2.83
318.15	3.35	3.33	3.33	3.49	3.32
323.15	3.87	3.87	3.80	4.03	3.89
Water + acetone (w_1 = 0.2000)					
283.15	1.09	1.12	0.99	0.98	1.23
288.15	1.26	1.25	1.18	1.15	1.40
293.15	1.42	1.42	1.40	1.34	1.58
298.15	1.63	1.62	1.66	1.56	1.80
303.15	1.88	1.88	1.95	1.84	2.07
308.15	2.19	2.19	2.28	2.17	2.40
313.15	2.58	2.59	2.66	2.59	2.81
318.15	3.12	3.08	3.09	3.18	3.31
323.15	3.66	3.69	3.58	3.72	3.83
Water + acetone (w_1 = 0.3000)					
283.15	1.00	0.99	0.93	0.91	0.82
288.15	1.13	1.13	1.09	1.06	0.95
293.15	1.28	1.29	1.28	1.22	1.08
298.15	1.47	1.48	1.50	1.42	1.26
303.15	1.68	1.70	1.74	1.65	1.46
308.15	1.97	1.97	2.01	1.94	1.73
313.15	2.32	2.29	2.32	2.29	2.07
318.15	2.70	2.67	2.68	2.66	2.50

Table 4 (*continued*)

T/K	$10^3 \cdot x_1^{exp}$	$10^3 \cdot x_1^{AP}$	$10^3 \cdot x_1^{\lambda h}$	$10^3 \cdot x_1^{lA}$	$10^3 \cdot x_1^{RK}$
323.15	3.10	3.13	3.07	3.02	2.96
Water + acetone (w_1 = 0.4000)					
283.15	0.87	0.88	0.80	0.83	0.82
288.15	1.01	1.00	0.96	0.97	0.95
293.15	1.15	1.15	1.14	1.12	1.08
298.15	1.33	1.33	1.35	1.30	1.25
303.15	1.54	1.55	1.59	1.52	1.45
308.15	1.81	1.82	1.87	1.79	1.71
313.15	2.16	2.14	2.19	2.13	2.05
318.15	2.55	2.54	2.55	2.50	2.45
323.15	3.03	3.03	2.97	2.94	2.89
Water + acetone (w_1 = 0.5000)					
283.15	0.79	0.79	0.71	0.78	0.86
288.15	0.90	0.90	0.85	0.90	0.98
293.15	1.04	1.04	1.03	1.04	1.12
298.15	1.20	1.21	1.23	1.21	1.30
303.15	1.40	1.42	1.46	1.41	1.50
308.15	1.67	1.67	1.73	1.67	1.77
313.15	1.99	1.99	2.04	1.97	2.11
318.15	2.41	2.39	2.40	2.36	2.51
323.15	2.86	2.88	2.81	2.76	2.96
Water + acetone (w_1 = 0.6000)					
283.15	0.71	0.72	0.63	0.74	0.78
288.15	0.82	0.82	0.77	0.85	0.89
293.15	0.95	0.95	0.94	0.98	1.03
298.15	1.12	1.12	1.13	1.15	1.20
303.15	1.32	1.32	1.36	1.34	1.41
308.15	1.56	1.57	1.63	1.58	1.67
313.15	1.89	1.89	1.94	1.88	1.99
318.15	2.32	2.28	2.29	2.27	2.41
323.15	2.76	2.78	2.71	2.65	2.87
Water + acetone (w_1 = 0.7000)					
283.15	0.63	0.64	0.55	0.69	0.60
288.15	0.73	0.73	0.68	0.80	0.70
293.15	0.85	0.85	0.83	0.93	0.82
298.15	1.01	1.00	1.02	1.08	0.97
303.15	1.20	1.19	1.23	1.26	1.16
308.15	1.43	1.43	1.49	1.47	1.40
313.15	1.73	1.74	1.79	1.75	1.70
318.15	2.13	2.12	2.14	2.10	2.11
323.15	2.62	2.62	2.54	2.52	2.59
Water + acetone (w_1 = 0.8000)					
283.15	0.55	0.55	0.49	0.65	0.45
288.15	0.65	0.64	0.60	0.75	0.55
293.15	0.76	0.76	0.75	0.87	0.65
298.15	0.91	0.91	0.92	1.01	0.79
303.15	1.07	1.09	1.12	1.18	0.95
308.15	1.32	1.32	1.36	1.40	1.18
313.15	1.61	1.60	1.64	1.66	1.46
318.15	1.95	1.96	1.97	1.95	1.83
323.15	2.41	2.41	2.36	2.33	2.30
Water + acetone (w_1 = 0.9000)					
283.15	0.43	0.43	0.40	0.60	0.48
288.15	0.55	0.53	0.51	0.70	0.59
293.15	0.64	0.65	0.64	0.81	0.69
298.15	0.81	0.80	0.80	0.96	0.86
303.15	0.95	0.99	1.00	1.10	1.00
308.15	1.24	1.21	1.24	1.34	1.29
313.15	1.51	1.50	1.52	1.58	1.57
318.15	1.84	1.85	1.85	1.86	1.89
323.15	2.28	2.28	2.25	2.22	2.33

[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}, $x_1^{\lambda h}$, x_1^{lA} and x_1^{RK} represent the calculated mole fraction solubility correlated by the modified Apelblat equation, λh equation, Jouyban-Acree model and CNIBS/R-K model, respectively.

