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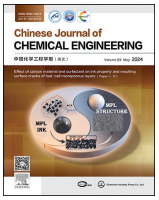

Full Length Article

Solubility determination and comparison of β-HMX and RDX in two binary mixed solvents (acetonitrile + water, nitric acid + water)

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Model
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ABSTRACT

In order to remove hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), the main impurity, in process of polymorphic transformation of octrahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), the solubility of β-HMX and RDX in acetonitrile (ACN) + water in the temperature range of 288.15–333.15 K and in nitric acid (HNO_3) + water in the temperature range of 298.15–333.15 K were measured by laser dynamic method. The results showed that the solubility of both β-HMX and RDX in binary mixed solvents increased monotonously as the temperature increase at a given solvent composition or with increasing of mole fraction of solvent (ACN and nitric acid). Solubility data were well correlated by the modified Apelblat equation, Jouyban-Acree model, Yaws equation and van't Hoff equation, and the Yaws equation achieved the best fitting results according to the relative error and the mean square error root. Furthermore, the solubility of β-HMX and RDX in binary mixed solvent was compared, based on the solubility difference and the solvent's own properties, the best separation degree of β-HMX and RDX was found when the mole fraction of nitric acid was 0.22 at room temperature, which provided data support for HMX crystallization in mixed solvent. The solubility differences between RDX and β-HMX in mixed solvents were explained from the formation of intermolecular and intramolecular hydrogen bonds.

1. Introduction

Octrahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX; CAS number: 2691-41-0; molecular formula: $C_4H_8N_8O_8$; molar mass: 296.17 $g \cdot mol^{-1}$) is a kind of high elemental explosive with superior detonation performance. The structure of HMX is illustrated in Fig. 1, which is widely used in charge the warhead, high performance solid propellant, and components of gun propellant [1]. Between room temperature and melting point, there are four solid phase polymorphs labeled as α-, β-, γ-, and δ-HMX [2]. According to the literature, different polymorphs of HMX have different physicochemical properties and detonation properties [3]. Since β-HMX has the largest density and the least mechanical sensitivity of the four polymorphs, it is the most stable crystal form at room temperature [4]; therefore, *β*-HMX became the product required by industry. However, the rough products obtained by industrial production are usually α-HMX and need to transform it into β-HMX.

Polymorphic transformation can be achieved by the solvent-non-solvent method [5,6], the principle of this method is that the substance dissolved in the solvent, then add non-solvent to reduce the solubility and produce supersaturation, after the solid precipitated, polymorphic transformation is carried out under appropriate conditions [7,8]. In the field of energetic materials, the solvent-non-solvent method is often used by researchers to refine various explosives [9–14]. In the process of polymorphic transformation, purity of the product must also be considered. In fact, the main impurity of HMX produced by acetic anhydride is hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX, as shown in Fig. 2), it is well known that HMX and RDX differ greatly in solubility in the same solvent, thus it is feasible to remove the RDX from β-HMX based on this solubility difference. When using the solvent-non-solvent approach to transcrystallize and remove RDX in the mixed solvent system, it is required to ascertain the solubility of β-HMX and RDX in the same mixed solvent in order to give data support for the screening of HMX transcrystallize solvent system. Solvents are selected based on the properties of HMX and RDX, and the solubility of HMX [15–20] and RDX [21–23] in previous literature.

In this study, the solubility of β-HMX and RDX in acetonitrile + water at the temperature range from 288.15 K to

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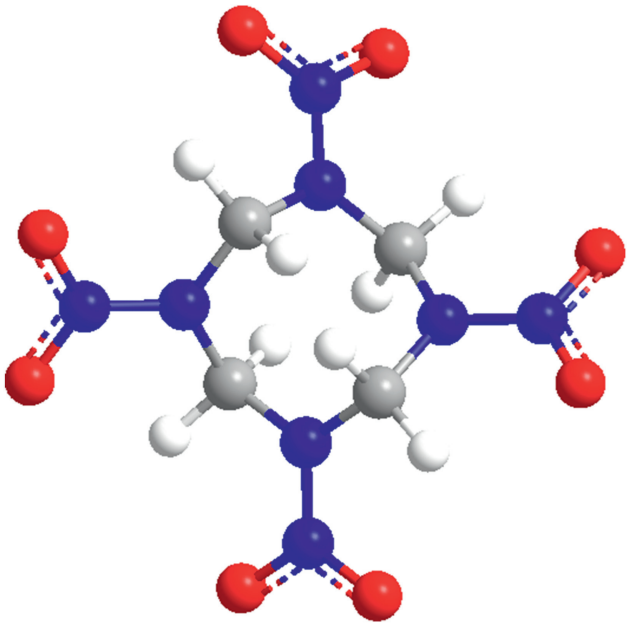

Fig. 1. The structure of HMX.

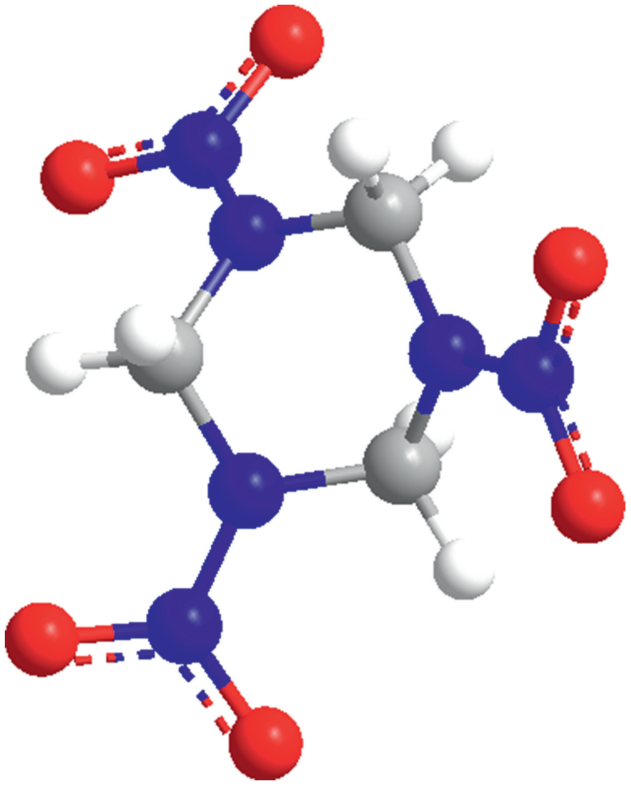

Fig. 2. The structure of RDX.

333.15 K and in nitric acid + water at the temperature range from 298.15 K to 333.15 K were measured by laser dynamic method [24]. Solubility data were then correlated by four thermodynamic models including the Apelblat equation, Yaws equation, van't Hoff equation and Jouyban-Acree model. Furthermore, the solubilities of β-HMX and RDX were compared, and the most suitable separation condition in the two mixed solvents was determined according to the solubility difference.

2. Experimental

2.1. Materials

β-HMX ($C_4H_8N_8O_8$, molecular weight 296.17 $g \cdot mol^{-1}$) obtained from Gansu Yinguang Chemical Industry Group Co. LTD., China, its purity was greater than 0.994, which was determined by high-performance liquid chromatography (HPLC). RDX ($C_3H_6N_6O_6$, molecular weight 222.12 $g \cdot mol^{-1}$) was prepared according to the procedures reported in the previous literature [2], the rough products were recrystallized with acetone, and its purity was measured to be greater than 0.995 by using HPLC. Acetonitrile was supplied by Tianjin Kemi Ou Chemical Reagent Co. LTD., and it was analytical grade without progressively purified. Deionized water is prepared by our laboratory. Detailed information about the materials used in this work was listed in Table 1.

2.2. X-ray powder diffraction

In order to analyze whether two substances have changed (transformation of crystal form, reaction, formation of solvent compounds, *etc.*) before and after the solubility measurement, the powder X-ray diffraction analysis (EMPYREAN, Netherland) was performed on the raw material and the equilibrium solid phases obtained from the solubility measurement. The solutes were precipitated after the system was cooled to room temperature after testing the solubility of β-HMX and RDX in various mass fractions of nitric acid and acetonitrile at temperatures ranging from 298.15 K to 323.15 K and from 288.15 K to 333.15 K. Then the equilibrium solid phase is obtained by vacuum filtration and drying at 50 °C.

It can be seen from Fig. 3 that the crystalline forms of β-HMX and RDX recovered from the solvent did not change and no solvent compounds were formed.

2.3. Solubility measurement

2.3.1. The preparation of mixed solvent

The experimental determination of the solubility of β-HMX and RDX in different concentrations of nitric acid involved dilution of concentrated nitric acid; the dilution process is described below.