Where x_1 represents the solubility of 3-nitropyrazole in binary solvents; x_2 is the mole fraction of water in binary mixed solvents; w_1 is the mass fraction of water in binary solvents mixtures; m_1, m_2, m_3, and M_1, M_2, M_3 represent the mass and molar mass of 3-nitropyrazole, water and (methanol, ethanol, 1-propanol and acetone), respectively.

3. Results and discussion

3.1. Solubility models

In order to demonstrate the error and evaluate the different models, the root-mean-square deviation (RMSD) is employed, which is expressed as Eq. (10).

$$RMSD = \left[\frac{\sum_{i=1}^{n}\left(x_i^c - x_i^e\right)^2}{N}\right]^{1/2} \quad (10)$$

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 3-nitropyrazole were correlated by the modified Apelblat equation [21–23]. It is simple and commonly to be written as follows:

$$\ln x_1 = A + \frac{B}{T} + C\ln T \quad (11)$$

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. Table 5 contains data of the model parameters A, B, C, 10^4RMSD and R^2.

3.1.2. λh equation

λh equation was proposed by Buchowski et al. that can give an excellent solubility correlation for most systems with only two variable parameters, λ and h. The equation can be written as [24]:

$$\frac{1}{x_1} - 1 = \frac{1}{\lambda}\left\{\exp\left[\lambda h\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] - 1\right\} \quad (12)$$

Where T_m represents the melting temperature of the corresponding solid. The values of model parameters λ, h, 10^4RMSD and R^2 are presented in Table 6.

3.1.3. Jouyban-Acree model

The Jouyban-Acree model [25,26] is a semi-empirical thermodynamic model that it is widely used to correlate the relationship between both temperature and solvent composition with the solubility. The equation can be expressed as:

$$\ln x_1 = A_1 + A_2/T + A_3\ln T + A_4x_2 + A_5x_2/T + A_6(x_2)^2/T + A_7(x_2)^3/T + A_8(x_2)^4/T + A_9x_2\ln T \quad (13)$$

Where A_1-A_9 are empirical model parameters. Table 7 contains the model parameters, 10^4RMSD and R^2.

3.1.4. CNIBS/R-K model

The CNIBS/R-K equation, which was proposed by Acree [27,28], is suitable for binary mixed systems. It is mainly used to describe the relationship between the solubility and the composition of mixed solvent when the temperature is constant, which can be expressed as follows:

$$\ln x_1 = B_0 + B_1x_2 + B_2x_2^2 + B_3x_2^3 + B_4x_2^4 \quad (14)$$

Table 5
Model parameters and 10^4RMSD of the modified Apelblat equation in different binary solvents.

w_1	A	B	C	10^4RMSD	R^2
Water + methanol					
0.1000	36.74	−5792.00	−3.89	3.18	0.9981
0.2000	−467.65	17482.63	70.91	1.14	0.9996
0.3000	−359.84	12489.24	54.92	0.28	0.9999
0.4000	−398.18	14115.39	60.68	0.97	0.9997
0.5000	−570.86	22019.44	86.31	1.12	0.9995
0.6000	−405.49	14316.37	61.78	0.56	0.9998
0.7000	−457.45	16808.12	69.38	0.40	0.9998
0.8000	−408.93	14396.86	62.20	0.26	0.9998
0.9000	−291.15	8693.58	44.86	0.26	0.9998
Water + ethanol					
0.1000	−298.07	10928.40	45.21	2.28	0.9995
0.2000	−365.97	13702.86	55.40	1.07	0.9998
0.3000	−425.46	16114.13	64.33	0.90	0.9997
0.4000	−431.36	16133.89	65.26	0.61	0.9996
0.5000	−306.54	10249.65	46.69	0.14	0.9999
0.6000	−244.07	7157.71	37.53	0.16	0.9999
0.7000	−116.74	1033.90	18.77	0.32	0.9997
0.8000	−343.1	11689.04	52.14	0.22	0.9994
0.9000	−268.83	7959.14	41.27	0.31	0.9988
Water + 1-propanol					
0.1000	−328.22	12368.34	49.61	2.03	0.9994
0.2000	−328.08	12100.86	49.71	1.66	0.9995
0.3000	−373.48	13885.54	56.58	2.27	0.9988
0.4000	−429.65	16160.89	65.05	1.61	0.9992
0.5000	−429.28	15962.02	65.04	0.87	0.9996
0.6000	−408.71	14818.15	62.03	0.39	0.9999
0.7000	−516.71	19552.99	78.12	0.42	0.9996
0.8000	−348.36	11554.79	53.15	0.11	0.9999
0.9000	−258.12	7074.93	39.93	0.47	0.9984
Water + acetone					
0.1000	−213.74	7251.71	32.16	0.29	0.9988
0.2000	−362.39	13713.33	54.40	0.20	0.9994
0.3000	−215.36	7174.28	32.43	0.16	0.9994
0.4000	−277.81	9801.89	41.83	0.09	0.9998
0.5000	−319.58	11575.02	48.10	0.11	0.9997
0.6000	−351.16	12884.17	52.86	0.15	0.9995
0.7000	−381.06	14102.91	57.37	0.06	0.9999
0.8000	−314.90	10993.43	47.57	0.07	0.9999
0.9000	−195.13	5245.31	29.91	0.17	0.9991

Table 6
Model parameters and the 10^4RMSD of the λh equation in different binary solvents.

w_1	λ	h	10^4RMSD	R^2
Water + methanol				
0.1000	1.40	3300.73	3.18	0.9981
0.2000	0.93	4724.45	3.81	0.9961
0.3000	0.96	4628.19	3.51	0.9965
0.4000	1.08	4300.05	4.11	0.9950
0.5000	0.93	4965.35	3.91	0.9940
0.6000	0.89	5359.74	2.71	0.9960
0.7000	0.54	8438.84	2.20	0.9948
0.8000	0.41	11628.68	1.17	0.9965
0.9000	0.56	9220.77	0.79	0.9984
Water + ethanol				
0.1000	0.51	5565.59	8.23	0.9938
0.2000	0.49	6615.63	6.57	0.9928
0.3000	0.44	8263.44	4.41	0.9930
0.4000	0.34	11481.66	2.72	0.9931
0.5000	0.21	19298.76	0.95	0.9972
0.6000	0.27	16354.43	0.71	0.9984
0.7000	0.36	13342.34	0.44	0.9994
0.8000	0.14	31965.23	0.62	0.9958
0.9000	0.19	24929.63	0.47	0.9975
Water + 1-propanol				
0.1000	0.35	7614.56	7.69	0.9918
0.2000	0.43	7156.40	6.36	0.9933
0.3000	0.49	6955.86	6.09	0.9918
0.4000	0.57	6673.90	5.20	0.9920
0.5000	0.53	7554.48	3.72	0.9935
0.6000	0.47	9182.82	2.43	0.9947
0.7000	0.37	12252.31	1.48	0.9955
0.8000	0.26	18752.95	0.57	0.9978
0.9000	0.38	13843.78	0.62	0.9974
Water + acetone				
0.1000	2.63×10^{-2}	91284.04	0.54	0.9958
0.2000	3.58×10^{-2}	77756.01	0.68	0.9935
0.3000	2.47×10^{-2}	103604.77	0.37	0.9972
0.4000	3.17×10^{-2}	90079.54	0.47	0.9955
0.5000	3.54×10^{-2}	85616.54	0.50	0.9946
0.6000	4.03×10^{-2}	79697.24	0.48	0.9949
0.7000	4.53×10^{-2}	75293.19	0.52	0.9937
0.8000	4.67×10^{-2}	75551.75	0.39	0.9959
0.9000	6.17×10^{-2}	63000.60	0.27	0.9980

Table 7
Model parameters and 10^4RMSD of Jouyban-Acree model in binary solvent systems.

Water + methanol		Water + ethanol		Water + 1-propanol		Water + acetone	
A_1	−87.85	A_1	−55.93	A_1	−52.54	A_1	−39.22
A_2	26.19	A_2	153.74	A_2	40.16	A_2	−2.86
A_3	14.54	A_3	9.13	A_3	8.52	A_3	5.58
A_4	−7.42	A_4	−59.72	A_4	−53.55	A_4	15138.62
A_5	11.13	A_5	34.26	A_5	5.05	A_5	330.05
A_6	324.15	A_6	−760.66	A_6	−287.66	A_6	−0.02
A_7	−319.81	A_7	212.90	A_7	−335.04	A_7	0.96
A_8	−405.29	A_8	850.94	A_8	−68.43	A_8	0.01
A_9	1.09	A_9	9.70	A_9	9.07	A_9	−2555.10
10^4RMSD	5.30	10^4RMSD	5.41	10^4RMSD	4.73	10^4RMSD	3.71
R^2	0.9905	R^2	0.9961	R^2	0.9968	R^2	0.9900

Where x_2 is the mole fraction of water in binary mixed solvents; B_0, B_1, B_2, B_3 and B_4 are the model parameters. The model parameters values of B_0, B_1, B_2, B_3, B_4, 10^4RMSD and R^2 are displayed in Table 8.

3.2. Solubility data

In four correlation models, it can be showed that small differences exist between the calculated values and experimental data at different temperature in mixed binary systems, which provide a convincing evidence for the accuracy of experimental data. According to Table 4, it can be seen clearly that the calculated values are close to the experimental values. From Tables 5-8, it can be observed easily that the average values of 10^4RMSD of selected four models: the modified Apelblat equation, λh equation, Jouyban-Acree model and CNIBS/R-K model are 0.70, 2.47, 4.79 and 1.51, respectively. In addition, the average values R^2 of 3-nitropyrazole within the experimental temperature range of these equations are 0.9995 (the modified Apelblat equation), 0.9954 (λh equation), 0.9934 (Jouyban-Acree model) and 0.9972 (CNIBS/R-K model). And the values of R^2 and the values of 10^4RMSD indicated that all the four equations can present a satisfactory fitting results in the mixed solvents and well correlated with experimental data of 3-nitropyrazole. Therefore, by comparing the data of 10^4RMSD and R^2, the correlation between solubility and temperature goodness order is the modified Apelblat equation > CNIBS/R-K mod-

Table 8
Model parameters and the 10^4RMSD of the CNIBS/R-K model in different binary solvents.