(1) Nitric acid dilution process

Fuming nitric acid with a mass fraction of 98% is commonly used in our laboratory, so the different concentrations of nitric acid used for the determination of solubility are diluted with 98% nitric acid.

Table 1
Detailed information of the materials used in the experiment

Chemical name	Source	Purity (mass faction)	Purification method	Method analysis
β-HMX	Gansu Yinguang Chemical Industry Group Co. LTD	>0.994	None	HPLC①
RDX	Prepared by us	>0.995	Recrystallization	HPLC①
Acetonitrile	Tianjin Kemi Ou Chemical Reagent Co. LTD	>0.995	None	GC②
Water	Prepared by us			

① High-performance liquid chromatography.
② Gas chromatography.

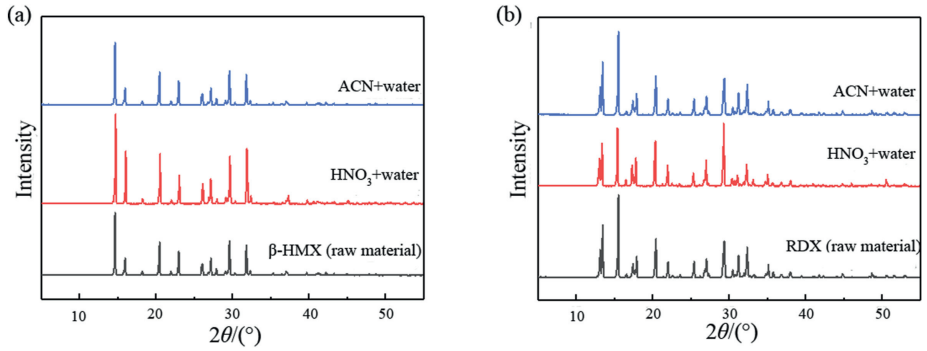

Fig. 3. The X-ray powder diffraction (PXRD) patterns: (a) PXRD patterns of the raw material of β-HMX and equilibrium solid phases of HMX in ACN + water and HNO_3+water. (b) PXRD patterns of the raw material of RDX and equilibrium solid phases of RDX in ACN + water and HNO_3+water.

This process is based on the principle of mass conservation, that is, the mass of pure nitric acid before and after dilution is unchanged. According to Eq. (1), the total amount of nitric acid with a certain mass fraction is determined, the mass of 98% nitric acid is calculated, and the mass of deionized water used for dilution is calculated. Then nitric acid is slowly added to water while stirring at a certain temperature. Control the rate at which nitric acid drops into the water to prevent the temperature from rising dangerously too fast.

$$w_1\rho_1V_1 = w_2\rho_2V_2 \tag{1}$$

where w_1 and w_2 are the mass fraction of nitric acid before and after dilution, ρ_1 and ρ_2 are the density of nitric acid before and after dilution, and V_1 and V_2 are the volume of nitric acid before and after dilution, respectively.

(2) Titration process of nitric acid concentration

Due to the error in the operation process, the obtained nitric acid concentration is not necessarily the theoretical concentration, and the accurate concentration needs to be calculated through titration analysis. The method specified in GB/T 337.1—2014 and GB/T 337.2—2014 was used to titrate concentrated nitric acid with mass fraction above 68% and dilute nitric acid with mass fraction below 68%, respectively.

The concentration of nitric acid in the above configuration was expressed as a mass fraction, which was converted to a mole fraction by the following equation.

$$x = \frac{wM_2}{mM_1 - w(M_1 - M_2)} \tag{2}$$

where x is the mole fraction, w represents the mass fraction, M_1 is the relative molecular mass of nitric acid, M_2 is the relative molecular mass of water, and m is the total mass of the solution.

2.3.2. Solubility measurement

The solubilities of β-HMX and RDX were determined with a laser monitoring [25–27]. The device must be opened and preheated for 30 min before the experiment may begin. The thermostat and stirring apparatus are turned on when the excess solute and a specific amount of solvent have been supplied to the crystallizer, and the temperature and stirring rate have been set. The laser indication is noted after the crystallizer's temperature reaches the predetermined point and stabilizes for 20 min. Once the laser indicator reaches its maximum and stays stable for 30 min, the solute is thought to have been completely dissolved, and the total amount of solute and solvent added is recorded. Next, add a small amount of solvent to the crystallizer gradually using a pipette, recording the amount of addition and laser indication each time. Final data processing includes calculating solubility and other properties for various temperature points based on the record data.

The solubility of substance in binary system expressed by mole fraction was calculated according to Eq. (3).

$$x = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \tag{3}$$

where m_1, m_2, m_3 are the mass of β-HMX or RDX, solvent, non-solvent, respectively. M_1, M_2, M_3 are the molar mass of β-HMX or RDX, solvent, non-solvent, respectively.

2.4. Models

2.4.1. The modified Apelblat equation

The modified Apelblat equation is derived from the Clausius Clapeyron equation [28], it applies to the case where the solubility of a solid substance in a solvent or mixed solvent varies with temperature. The equation can be expressed as Eq. (4).

$$\ln x = A + B/T + C\ln T \tag{4}$$

where x is the mole fraction solubility of β-HMX or RDX; A, B and C are the model parameters; T is the absolute temperature (K).

2.4.2. Modified Jouyban-Acree model

The Jouyban-Acree model is the equation proposed by Jouyban-Gharamaleki and his colleagues for the solubility of a substance in a binary mixture of solvents as a function of solvent composition and temperature [29], and the modified Jouyban-Acree model can be expressed by the following Eq. (5):

$$\ln x = A_1 + A_2/T + A_3\ln T + A_4x_1 + A_5x_1/T + A_6x_1^2/T + A_7x_1^3/T + A_8x_1^4/T + A_9x_1\ln T \tag{5}$$

where x is the mole fraction solubility of β-HMX or RDX; x_1 represents the mole fraction of solvent; A_1 to A_9 are the model parameters; T is the absolute temperature (K).

Table 2
Experimental and fitted solubility of β-HMX in binary mixed system (ACN + H_2O) within the temperature range from 298.15 K to 338.15 K under 0.1 MPa