T/K	B_0	B_1	B_2	B_3	B_4	10^4RMSD	R^2
Water + methanol							
283.15	−5.49	−1.08	4.07	−8.70	3.43	0.19	0.9965
288.15	−5.16	−2.36	8.97	−16.10	7.31	0.69	0.9971
293.15	−4.87	−3.64	14.63	−25.41	12.37	1.13	0.9973
298.15	−4.62	−4.07	16.27	−28.11	13.95	0.61	0.9972
303.15	−4.19	−6.29	24.07	−39.16	19.43	1.79	0.9979
308.15	−3.66	−9.32	34.11	−52.65	25.76	2.12	0.9978
313.15	−3.53	−8.09	29.55	−45.86	22.41	1.81	0.9964
318.15	−3.27	−8.48	31.64	−49.52	24.43	4.11	0.9973
323.15	−3.12	−7.91	30.79	−49.17	24.50	1.63	0.9973
Water + ethanol							
283.15	−3.91	−1.82	−16.72	24.90	−10.18	0.42	0.9995
288.15	−3.79	−1.95	−15.50	23.16	−9.39	2.33	0.9993
293.15	−3.69	−1.59	−16.69	25.95	−11.32	4.22	0.9990
298.15	−3.64	−0.23	−23.02	38.14	−18.78	1.08	0.9987
303.15	−3.57	0.64	−25.01	39.91	−19.14	8.43	0.9985
308.15	−3.35	0.04	−23.16	38.66	−19.31	1.85	0.9984
313.15	−3.19	−0.05	−22.18	37.06	−18.38	6.36	0.9980
318.15	−3.08	0.72	−23.61	37.90	−18.36	3.71	0.9975
323.15	−2.97	1.32	−25.04	39.87	−19.45	0.46	0.9971
Water + 1-propanol							
283.15	−4.25	−1.47	−5.09	6.89	−5.15	0.07	0.9995
288.15	−4.05	−2.36	−1.15	0.86	−1.99	0.28	0.9995
293.15	−3.86	−3.36	4.07	−8.27	3.41	0.35	0.9994
298.15	−3.77	−2.99	3.51	7.93	3.48	0.15	0.9993
303.15	−3.64	−3.01	4.47	−9.71	4.48	0.18	0.9990
308.15	−3.51	−3.01	5.78	−13.01	6.86	0.16	0.9991
313.15	−3.45	−1.75	1.31	−6.20	3.36	0.05	0.9989
318.15	−3.19	−2.89	6.60	−14.34	7.57	0.52	0.9971
323.15	−2.99	−3.53	10.64	−21.49	11.54	0.37	0.9987
Water + acetone							
283.15	−2.28	−41.78	128.37	−164.55	73.48	0.57	0.9951
288.15	−2.41	−39.22	120.28	−154.38	69.18	1.81	0.9949
293.15	−2.48	−37.33	113.96	−145.58	64.95	2.04	0.9946
298.15	−2.57	−35.19	107.36	−137.21	61.35	0.94	0.9942
303.15	−2.62	−33.27	100.68	−127.59	56.57	0.95	0.9942
308.15	−2.64	−31.73	96.40	−122.80	54.86	0.90	0.9939
313.15	−2.82	−28.50	86.11	−109.25	48.64	0.30	0.9934
318.15	−3.00	−25.07	74.68	−93.54	41.14	1.19	0.9956
323.15	−3.19	−21.76	63.87	−78.91	34.31	0.52	0.9960

el > λh equation > Jouyban-Acree model, which indicated that the modified Apelblat equation correlated the relationship between equilibrium solubility and temperature is more suitable for equation research and fitting the solubility values of 3-nitropyrazole in the binary systems than other three models. The results mentioned above suggest that the fitted models and the values of solubility in this study provide a certain foundation for the crystallization process of 3-nitropyrazole in the future.

For further study of 3-nitropyrazole solubility behavior, Hansen solubility parameters of selected solvents and 3-nitropyrazole were investigated in this work. From Table 2, values of δ_t for methanol, ethanol and 1-propanol are mainly contributed by δ_h. However, values of δ_t for water and acetone are mainly contributed by δ_d. It indicates that the major forces of methanol, ethanol and 1-propanol differ from theses of water and acetone. Therefore, solubility of 3-nitropyrazole in methanol, ethanol and 1-propanol is higher than that in water and acetone. In addition, values of $\Delta\delta_t$ between 3-nitropyrazole and binary solvents (water + methanol, ethanol, 1-propanol and acetone) decrease as the mass fraction of water decreases. For four binary solvents, the difference of δ_d between mixed solvent and 3-nitropyrazole reduces as mass fraction of water decreases. So the solubility of 3-nitropyrazole increases with the decrease of mass fraction of water.

Solubility of 3-nitropyrazole in four binary solvents (water + methanol, ethanol, 1-propanol and acetone) with different mass fraction of water was presented in Table 4 and Figs. 6-9. The results further illustrate that the solubility of 3-nitropyrazole is a function of temperature and increases with the increasing temperature, while decreases with the rising water mass fraction ranging from 0.1000 to 0.9000 at a constant temperature. As the mass fraction of water increases, the interaction of water and organic solvent will be weakened. So the solubility of 3-nitropyrazole decreases with

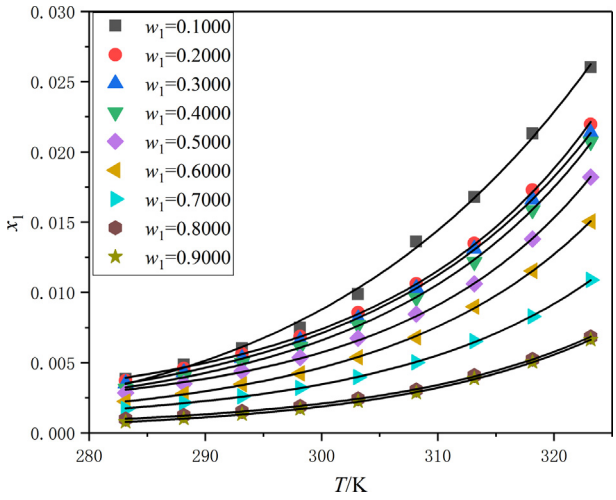

Fig. 6. Experimental data correlated by the modified Apelblat equation for 3-nitropyrazole in (water + methanol) binary solvent mixtures.

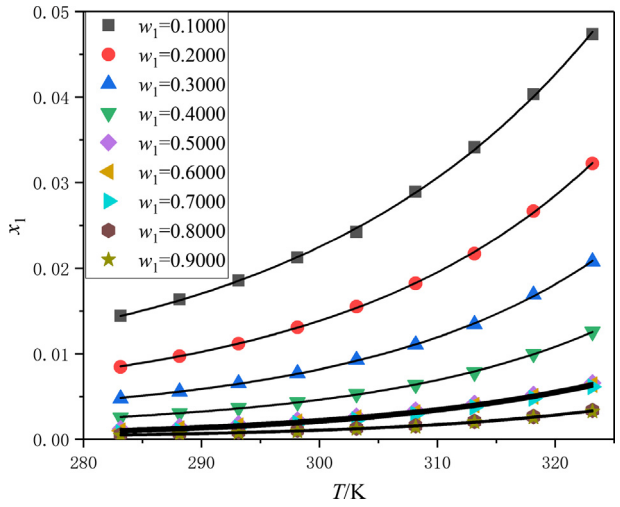

Fig. 7. Experimental data correlated by the modified Apelblat equation for 3-nitropyrazole in (water + ethanol) binary solvent mixtures.

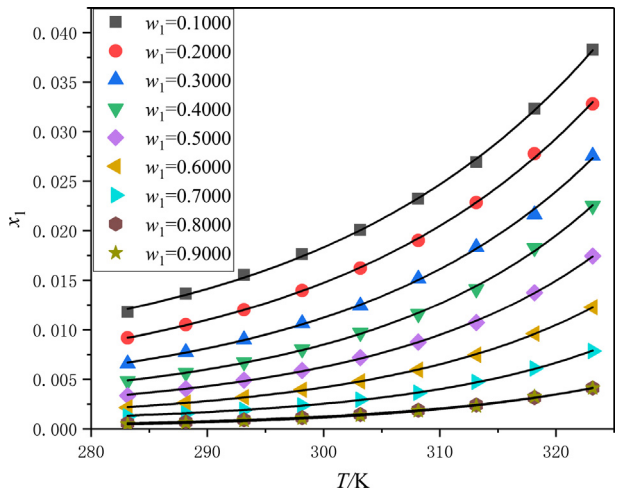

Fig. 8. Experimental data correlated by the modified Apelblat equation for 3-nitropyrazole in (water + 1-propanol) binary solvent mixtures.

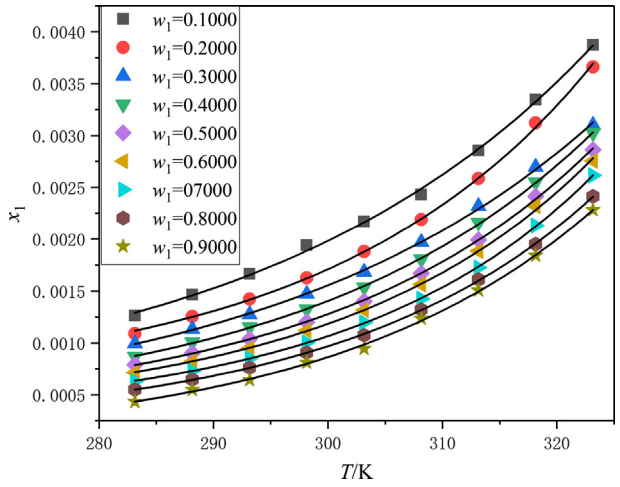

Fig. 9. Experimental data correlated by the modified Apelblat equation for 3-nitropyrazole in (water + acetone) binary solvent mixtures.

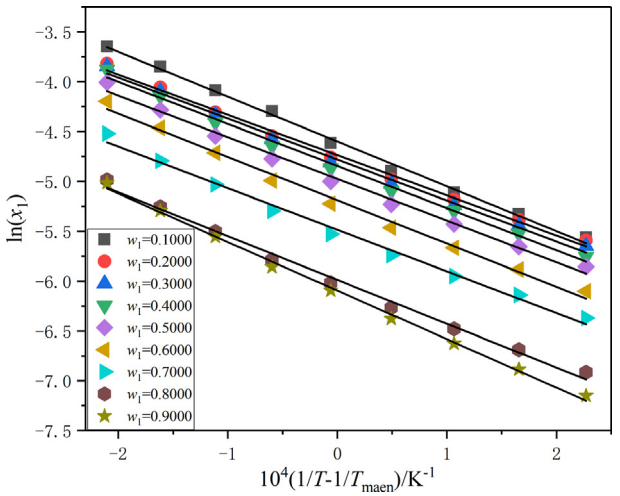

Fig. 10. lnx_1 of 3-nitropyrazole in (water + methanol) binary solvent mixtures against $10^4(1/T\text{-}1/T_{mean})$.