T/K	$1000x_{exp}$	The Apelblat equation		Jouyban-Acree equation		Yaws model		van't Hoff model	
		$1000x_{cal}$	RD	$1000x_{cal}$	RD	$1000x_{cal}$	RD	$1000x_{cal}$	RD
$x_{ACN} = 0.80$									
298.15	2.0795	2.0879	−0.0040	2.0960	−0.0080	2.0892	−0.0047	2.0119	0.0325
303.15	2.4633	2.4144	0.0198	2.4183	0.0183	2.4140	0.0200	2.3731	0.0366
308.15	2.7023	2.7920	−0.0332	2.7918	−0.0331	2.7907	−0.0327	2.7843	−0.0304
313.15	3.2507	3.2281	0.0069	3.2246	0.0080	3.2269	0.0073	3.2502	0.0002
318.15	3.7858	3.7317	0.0143	3.7258	0.0159	3.7312	0.0144	3.7755	0.0027
323.15	4.3076	4.3128	−0.0012	4.3061	0.0003	4.3133	−0.0013	4.3655	−0.0134
328.15	4.9612	4.9828	−0.0044	4.9778	−0.0034	4.9842	−0.0046	5.0254	−0.0129
333.15	5.7408	5.7550	−0.0025	5.7550	−0.0025	5.7561	−0.0027	5.7607	−0.0035
338.15	6.6572	6.6442	0.0020	6.6539	0.0005	6.6430	0.0021	6.5769	0.0121
$x_{ACN} = 0.64$									
298.15	1.3126	1.3019	0.0081	1.2746	0.0289	1.3036	0.0069	1.2308	0.0623
303.15	1.5049	1.5111	−0.0041	1.4937	0.0075	1.5111	−0.0041	1.4711	0.0224
308.15	1.7292	1.7574	−0.0163	1.7497	−0.0119	1.7565	−0.0158	1.7482	−0.0110
313.15	2.0579	2.0474	0.0051	2.0487	0.0045	2.0464	0.0056	2.0660	−0.0039
318.15	2.4127	2.3890	0.0098	2.3976	0.0063	2.3886	0.0100	2.4288	−0.0067
323.15	2.8063	2.7917	0.0052	2.8045	0.0006	2.7921	0.0051	2.8411	−0.0124
328.15	3.2357	3.2662	−0.0094	3.2785	−0.0132	3.2674	−0.0098	3.3075	−0.0222
333.15	3.8263	3.8257	0.0002	3.8304	−0.0011	3.8266	−0.0001	3.8329	−0.0017
338.15	4.4905	4.4853	0.0011	4.4723	0.0041	4.4839	0.0015	4.4225	0.0151
$x_{ACN} = 0.51$									
298.15	0.6936	0.6894	0.0062	0.7261	−0.0468	0.6746	0.0274	0.7315	−0.0546
303.15	0.8326	0.8325	0.0002	0.8639	−0.0376	0.8235	0.0110	0.8679	−0.0423
308.15	1.0160	1.0016	0.0142	1.0267	−0.0105	0.9987	0.0171	1.0290	−0.0128
313.15	1.1971	1.2008	−0.0031	1.2185	−0.0179	1.2037	−0.0055	1.2193	−0.0186
318.15	1.3981	1.4346	−0.0261	1.4444	−0.0331	1.4423	−0.0316	1.4439	−0.0328
323.15	1.7008	1.7084	−0.0045	1.7099	−0.0054	1.7186	−0.0105	1.7087	−0.0046
328.15	2.0686	2.0279	0.0197	2.0218	0.0226	2.0370	0.0153	2.0205	0.0232
333.15	2.3974	2.3997	−0.0010	2.3875	0.0041	2.4020	−0.0019	2.3873	0.0042
338.15	2.8226	2.8313	−0.0031	2.8157	0.0024	2.8186	0.0014	2.8186	0.0014
$x_{ACN} = 0.40$									
298.15	0.3924	0.3960	−0.0092	0.3709	0.0548	0.3966	−0.0106	0.3685	0.0609
303.15	0.4633	0.4683	−0.0108	0.4485	0.0320	0.4682	−0.0106	0.4516	0.0252
308.15	0.5673	0.5552	0.0214	0.5412	0.0461	0.5549	0.0220	0.5499	0.0307
313.15	0.6679	0.6599	0.0120	0.6517	0.0243	0.6595	0.0126	0.6653	0.0038
318.15	0.7669	0.7859	−0.0248	0.7832	−0.0212	0.7857	−0.0245	0.8002	−0.0434
323.15	0.9511	0.9379	0.0139	0.9393	0.0124	0.9380	0.0137	0.9569	−0.0061
328.15	1.1133	1.1211	−0.0070	1.1244	−0.0100	1.1216	−0.0075	1.1381	−0.0223
333.15	1.3435	1.3423	0.0009	1.3434	0.0001	1.3427	0.0006	1.3466	−0.0023
338.15	1.6101	1.6092	0.0005	1.6021	0.0049	1.6087	0.0008	1.5853	0.0154
$x_{ACN} = 0.31$									
298.15	0.1806	0.1826	−0.0113	0.1672	0.0743	0.1827	−0.0115	0.1848	−0.0234
303.15	0.2324	0.2241	0.0357	0.2057	0.1151	0.2241	0.0355	0.2254	0.0300
308.15	0.2700	0.2728	−0.0101	0.2523	0.0658	0.2728	−0.0103	0.2732	−0.0117
313.15	0.3297	0.3295	0.0005	0.3086	0.0640	0.3295	0.0005	0.3291	0.0019
318.15	0.3873	0.3952	−0.0205	0.3764	0.0281	0.3952	−0.0205	0.3941	−0.0175
323.15	0.4648	0.4708	−0.0130	0.4580	0.0147	0.4708	−0.0128	0.4693	−0.0097
328.15	0.5723	0.5572	0.0263	0.5557	0.0290	0.5572	0.0264	0.5559	0.0287
333.15	0.6531	0.6554	−0.0036	0.6726	−0.0299	0.6554	−0.0035	0.6551	−0.0031
338.15	0.7642	0.7664	−0.0029	0.8121	−0.0627	0.7665	−0.0031	0.7683	−0.0054

Note: Values of the standard uncertainty u are $u(x) = 0.02$, $u(T) = 0.05$ K, $u(p) = 0.02$ MPa. X_{exp} is the experimental solubility; X_{cal} represent the calculated mole fraction solubility correlated by the modified Apelblat equation, Jouyban-Acree equation, Yaws model and van't Hoff equation, respectively.

Table 3
Experimental and fitted solubility of β-HMX in binary mixed system (HNO_3 + H_2O) within the temperature range from 298.15 K to 323.15 K under 0.1 MPa

T/K	$1000x_{exp}$	The Apelblat equation		Jouyban-Acree equation		Yaws model		van't Hoff model	
		$1000x_{cal}$	RD	$1000x_{cal}$	RD	$1000x_{cal}$	RD	$1000x_{cal}$	RD
$x_{HNO_3} = 0.72$									
298.15	6.6946	6.5266	0.0251	6.6308	0.0095	6.6946	0.0000	6.4771	0.0325
303.15	7.1474	7.1435	0.0005	7.1392	0.0011	7.1341	0.0019	7.1442	0.0004
308.15	7.6909	7.8232	−0.0172	7.7531	−0.0081	7.7103	−0.0025	7.8550	−0.0213
313.15	8.4163	8.5718	−0.0185	8.4874	−0.0084	8.4391	−0.0027	8.6105	−0.0231
318.15	9.3874	9.3960	−0.0009	9.3608	0.0028	9.3422	0.0048	9.4113	−0.0026
323.15	10.429	10.303	0.0121	10.396	0.0032	10.258	0.0164	10.443	−0.0013
$x_{HNO_3} = 0.53$									
298.15	1.0913	1.0922	−0.0008	1.1066	−0.0139	1.0949	−0.0033	1.0800	0.0104

(*continued on next page*)

Table 3 (*continued*)

T/K	$1000x_{exp}$	The Apelblat equation		Jouyban-Acree equation		Yaws model		van't Hoff model	
		$1000x_{cal}$	RD	$1000x_{cal}$	RD	$1000x_{cal}$	RD	$1000x_{cal}$	RD
303.15	1.2463	1.2501	−0.0030	1.2512	−0.0039	1.2501	−0.0030	1.2493	−0.0024
308.15	1.4429	1.4311	0.0082	1.4231	0.0137	1.4295	0.0093	1.4384	0.0031
313.15	1.6452	1.6387	0.0039	1.6274	0.0108	1.6367	0.0051	1.6487	−0.0021
318.15	1.8506	1.8766	−0.0140	1.8705	−0.0108	1.8758	−0.0136	1.8816	−0.0167
323.15	2.1616	2.1490	0.0058	2.1600	0.0007	2.1511	0.0049	2.1387	0.0106
$x_{HNO_3} = 0.42$									
298.15	0.2792	0.2820	−0.0101	0.3054	−0.0939	0.2771	0.0076	0.2814	−0.0079
303.15	0.3402	0.3423	−0.0061	0.3568	−0.0486	0.3412	−0.0028	0.3419	−0.0048
308.15	0.4118	0.4130	−0.0030	0.4185	−0.0162	0.4149	−0.0075	0.4127	−0.0022
313.15	0.4977	0.4955	0.0043	0.4927	0.0100	0.4986	−0.0019	0.4952	0.0051
318.15	0.5981	0.5913	0.0113	0.5822	0.0265	0.5928	0.0088	0.5908	0.0122
323.15	0.6952	0.7020	−0.0097	0.6901	0.0073	0.6976	−0.0034	0.7009	−0.0082
$x_{HNO_3} = 0.30$									
298.15	0.1102	0.1084	0.0156	0.0776	0.2957	0.1107	−0.0052	0.1067	0.0313
303.15	0.1211	0.1220	−0.0071	0.0938	0.2252	0.1214	−0.0027	0.1214	−0.0024
308.15	0.1357	0.1372	−0.0116	0.1138	0.1614	0.1350	0.0047	0.1376	−0.0140
313.15	0.1533	0.1544	−0.0073	0.1382	0.0985	0.1520	0.0085	0.1552	−0.0126
318.15	0.1722	0.1738	−0.0092	0.1682	0.0232	0.1730	−0.0046	0.1745	−0.0134
323.15	0.1987	0.1956	0.0156	0.2051	−0.0321	0.1989	−0.0009	0.1955	0.0162
$x_{HNO_3} = 0.22$									
298.15	0.0247	0.0236	0.0467	0.0344	−0.3919	0.0242	0.0216	0.0232	0.0606
303.15	0.0294	0.0303	−0.0278	0.0426	−0.4457	0.0304	−0.0332	0.0302	−0.0244
308.15	0.0387	0.0387	−0.0005	0.0527	−0.3621	0.0384	0.0058	0.0388	−0.0038
313.15	0.0492	0.0493	−0.0011	0.0652	−0.3252	0.0488	0.0085	0.0495	−0.0064
318.15	0.0620	0.0625	−0.0087	0.0808	−0.3038	0.0622	−0.0033	0.0627	−0.0118
323.15	0.0796	0.0791	0.0054	0.1003	−0.2603	0.0796	0.0000	0.0789	0.0086

Note: Values of the standard uncertainty u are $u(x) = 0.02$, $u(T) = 0.05$ K, $u(p) = 0.02$ MPa. X_{exp} is the experimental solubility; X_{cal} represent the calculated mole fraction solubility correlated by the modified Apelblat equation, Jouyban-Acree equation, Yaws model and van't Hoff equation, respectively.