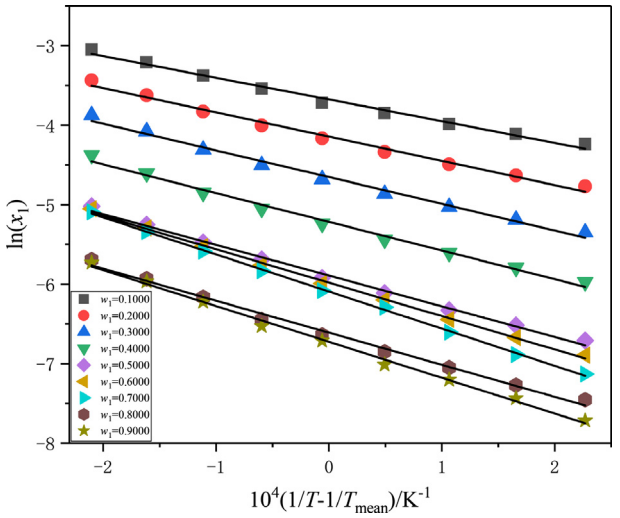

Fig. 11. lnx_1 of 3-nitropyrazole in (water + ethanol) binary solvent mixtures against $10^4(1/T\text{-}1/T_{mean})$.

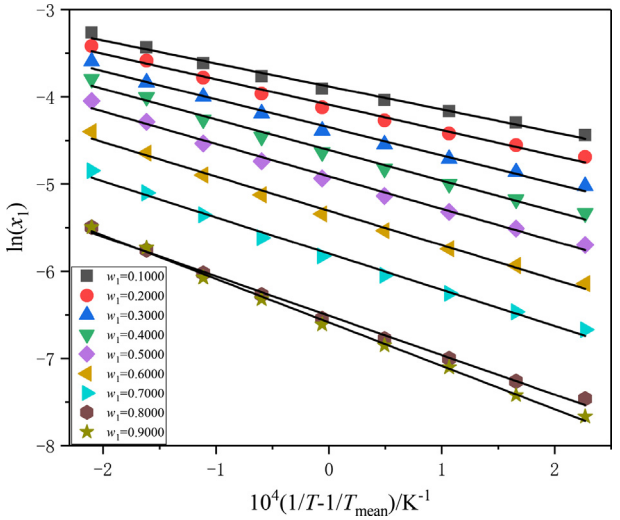

Fig. 12. lnx_1 of 3-nitropyrazole in (water + 1-propanol) binary solvent mixtures against $10^4(1/T\text{-}1/T_{mean})$.

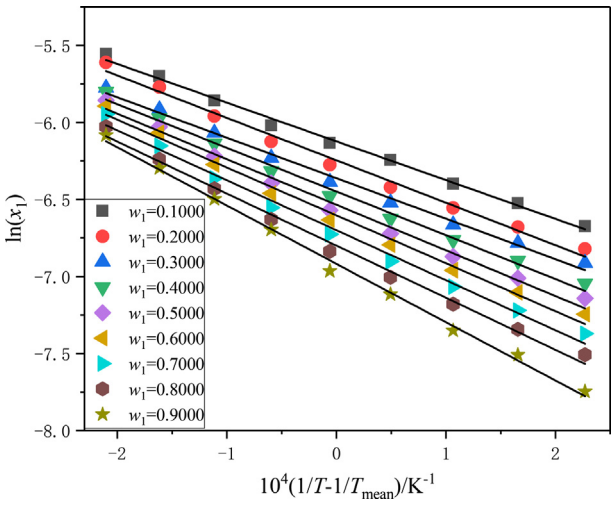

Fig. 13. lnx_1 of 3-nitropyrazole in (water + acetone) binary solvent mixtures against $10^4(1/T\text{-}1/T_{mean})$.

the increasing mass fraction of water in the determined temperature. At a given temperature and mass fraction of water, the solubility order of 3-nitropyrazole in four binary solvents is water + ethanol (w_1 = 0.1000) > water + 1-propanol (w_1 = 0.1000) > water + methanol (w_1 = 0.1000) > water + acetone (w_1 = 0.1000) in general. It can be inferred that the solubility order of 3-nitropyrazole is ethanol > 1-propanol > methanol > acetone > water. However, the polarity order of pure solvents is water (100) > methanol (76.2) > ethanol (65.4) > 1-propanol (61.7) > acetone (35.5) [29], which is not strictly consistent with the solubility sequence of 3-nitropyrazole. The principle of 'like dissolves like' rule was not obvious. Generally, polarity mainly influences the strength of solute–solvent Van der Waals interactions. Whereas, hydrogen-bonding may also play an important role in the solute–solvent interactions. For instance, a similar phenomenon has been revealed in other compounds, such as EA [30], CNP [31] and FM [32]. Obviously, dissolution is a complex process and polarity is not the unique factor to affect it. In fact, many factors (e.g., molecular geometry, molecule polarity, molecule size, solute–solvent and solvent–solvent interactions, dielectric constant, ionization constant [33] and surface tension of different solvents) might affect the solute solubility dissolved in a solvent. A similar phenomenon was identified the solubility measurement of other compounds (e.g., sorbic acid [34] and sulbactam [35]).

According to Mauricio A. Filippa [29], dissolution process can be divided into three steps: First, the bonds between adjacent solute molecules are broken. Next, some hollow space are produced in solvent. After that, the hollow space are filled by solute molecules. Therefore, the E_{inter} plays a key role in solubility behavior. In this work, solute–solvent interaction was analyzed by using Dmol^3 module. Fig. 5 displays interactions between 3-nitropyrazole and methanol + water (a), ethanol + water (b), 1-propanol + water (c)

Table 9
$\%\zeta_H$, $\%\zeta_S$, standard molar enthalpy, entropy and Gibbs energy of 3-nitropyrazole in four binary solvents at mean temperature (302.60 K) and P = 0.1 MPa.

w_1	$\Delta_{dis}H^o$/(kJ mol^{-1})	$\Delta_{dis}S^o$/(J K^{-1} mol^{-1})	$\Delta_{dis}G^o$/(kJ mol^{-1})	$\%\zeta_H$	$\%\zeta_S$
Water + methanol					
0.1000	37.39	85.33	11.57	59.15	40.85
0.2000	33.57	71.57	11.92	60.79	39.21
0.3000	34.22	73.33	12.03	60.66	39.34
0.4000	35.15	75.86	12.19	60.49	39.51
0.5000	34.77	73.55	12.52	60.97	39.03
0.6000	36.11	76.19	13.06	61.03	38.97
0.7000	34.74	69.19	13.80	62.39	37.61
0.8000	36.57	71.06	15.07	62.97	37.03
0.9000	40.49	83.12	15.34	61.68	38.32
Water + ethanol					
0.1000	22.74	44.57	9.25	62.77	37.23
0.2000	25.37	49.38	10.43	62.93	37.07
0.3000	27.90	53.50	11.71	63.28	36.72
0.4000	30.02	56.58	12.89	63.68	36.32
0.5000	32.15	57.28	14.82	64.98	35.02
0.6000	34.92	65.67	15.05	63.73	36.27
0.7000	38.81	77.59	15.33	62.31	37.69
0.8000	33.50	55.75	16.63	66.51	33.49
0.9000	37.49	67.99	16.92	64.57	35.43
Water + 1-propanol					
0.1000	21.95	40.28	9.76	64.30	35.70
0.2000	24.29	46.29	10.29	63.43	36.57
0.3000	26.79	52.37	10.94	62.83	37.17
0.4000	29.16	58.05	11.60	62.41	37.59
0.5000	30.95	61.44	12.36	62.47	37.53
0.6000	32.74	64.09	13.35	62.80	37.20
0.7000	34.47	65.72	14.58	63.42	36.58
0.8000	37.60	70.15	16.37	63.92	36.08
0.9000	41.42	82.13	16.57	62.50	37.50
Water + acetone					
0.1000	20.91	18.21	15.40	79.15	20.85
0.2000	22.92	23.80	15.71	76.09	23.91
0.3000	21.86	19.34	16.01	78.88	21.12
0.4000	23.60	24.39	16.22	76.18	23.82
0.5000	24.61	26.99	16.44	75.08	24.92
0.6000	28.95	40.76	16.61	70.12	29.88
0.7000	26.97	33.41	16.86	72.73	27.27
0.8000	28.11	36.35	17.11	71.87	28.13
0.9000	31.47	46.48	17.40	69.11	30.89

and acetone + water (d), respectively. Hydrogen bonds are built between solvent and solute molecules according to the calculations, while the H···Acceptor distances (shown in Fig. 5) imply that hydrogen bonds are the main origin of intermolecular interactions in the studied cases [36]. The order of hydrogen bonds distance (Å) is 3-nitropyrazole-ethanol–water (1.433, 2.342) < 3-nitropyrazole-1-propanol-water (1.678, 2.342) < 3-nitropyrazole-methanol–water (2.004, 2.342) < 3-nitropyrazole-acetone–water (2.576, 2.342). The weakening of the (solute + solvent) interactions gives rise to the elongation of H···Acceptor distances. It illustrates that a high solubility in ethanol + water can be mainly attributed to a strong hydrogen bond interactions between 3-nitropyrazole and ethanol/water. When 3-nitropyrazole interacted with ethanol + water, the atom H of amino group (H-bond donor) in pyrazole form hydrogen bond with the atom O of hydroxyl group (H-bond acceptor) in ethanol + water. It is reasonable since the delocalized electron pyrazole ring attracts the lone pair electrons of nitrogen of amino group along with the CAO bond so that the electron density around O decreases and H atom becomes more positive [37]. As is shown in Table 3, order of E_{inter} is same to that of solubility order. For binary solvents, the order of E_{inter} is water + ethanol (57.76 kJ·mol^{-1}) > water + 1-propanol (34.13 kJ·mol^{-1}) > water + methanol (26.26 kJ·mol^{-1}) > water + acetone (21.00 kJ·mol^{-1}). A larger value of E_{inter} indicates a stronger interaction force. Stronger solute–solvent interaction indicates stronger dissolution ability of 3-nitropyrazole in selected solvents [38,39].