Table 4
Experimental and fitted solubility of RDX in binary mixed system (ACN + H_2O) within the temperature range from 298.15 K to 338.15 K under 0.1 MPa

T/K	$1000x_{exp}$	The Apelblat equation		Jouyban-Acree equation		Yaws model		van't Hoff model	
		$1000x_{cal}$	RD	$1000x_{cal}$	RD	$1000x_{cal}$	RD	$1000x_{cal}$	RD
$x_{ACN} = 0.80$									
298.15	6.6614	6.5851	0.0115	6.6861	−0.0037	6.5860	0.0113	6.5660	0.0143
303.15	7.9469	7.9321	0.0019	7.9926	−0.0057	7.9324	0.0018	7.9208	0.0033
308.15	9.3081	9.5004	−0.0207	9.5189	−0.0226	9.5002	−0.0206	9.4972	−0.0203
313.15	11.216	11.317	−0.0090	11.296	−0.0072	11.317	−0.0090	11.322	−0.0094
318.15	13.785	13.411	0.0271	13.359	0.0309	13.411	0.0271	13.422	0.0263
323.15	15.648	15.815	−0.0107	15.746	−0.0063	15.815	−0.0106	15.829	−0.0115
328.15	18.566	18.561	0.0002	18.501	0.0035	18.561	0.0002	18.573	−0.0004
333.15	21.668	21.687	−0.0009	21.671	−0.0002	21.687	−0.0009	21.689	−0.0010
338.15	25.241	25.229	0.0005	25.309	−0.0027	25.229	0.0005	25.212	0.0012
$x_{ACN} = 0.64$									
298.15	4.4260	4.6303	−0.0462	4.5365	−0.0250	4.6298	−0.0460	4.4515	−0.0058
303.15	5.4861	5.4936	−0.0014	5.4315	0.0100	5.4907	−0.0008	5.3884	0.0178
308.15	6.8054	6.5116	0.0432	6.4827	0.0474	6.5081	0.0437	6.4822	0.0475
313.15	7.7429	7.7106	0.0042	7.7141	0.0037	7.7084	0.0045	7.7521	−0.0012
318.15	9.0912	9.1211	−0.0033	9.1527	−0.0068	9.1215	−0.0033	9.2188	−0.0140
323.15	10.812	10.779	0.0031	10.829	−0.0015	10.782	0.0028	10.904	−0.0085
328.15	12.536	12.724	−0.0150	12.777	−0.0193	12.729	−0.0154	12.832	−0.0237
333.15	14.995	15.004	−0.0006	15.037	−0.0028	15.008	−0.0009	15.027	−0.0022
338.15	17.747	17.675	0.0041	17.650	0.0054	17.669	0.0044	17.516	0.0130
$x_{ACN} = 0.51$									
298.15	3.2741	3.2145	0.0182	3.1168	0.0480	3.2201	0.0165	2.9864	0.0879
303.15	3.7143	3.7831	−0.0185	3.7401	−0.0069	3.7833	−0.0186	3.6465	0.0183
308.15	4.4533	4.4660	−0.0029	4.4762	−0.0051	4.4631	−0.0022	4.4237	0.0066
313.15	5.3298	5.2867	0.0081	5.3432	−0.0025	5.2832	0.0088	5.3336	−0.0007
318.15	6.1909	6.2740	−0.0134	6.3622	−0.0277	6.2719	−0.0131	6.3929	−0.0326
323.15	7.5594	7.4625	0.0128	7.5571	0.0003	7.4632	0.0127	7.6197	−0.0080
328.15	8.8516	8.8945	−0.0049	8.9550	−0.0117	8.8978	−0.0052	9.0335	−0.0206
333.15	10.640	10.621	0.0018	10.587	0.0050	10.624	0.0015	10.655	−0.0014
338.15	12.693	12.703	−0.0008	12.488	0.0161	12.700	−0.0005	12.507	0.0147
$x_{ACN} = 0.40$									
298.15	1.7645	1.7577	0.0039	1.7225	0.0238	1.7598	0.0027	1.6949	0.0394
303.15	2.0915	2.1103	−0.0090	2.0804	0.0053	2.1106	−0.0091	2.0719	0.0094
308.15	2.6319	2.5289	0.0392	2.5065	0.0476	2.5281	0.0395	2.5163	0.0439
313.15	3.0091	3.0249	−0.0052	3.0128	−0.0012	3.0236	−0.0048	3.0371	−0.0093
318.15	3.4425	3.6116	−0.0491	3.6131	−0.0495	3.6105	−0.0488	3.6441	−0.0585

(*continued on next page*)

Table 4 (*continued*)

T/K	$1000x_{exp}$	The Apelblat equation		Jouyban-Acree equation		Yaws model		van't Hoff model	
		$1000x_{cal}$	RD	$1000x_{cal}$	RD	$1000x_{cal}$	RD	$1000x_{cal}$	RD
323.15	4.2805	4.3043	−0.0056	4.3231	−0.0100	4.3040	−0.0055	4.3478	−0.0157
328.15	5.2994	5.1209	0.0337	5.1614	0.0260	5.1214	0.0336	5.1595	0.0264
333.15	6.0447	6.0817	−0.0061	6.1489	−0.0172	6.0826	−0.0063	6.0915	−0.0077
338.15	7.1881	7.2104	−0.0031	7.3100	−0.0170	7.2102	−0.0031	7.1565	0.0044
$x_{ACN} = 0.31$									
298.15	0.7907	0.7947	−0.0050	0.8560	−0.0825	0.7942	−0.0044	0.8305	−0.0503
303.15	1.0542	1.0074	0.0444	1.0430	0.0107	1.0076	0.0442	1.0309	0.0221
308.15	1.2156	1.2615	−0.0377	1.2678	−0.0430	1.2620	−0.0382	1.2707	−0.0453
313.15	1.5493	1.5612	−0.0077	1.5377	0.0075	1.5618	−0.0081	1.5558	−0.0042
318.15	1.9419	1.9109	0.0159	1.8607	0.0418	1.9112	0.0158	1.8929	0.0252
323.15	2.2597	2.3146	−0.0243	2.2468	0.0057	2.3143	−0.0242	2.2891	−0.0130
328.15	2.8352	2.7758	0.0210	2.7070	0.0452	2.7750	0.0212	2.7522	0.0293
333.15	3.2829	3.2976	−0.0045	3.2547	0.0086	3.2969	−0.0043	3.2907	−0.0024
338.15	3.8784	3.8826	−0.0011	3.9051	−0.0069	3.8833	−0.0013	3.9139	−0.0092

Note: Values of the standard uncertainty u are $u(x) = 0.02$, $u(T) = 0.05$ K, $u(p) = 0.02$ MPa. X_{exp} is the experimental solubility; X_{cal} represent the calculated mole fraction solubility correlated by the modified Apelblat equation, Jouyban-Acree equation, Yaws model and van't Hoff equation, respectively.