4. Thermodynamic properties

The standard molar enthalpy ($\Delta_{dis}H^o$) [40] could be related to the temperature and the solubility with Eq. (15).

$$\Delta_{dis}H^O = -R \times \left(\frac{\partial \ln x_1}{\partial(1/T)}\right) \tag{15}$$

Over a limited temperature interval, the standard molar enthalpy ($\Delta_{dis}H^o$) would be valid for the mean temperature (T_{mean} = 302.60 K, in the present work) [41]. Therefore, Eq. (16) can be presented as:

$$\Delta_{dis}H^O = -R \times \left(\frac{\partial \ln x_1}{\partial(1/T - 1/T_{mean})}\right) \tag{16}$$

The standard molar Gibbs energy ($\Delta_{dis}G^o$) can be calculated by the following equation [42]:

$$\Delta_{dis}G^O = -RT_{mean} \times intercept \tag{17}$$

Where the intercept is obtained in plots of $\ln x_1$ versus ($1/T - 1/T_{mean}$). The standard molar entropy ($\Delta_{dis}S^o$) is obtained by [43]:

$$\Delta_{dis}S^O = \frac{\Delta_{dis}H^O - \Delta_{dis}G^O}{T_{mean}} \tag{18}$$

The $\%\zeta_H$ and $\%\zeta_S$ represent the comparison of the relative contribution to the standard Gibbs energy by enthalpy and entropy in the solution process [44,45], respectively.

$$\%\zeta_H = \frac{|\Delta_{mix}H|}{|\Delta_{mix}H| + |T_m\Delta_{mix}S|} \times 100 \tag{19}$$

$$\%\zeta_S = \frac{|T\Delta_{mix}S|}{|\Delta_{mix}H| + |T\Delta_{mix}S|} \times 100 \tag{20}$$

The curves of $\ln x_1$ vs ($1/T - 1/T_{mean}$) in four binary solvent mixtures were displayed in Figs. 10–13. The data of $\%\zeta_H$ and $\%\zeta_S$ is listed in Table 9 together with $\Delta_{dis}G^o$, $\Delta_{dis}H^o$ and $\Delta_{dis}S^o$. It is clear that the values of $\Delta_{dis}H^o$ and $\Delta_{dis}S^o$ are all positive, which indicate that the dissolution process of 3-nitropyrazole is endothermic and driven by entropy [46,47]. The values of $\Delta_{dis}G^o$ are all positive, which indicates that 3-nitropyrazole in all solvents investigated is a non-spontaneous and favorable process [48,49]. Meanwhile, it is found that the lower the value of $\Delta_{dis}G^o$, the greater the 3-nitropyrazole solubility, which conforms to the general thermodynamic principle [50]. In brief, these results are helpful for the optimization of the mixing and crystallization processes of 3-nitropyrazole. Moreover, it can be observed that all the values of $\%\zeta_H$ were greater than those of $\%\zeta_S$ in the 4 kinds of binary mixed solvents, revealing that $\Delta_{dis}H^o$ is the main factor affecting $\Delta_{dis}G^o$ [51].

5. Conclusions

In this paper, the solubility of 3-nitropyrazole was measured by the dynamic laser method in four binary solvents such as (water + methanol), (water + ethanol), (water + 1-propanol) and (water + acetone) in the temperature range from 283.15 K to 323.15 K. It is easy to be found that the solubility of 3-nitropyrazole generally increases with the increasing temperature in binary system at constant solvent and decreases with the increasing in the mass fraction of water. Moreover, the dissolving capacity of 3-nitropyrazole in four binary solvent mixtures at constant temperature ranked as water + ethanol (w_1 = 0.1000) > water + 1-propanol (w_1 = 0.1000) > water + methanol (w_1 = 0.1000) > water + acetone (w_1 = 0.1000). Hansen solubility parameters were employed to provide a reasonable illustration for the solubility order of 3-nitropyrazole in the 4 binary mixed solvents, and the order of 3-nitropyrazole solubility in each binary solvent mixture is the result of the combined effects of hydrogen bonding, dispersion and polarity. And solute–solvent interaction was calculated by molecular simulation to investigate the solubility behavior deeply. The analytic results show that solubility behavior can be explained well by them. In addition, the data of experiment was correlated by the modified Apelblat equation, λh equation, Jouyban-Acree model and CNIBS/R-K model, which have been verified to be capable of the correlation of the solubility of 3-nitropyrazole in binary system. In general, the four models give a very satisfactory results, and the modified Apelblat equation shows best consistency with the experimental data than the other three equations by comparing the 10^4RMSD and R^2 in different binary solvents. Meanwhile, the thermodynamic properties of solution in different binary solvent mixtures, such as the standard molar Gibbs energy ($\Delta_{dis}G^o$), standard molar enthalpy ($\Delta_{dis}H^o$) and standard molar entropy ($\Delta_{dis}S^o$) were obtained and discussed. According to the data fitting, the mixing process of 3-nitropyrazole in all solvents investigated is a non-spontaneous, and the main contribution of $\Delta_{dis}G^o$ comes from the positive enthalpy. Furthermore, the solubility data and correlation results are worthwhile and very useful for choosing a suitable solvent for the purification process of 3-nitropyrazole on an industrial scale and further theoretical studies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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