Table 5
Experimental and fitted solubility of RDX in binary mixed system ($HNO_3 + H_2O$) within the temperature range from 298.15 K to 323.15 K under 0.1 MPa

T/K	$1000x_{exp}$	The Apelblat equation		Jouyban-Acree equation		Yaws model		van't Hoff model	
		$1000x_{cal}$	RD	$1000x_{cal}$	RD	$1000x_{cal}$	RD	$1000x_{cal}$	RD
$x_{HNO_3} = 0.72$									
298.15	24.990	24.644	0.0139	24.828	0.0065	24.816	0.0070	24.461	0.0212
303.15	26.416	26.692	−0.0104	26.683	−0.0101	26.677	−0.0099	26.699	−0.0107
308.15	28.710	28.937	−0.0079	28.8140	−0.0036	28.818	−0.0038	29.060	−0.0122
313.15	31.459	31.399	0.0019	31.252	0.0066	31.264	0.0062	31.544	−0.0027
318.15	34.138	34.096	0.0012	34.034	0.0030	34.045	0.0027	34.152	−0.0004
$x_{HNO_3} = 0.53$									
298.15	6.0032	5.8398	0.0272	5.8139	0.0315	5.9367	0.0111	5.7691	0.0390
303.15	6.5796	6.6708	−0.0139	6.6366	−0.0087	6.6743	−0.0144	6.6658	−0.0131
308.15	7.5316	7.6251	−0.0124	7.5914	−0.0079	7.5673	−0.0047	7.6658	−0.0178
313.15	8.7022	8.7204	−0.0021	8.6997	0.0003	8.6444	0.0066	8.7766	−0.0085
318.15	9.9763	9.9774	−0.0001	9.9865	−0.0010	9.9403	0.0036	10.006	−0.0029
323.15	11.466	11.419	0.0041	11.481	−0.0013	11.497	−0.0027	11.361	0.0092
$x_{HNO_3} = 0.42$									
298.15	1.3217	1.2862	0.0269	1.4068	−0.0644	1.2906	0.0236	1.2658	0.0423
303.15	1.5263	1.5701	−0.0287	1.6789	−0.0999	1.5768	−0.0331	1.5729	−0.0305
308.15	1.9452	1.9181	0.0139	2.0039	−0.0302	1.9277	0.0090	1.9407	0.0023
313.15	2.3459	2.3448	0.0004	2.3921	−0.0197	2.3572	−0.0048	2.3785	−0.0139
318.15	2.9172	2.8679	0.0169	2.8556	0.0211	2.8822	0.0120	2.8965	0.0071
323.15	3.5091	3.5090	0.0000	3.4085	0.0287	3.5229	−0.0039	3.5059	0.0009
$x_{HNO_3} = 0.30$									
298.15	0.3405	0.3737	−0.0976	0.3512	−0.0313	0.3588	−0.0538	0.3715	−0.0910
303.15	0.4712	0.4658	0.0115	0.4387	0.0689	0.4624	0.0187	0.4653	0.0125
308.15	0.5952	0.5775	0.0299	0.5471	0.0808	0.5839	0.0190	0.5785	0.0281
313.15	0.7179	0.7125	0.0075	0.6812	0.0511	0.7239	−0.0084	0.7143	0.0050
318.15	0.8932	0.8749	0.0204	0.8466	0.0521	0.8821	0.0123	0.8762	0.0190
323.15	1.0507	1.0696	−0.0179	1.0504	0.0004	1.0580	−0.0069	1.0679	−0.0163
$x_{HNO_3} = 0.22$									
298.15	0.2106	0.2049	0.0270	0.1807	0.1422	0.2066	0.0190	0.2013	0.0445
303.15	0.2388	0.2495	−0.0449	0.2317	0.0295	0.2499	−0.0465	0.2492	−0.0435
308.15	0.3043	0.3039	0.0014	0.2963	0.0262	0.3033	0.0033	0.3063	−0.0067
313.15	0.3756	0.3703	0.0142	0.3779	−0.0061	0.3693	0.0167	0.3742	0.0039
318.15	0.4577	0.4512	0.0141	0.4806	−0.0501	0.4509	0.0148	0.4541	0.0078
323.15	0.5464	0.5500	−0.0066	0.6095	−0.1155	0.5516	−0.0095	0.5479	−0.0028

Note: Values of the standard uncertainty u are $u(x) = 0.02$, $u(T) = 0.05$ K, $u(p) = 0.02$ MPa. X_{exp} is the experimental solubility; X_{cal} represent the calculated mole fraction solubility correlated by the modified Apelblat equation, Jouyban-Acree equation, Yaws model and van't Hoff equation, respectively.

2.4.3. Yaws model

The Yaws model relates the temperature to the solubility in solvents [30] and can be expressed as Eq. (6):

$$\ln x = A + B/T + C/T^2 \quad (6)$$

where x represents the mole fraction solubility of β-HMX or RDX; A, B and C are the model parameters; T is the absolute temperature (K).

2.4.4. van't Hoff model

The van't Hoff equation describes the relationship between the natural logarithm of the molar fraction solubility of a saturated

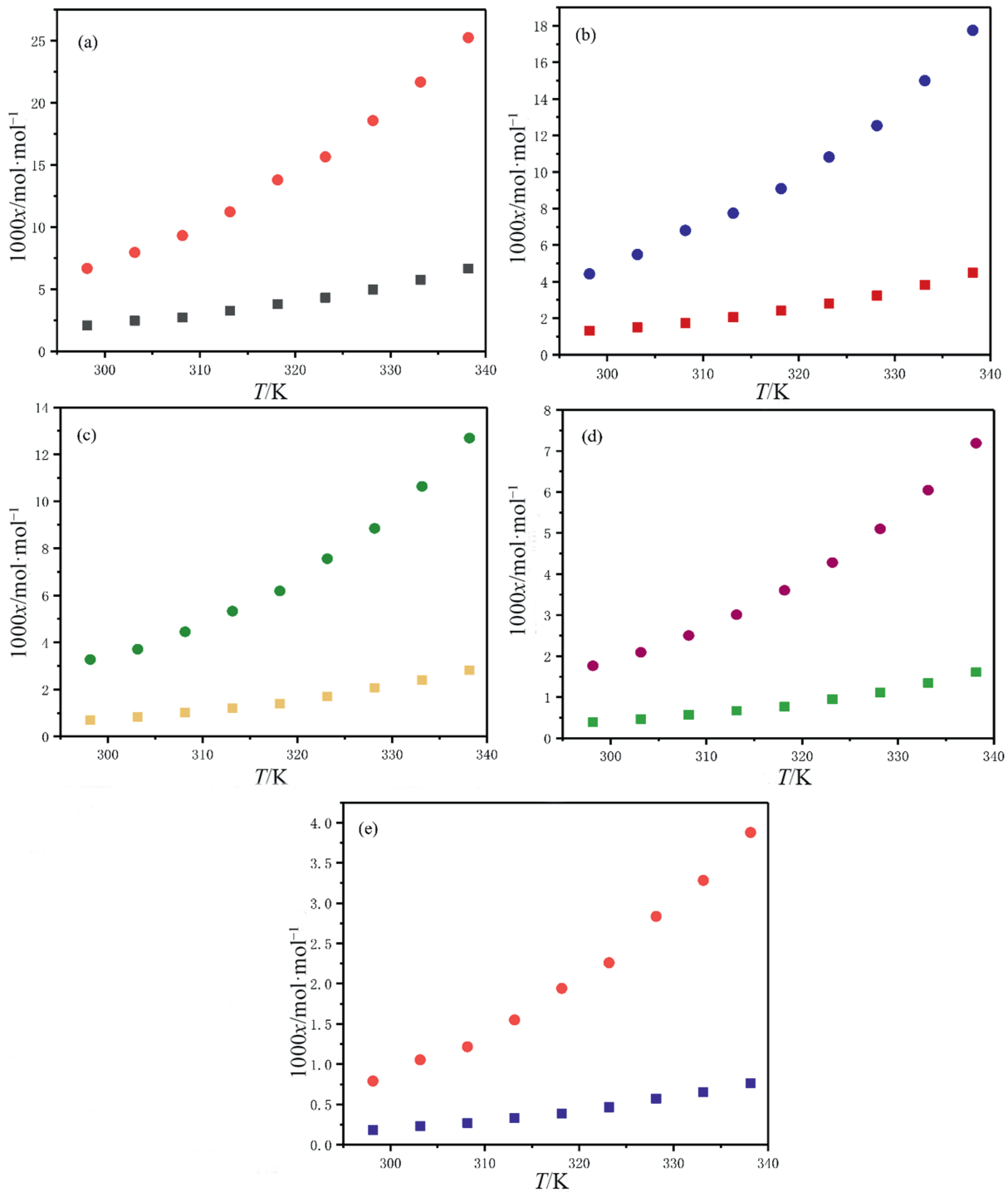

Fig. 4. Comparison of the solubility of β-HMX and RDX in the same proportion acetonitrile + water at the temperature from 298.15 K to 338.15 K under 0.1 MPa. (a) $x_{ACN} = 0.80$; (b) $x_{ACN} = 0.64$; (c) $x_{ACN} = 0.51$; (d) $x_{ACN} = 0.40$; (e) $x_{ACN} = 0.31$; ●, RDX; ■, β-HMX.

solution and the reciprocal of the absolute temperature [31]. It is a well-established semi-empirical model and can be expressed as Eq. (7)

$$\ln x = A + B/T \tag{7}$$

where x is the mole fraction solubility of β-HMX/RDX; A, B and C are the model parameters; T is the absolute temperature (K).

2.4.5. Evaluation of models

The solubility data were correlated with the above four equations. In order to evaluate the applicability and accuracy of the four models, the relative deviation (RD) and root-mean-square deviation (RMSE) were used to evaluate the relevant results [27]. RD and RMSE are shown as Eq. (8) and Eq. (9).

$$RD = (x_{exp} - x_{cal}) / x_{exp} \tag{8}$$

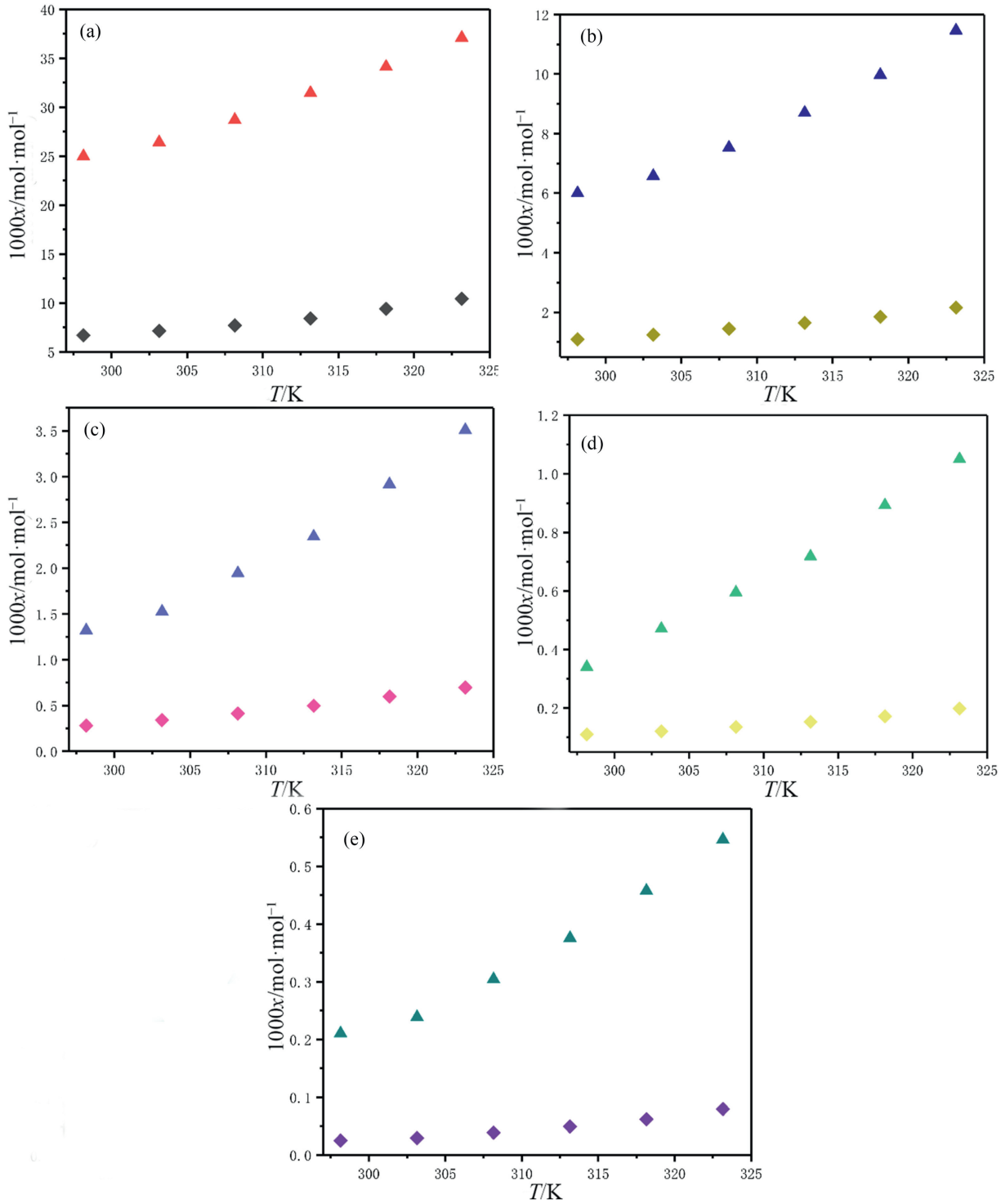

Fig. 5. Comparison of the solubility of β-HMX and RDX in the same proportion nitric acid + water at the temperature from 298.15 K to 323.15 K under 0.1 MPa. (f) x_{HNO_3} = 0.72; (g) x_{HNO3} = 0.53; (h) x_{HNO_3} = 0.42; (i) x_{HNO_3} = 0.30; (j) x_{HNO_3} = 0.22; ▲, RDX; ◆, β-HMX.

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{N} \left(x_{\mathrm{exp}} - x_{\mathrm{cal}}\right)^2}{N}} \quad (9)$$

where x_{exp} and x_{cal} are the mole fraction solubility of experimental and calculated values, respectively; N is the total number of experiment points.

3. Results and Discussion

3.1. Comparison and correlation of solubility data

Tables 2–5 list the experimental solubility values of β-HMX and RDX in binary mixed solvents. Figs. 4 and 5 show the comparative solubility of β-HMX and RDX in the same ratio of

Table 6
Model parameters, R^2 and RMSE of the modified Apelblat equation in different binary solvent

Substance	Solvent (x_1)	A	B	C	$R^{2①}$	RMSE②
β-HMX	ACN + H_2O					
	0.80	−107.33	2612.90	17.43	0.9992	0.04
	0.64	−161.32	4955.47	25.44	0.9997	0.02
	0.51	−49.55	−692.79	9.04	0.9992	0.02
	0.40	−193.34	6051.77	30.21	0.9994	0.01
	0.31	43.95	−5188.30	−4.96	0.9987	0.01
	HNO_3 + H_2O					
	0.72	−87.41	2305.88	13.10	0.9914	0.12
	0.53	−115.04	2778.17	17.36	0.9987	0.01
	0.42	−4.92	−3121.01	1.27	0.9991	0.00
	0.30	−104.63	2475.81	15.30	0.9965	0.00
	0.22	−106.98	491.41	16.62	0.9989	0.00
RDX	ACN + H_2O					
	0.80	4.68	−2983.90	1.27	0.9993	0.16
	0.64	−103.04	2062.22	17.14	0.9989	0.14
	0.51	−197.70	6413.74	31.13	0.9997	0.06
	0.40	−90.04	1254.00	15.16	0.9973	0.09
	0.31	130.82	−9518.90	−17.40	0.9987	0.04
	HNO_3 + H_2O					
	0.72	−87.73	2540.76	13.25	0.9976	0.21
	0.53	−121.27	3162.32	18.52	0.9979	0.09
	0.42	−176.74	4562.12	27.17	0.9982	0.03
	0.30	−45.46	−1696.01	7.59	0.9938	0.02
	0.22	−168.68	4159.93	25.67	0.9973	0.01

Note: x_1 is the mole fraction of solvent, such as acetonitrile and nitric acid.
① R^2 is the correlation coefficient.
② RMSE is the root-mean-square deviation.

Table 8
Model parameters, R^2 and RMSE of the Yaws equation in different binary solvent

Substance	Solvent (x_1)	A	B	C	$R^{2①}$	RMSE②
β-HMX	ACN + H_2O					
	0.80	19.32	−8518.50	8.88×10^5	0.9992	0.04
	0.64	23.59	−11311.00	1.30×10^6	0.9997	0.02
	0.51	16.25	−6538.00	4.72×10^5	0.9992	0.02
	0.40	26.20	−13254.00	1.54×10^6	0.9994	0.01
	0.31	8.00	−2069.60	-2.45×10^5	0.9987	0.01
	HNO_3 + H_2O					
	0.72	29.51	−19588.66	2.77×10^6	0.9997	0.02
	0.53	12.44	−9145.46	1.01×10^6	0.9978	0.01
	0.42	−6.60	2865.40	-9.96×10^5	0.9996	0.00
	0.30	28.39	−20849.71	2.88×10^6	0.9994	0.00
	0.22	28.09	−19085.34	2.25×10^6	0.9993	0.00
RDX	ACN + H_2O					
	0.80	13.90	−3803.70	6.63×10^4	0.9993	0.16
	0.64	21.36	−8790.30	8.58×10^5	0.9989	0.14
	0.51	28.60	−13533.00	1.60×10^6	0.9997	0.06
	0.40	20.29	−8516.80	7.86×10^5	0.9974	0.09
	0.31	4.40	1588.81	-8.86×10^5	0.9986	0.04
	HNO_3 + H_2O					
	0.72	14.37	−9533.51	1.24×10^6	0.9985	0.17
	0.53	25.29	−16137.31	2.11×10^6	0.9991	0.06
	0.42	19.01	−11748.23	1.22×10^6	0.9985	0.03
	0.30	−15.07	8952.57	-2.03×10^6	0.9979	0.01
	0.22	21.97	−14822.08	1.71×10^6	0.9970	0.01

Note: x_1 is the mole fraction of solvent, such as acetonitrile and nitric acid.
① R^2 is the correlation coefficient.
② RMSE is the root-mean-square deviation.

acetonitrile + water and nitric acid + water, respectively, from which it can be seen that the solubility of β-HMX in both solvent mixtures is smaller than that of RDX. In the acetonitrile + water system, the solubility of β-HMX changed slightly with temperature, while that of RDX changed significantly. At room temperature, the solubility difference between β-HMX and RDX was 3.2–4.72 times. When the acetonitrile molar fraction was 0.51, the solubility difference between β-HMX and RDX reached the maximum at room temperature. Therefore, acetonitrile + water could be selected to separate RDX from β-HMX under this condition. In the nitric acid + water system, the solubility difference between β-HMX and RDX is more obvious, especially when the mole fraction of nitric acid is 0.22, the difference is 8.53 times at room temperature, indicating that the separation effect of β-HMX and RDX is better in low concentration of nitric acid. Experiments have shown that α-HMX can be converted to β-HMX in the mixed solvent system of acetonitrile + water and nitric acid + water, if it is to be applied in industrial production, then the choice of solvent is crucial, acetonitrile belongs to cyanide organic substances, high toxicity, high harm to human body, not suitable for large-scale production. While nitric acid is an inorganic acid, it is often used as nitration agent in industrial synthesis of nitroamine explosives, which has low cost and is easy to deal with. Moreover, the solubility difference between β-HMX and RDX in low concentration nitric acid is larger than that in acetonitrile + water. Therefore, the system of nitric acid + water is more suitable as the transformation solvent system of α-HMX.

As can be seen from Tables 2–5, the solubility values calculated by the equations obtained from the four correlation models are in good agreement with the experimental values. According to Tables 6–9, the solubility data of β-HMX in two mixed solvents (acetonitrile + water, nitric acid + water) at different temperatures with the average RMSE of four models are 0.02 (modified Apelblat equation), 0.01 (Yaws model), 0.03 (modified Jouyban-Acree equation), 0.03 (van't Hoff equation), respectively. Similarly, the

Table 7
Model parameters, R^2 and RMSE of the modified Jouyban-Acree equation in different binary solvent

β-HMX				RDX			
ACN + H_2O		HNO_3 + H_2O		ACN + H_2O		HNO_3 + H_2O	
A_1	−61.94	A_1	−158.00	A_1	−122.81	A_1	−93.27
A_2	−2667.96	A_2	2889.09	A_2	1801.79	A_2	−497.81
A_3	10.97	A_3	25.18	A_3	19.99	A_3	16.28
A_4	−74.68	A_4	−154.22	A_4	104.77	A_4	−106.06
A_5	14932.76	A_5	9616.63	A_5	−3706.86	A_5	7077.67
A_6	−19709.52	A_6	4387.77	A_6	8453.95	A_6	4227.16
A_7	18393.55	A_7	−937.07	A_7	−18663.22	A_7	8914.03
A_8	−6812.08	A_8	−2702.76	A_8	10744.15	A_8	−12930.89
A_9	10.72	A_9	22.07	A_9	−15.35	A_9	14.09
$R^{2①}$	0.9997	$R^{2①}$	0.9999	$R^{2①}$	0.9995	$R^{2①}$	0.9999
RMSE②	0.03	RMSE②	0.03	RMSE②	0.12	RMSE②	0.09

① R^2 is the correlation coefficient.
② RMSE is the root-mean-square deviation.

Table 9
Model parameters, R^2 and RMSE of the van't Hoff equation in different binary solvent

Substance	Solvent (x_1)	A	B	$R^{2①}$	RMSE②
β-HMX	ACN + H_2O				
	0.80	10.71	−2985.53	0.9983	0.01
	0.64	11.02	−3223.75	0.9979	0.05
	0.51	11.69	−3603.85	0.9991	0.02
	0.40	11.34	−3677.63	0.9976	0.02
	0.31	10.36	−3591.22	0.9987	0.01
	HNO_3 + H_2O				
	0.72	0.90	−1772.14	0.9858	0.15
	0.53	2.00	−2633.16	0.9979	0.02
	0.42	3.62	−3516.60	0.9992	0.00
	0.30	−1.32	−2332.83	0.9936	0.00
	0.22	5.13	−4709.56	0.9982	0.00
RDX	ACN + H_2O				
	0.80	13.26	−3391.10	0.9993	0.16
	0.64	13.07	−3452.70	0.9983	0.18
	0.51	13.20	−3609.80	0.9977	0.15
	0.40	12.70	−3630.50	0.9969	0.10
	0.31	12.92	−3907.50	0.9982	0.04
	HNO_3 + H_2O				
	0.72	1.60	−1582.91	0.9950	0.29
	0.53	3.60	−2611.57	0.9955	0.13
	0.42	6.50	−3926.04	0.9981	0.03
	0.30	5.75	−4069.24	0.9947	0.02
	0.22	4.43	−3859.74	0.9974	0.01

Note: x_1 is the mole fraction of solvent, such as acetonitrile and nitric acid.
① R^2 is the correlation coefficient.
② RMSE is the root-mean-square deviation.

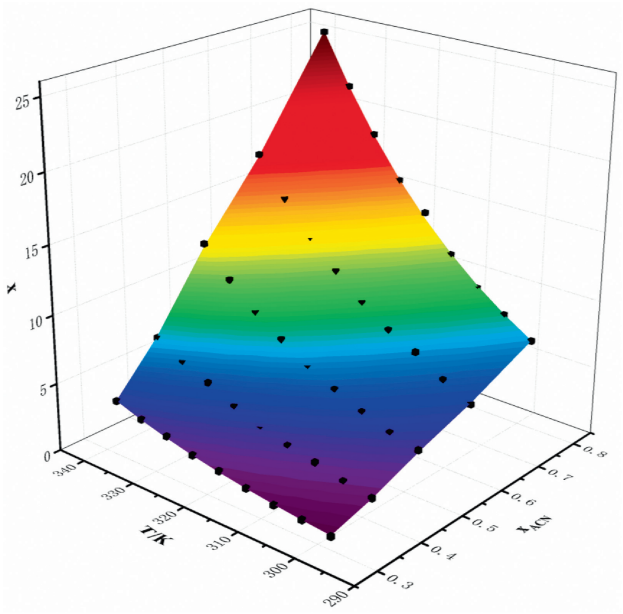

Fig. 7. The mole fraction solubility of RDX in binary system ACN + H_2O correlated by the Jouyban-Acree model. The points represent the experimental values, and the surface represents the results fitted by the Jouyban-Acree model.

solubility data of RDX in two mixed solvents at different temperatures with the average RMSE of four models are 0.09 (modified Apelblat equation), 0.08 (Yaws model), 0.13 (modified Jouyban-Acree equation), 0.11 (van't Hoff equation), respectively. From the above, the average RMSE obtained by the Yaws model was smaller than the other three models, so the Yaws model fitted the β-HMX and RDX in the two solvent mixtures best. The solubility values and experimental equations of β-HMX and RDX will be used as the basic data and models for the HMX polymorphic transformation process, providing the necessary support for industrial design and further theoretical studies.

The trend of solubility of β-HMX and RDX in the mixed solvents with temperature can be seen from Figs. 6–9. In the binary mixed solvents with constant non-solvent composition, the solubility of the two increases with the increase of temperature, which indicates that β-HMX and RDX exhibit the characteristic of heat absorption

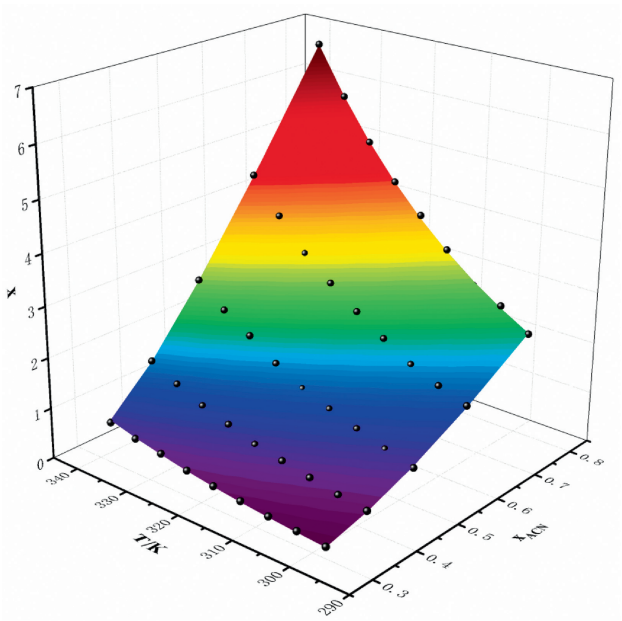

Fig. 6. The mole fraction solubility of β-HMX in binary system ACN + H_2O correlated by the Jouyban-Acree model. The points represent the experimental values, and the surface represents the results fitted by the Jouyban-Acree model.

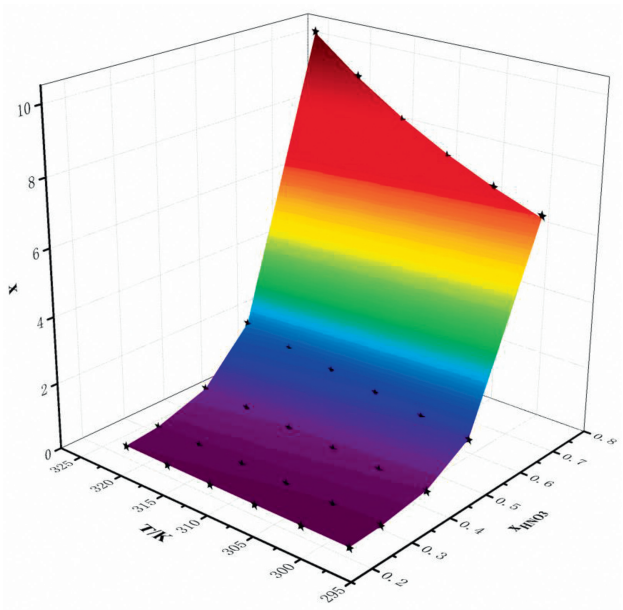

Fig. 8. The mole fraction solubility of β-HMX in binary system HNO_3 + H_2O correlated by the Jouyban-Acree model. The points represent the experimental values, and the surface represents the results fitted by the Jouyban-Acree model.

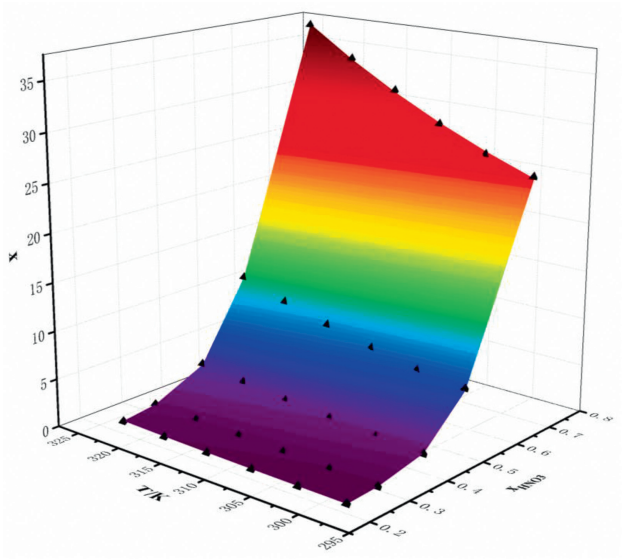

Fig. 9. The mole fraction solubility of RDX in binary system $HNO_3 + H_2O$ correlated by the Jouyban-Acree model. The points represent the experimental values, and the surface represents the results fitted by the Jouyban-Acree model.

of the solute and solvent, and hydrogen bonding. The difference in solubility between β-HMX and RDX in binary mixed solvents is caused by the different hydrogen bond formation. In 1970, Choi and Boutin [32] conducted a neutron diffraction study on the crystal structure of β-HMX, and reported that several non-bonded short intramolecular and intermolecular distances appeared in β-HMX. In the molecule, most of the hydrogen atoms in the methylene group are located close to the oxygen atoms in the nitramine group, which is prone to forming intramolecular hydrogen bonds. However, in RDX, the orientation of methylene group and nitro group is different, resulting in a distance between hydrogen atoms and oxygen atoms, which is not easy to form intramolecular hydrogen bonds. In 2009, Millar *et al.* [33] studied the crystal structure of RDX. It is pointed out that weak C—H···O intermolecular interactions link the two molecules within each lattice, showing weak intermolecular hydrogen bonds. This indicates that RDX is more likely to form intermolecular hydrogen bonds with solvents and be encapsulated by solvent molecules, showing a strong solvation effect, while β-HMX is easy to form intramolecular hydrogen bonds and has a strong wrapping force, which makes it difficult to break the intramolecular hydrogen bonds of HMX in solvents, leading to a weak solvation ability. Therefore, RDX has a higher solubility in mixed solvents than β-HMX.

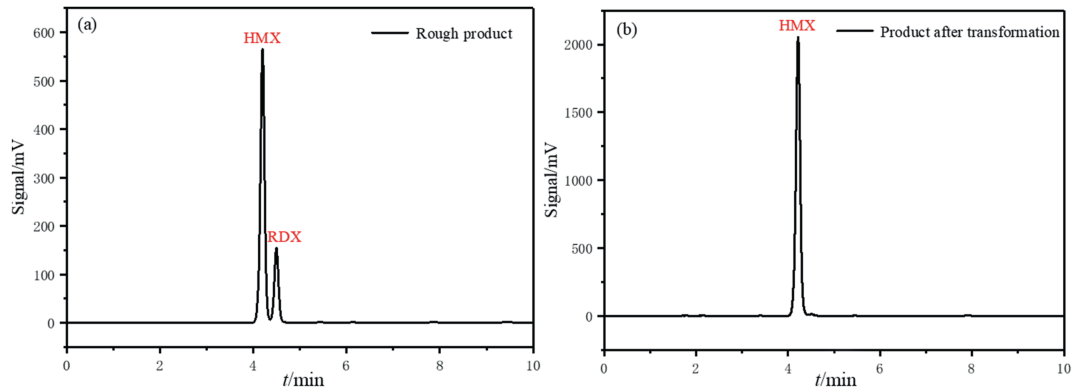

Fig. 10. HPLC analysis for comparison of HMX before and after transformation of crystal form: (a) rough product; (b) transcrystallite.

when dissolved in the binary mixed solvents. And at the same temperature, the solubility of both substances in the binary mixed solvent increased with the increase of solvent mass fraction.

3.2. Analysis of crystal transformation

The crude α-HMX (prepared by the acetic anhydride method without pyrolysis, purity, 78.5%) was dissolved in 98% nitric acid. When it was completely dissolved, the solution was slowly dripping into boiling deionized water (the amount of water used was just mixed with nitric acid to become nitric acid with a mass fraction of 50%), stirring for 1 h after all solid precipitation. It was dropped to room temperature and filtered to dry to obtain β-HMX. It can be seen from Fig. 10 that the purity of β-HMX was greater than 99.2% after crystal transformation.

3.3. Discussion of comparison

The factors affecting the solubility are complex, including the polarity of the selected solvent, the intermolecular interaction force

4. Conclusions

In this paper, the solubilities of β-HMX and RDX in the binary mixed solvent nitric acid + water in the range of 298.15–323.15 K and in the binary mixed solvent acetonitrile + water at 288.15 K to 333.15 K, respectively, were determined by using a laser dynamic monitoring technique. The results showed that the solubilities of both β-HMX and RDX in the binary mixed solvents increased with the increase of temperature and the content of solvents (acetonitrile and nitric acid); the solubilities of β-HMX were smaller than those of RDX at the same ratio and temperature of the same binary mixed solvents. The modified Apelblat equation, Yaws equation, Jouyban-Acree model and van't Hoff equation were used to correlate the experimental data of solubility, and the calculated values obtained with the four correlation models were in good agreement with the experimental values. By comparing the RMSE values in different binary solvent mixtures, it was found that the Yaws equation correlated the experimental data best, which is a guideline for fitting and expanding the application of experimental solubility data. In addition, by comparing the solubility differences of

β-HMX and RDX in different ratios of binary mixed solvents, the optimal separation conditions of β-HMX and RDX in two mixed solvents were determined, and nitric acid + water was selected as the optimal solvent system for HMX conversion according to the solubility differences and solvent properties. And the differences in the solubility of RDX and β-HMX in mixed solvents were attributed to the differences in the formation of intermolecular and intramolecular hydrogen bonds.

Declaration of 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.

Data Availability

Data will be made available on request.

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