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Simulation of the Dissolution Characteristics of RDX in Ethyl Acetate-Water Binary Mixed Solvent

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Abstract: To research the dissolution characteristics of Hexogen (RDX) in ethyl acetate - water binary system, the solubility of RDX at temperatures ranging from 298.15 to 338.15 K was measured The experimental data were fitted using Apelblat equation, CNIBS/R-K model and Jouyban-Acree equation. The standard enthalpy of dissolution, entropy of dissolution and Gibbs free energy were calculated. To study the dissolution mechanism, the solubility parameters of RDX in ethyl acetate-water binary mixed solvent were calculated by molecular dynamics simulation method. Results show that the solubility of RDX increases with the increase of temperature and water content. The fitting values of empirical equation are basically consistent with the experimental ones. The experimental solubility data, model parameters, thermodynamic properties and solubility parameters provide basic data and models for the recovery process of RDX and HMX.

Key words: hexogen(RDX); solubility; solubility parameter; thermodynamic properties

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1 Introduction

Octogen(HMX), with eight-membered ring of nitramine structure, is a kind of preferable single explosive judged from high density, high detonation velocity and good thermal stability. It has wide applications in rocket propellant, ammunition and weapons. HMX can be prepared in many methods[1], among which acetic anhydride method with simple process, easy operation and production safety is popularized. In the production process of HMX by acetic anhydride method, a mass of "waste explosive" is produced, and the so-called "waste explosive" is a mixture containing RDX, HMX and multiple by products, which precipitates from waste acid and waste solvents[2]. The interactions between RDX and HMX of "waste explosive" are mainly consist of van der Waals(vdW) force and electrostatic, which can be broken easily that makes it possible to separate the RDX and HMX. Since 1960s, the research of separation of RDX and HMX has entered a period of rapid development[2-3]. The representative methods are solvent method, crystallization with waste acid or nitric acid, mechanical separating method and complexation with cyclohexanone or dimethylformamide.

Nowadays, crystallization with ethyl acetate (EtOAc) that has mature recovery technology and obvious difference in solubility of RDX and HMX is selected to separate the RDX and HMX. Then HMX of high quality is obtained by rotating crystal method[4] and RDX of multi-granularity can be obtained through evaporative crystallization with acetone and water[5].

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The solubility is an extremely significant thermodynamic parameter for crystallization and calculation of other thermodynamic parameters. Because EtOAc is used in the separation of RDX and HMX, the measurement of the solubility of EtOAc is very important. In addition, the moisture content of raw material is pretreated to be below 25 percent, to leave out the drying process, during which we must consider the influence of moisture on solubility, so it is necessary to measure the solubility of RDX in ethyl acetate-water mixed solvents with different mole ratios. The solubility results will support the design and operation of the HMX recycling process.

In addition, molecular dynamics(MD) with provision of atomic-scale information has become a powerful simulation technique. Some researchers have simulated the solubility parameter[6-8] by MD method to explore the effect of components on solubility.

In the present work, we report the solubility of RDX in ethyl acetate-water mixture measured with a gravimetric method and the solubility parameter calculated using MD simulation. This is quite useful in the study of recycling process of RDX and HMX.

2 Materials and methodology

2.1 Materials

RDX (99.7%) was supplied by Research Institute of Gansu Yin Guang Chemical Industry Group Co.Ltd. Ethyl acetate (99.5%) without further purification was purchased from Sinopharm Chemical Reagent Co.Ltd. Deionized water was provided by laboratory-made.

2.2 Solubility measurements

40 g RDX and 200 g EtOAc were added into a 500 mL flask with three necks under 300 $r \cdot min^{-1}$ with an agitator made from polytetrafluoroethylene at temperatures ranging from 298.15 K to 338.15 K. A thermostatic water bath(Shanghai Bilon Precision Instrument Co. Ltd., China) was used to control the temperature with an uncertainty of 0.05 K. A condenser was used to prevent evaporation of solvent during the experiments. After 120 min, the agitation was switched off and the solution was stood for 120 min. Then 5 mL of solution was sampled into a bottle weighed before hand, and the mass of solution could be calculated after the total mass was measured. Similarly, the mass of solute could be calculated after the solvent evaporated completely. Each mass was determined using an analytical balance (Mettler Toledo XS 105DU, Switzerland) with an uncertainty of 0.0001 g. The same solubility experiments were repeated three times to obtain the mean values. The operations above were repeated with the mole ratio of water ranging from 0.0000 to 0.1280.

2.3 Computation

MD simulation in present work was performed using Forcite module and Amorphous Cell in Materials Studio 6.0 package[9]. The single crystal structure of RDX was obtained from the Cambridge Structural Database(CCDC: 705291)[10]. All the geometry was optimized by Conjugate gradient algorithm in COMPASS force field. The comparison of the experimental lattice parameters and the optimized values of RDX are listed in Table 1. It can be illustrated that the relative error between the optimized lattice parameters and the experimental values is within 5%, demonstrating that COMPASS force field is suitable for the simulation of RDX.

Table 1 Comparison of the experimental lattice parameters and the optimized values of RDX

lattice parameter	experimental value[10]	optimized value	relative error/%
a/Å	13.182	13.450	−2.033
b/Å	11.574	11.283	2.514
c/Å	10.709	10.225	4.520
β/(°)	90.000	90.000	0.000

The solubility parameter (δ) of a material is defined as square root of its cohesive energy density, and the molar cohesive energy is the energy associated with all the molecular interactions in a mole of the material[11]. According to the solubility parameter similarity rule, if the difference of solute and solvent is small, the solute will prefer to dissolve into the solvent[12]. Therefore, the solubility parameter of

RDX and ethyl acetate-water is calculated to evaluate the miscibility. The supercell of RDX and AC models of pure EtOAc and EtOAc/water system are displayed in Fig.1.

With COMPASS force field, a MD simulation of 200 psis was conducted under NPT (constant number of particles, pressure, and temperature) ensemble to equilibrate the AC structure of pure EtOAc and EtOAc/water binary system, and then another MD simulation of 200 psis was performed under NVT ensemble to calculate the solubility parameter. The periodic boundary condition was applied to all the simulations. Andersen thermostat[13] and Berendsen barostat[14] were selected to control the temperature and pressure, respectively. The Verlet velocity time integration method[15] with a time step of 1 fs was adopted to integrate the Newtonian equation of motion. The electrostatic interactions were calculated by the Ewald method[16] with an accuracy of 0.0001 kcal·mol^{-1}, and the van der Waals interactions were calculated by the atom-based method with a cutoff distance of 15.5 Å.

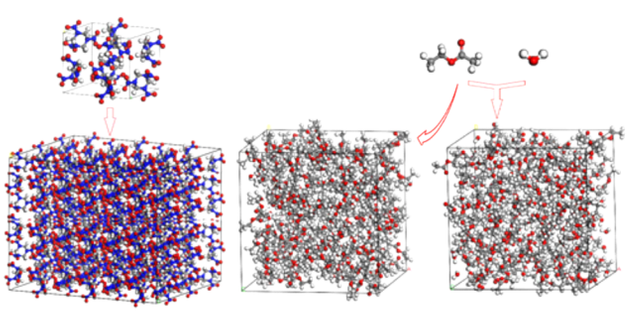

Fig.1 The super cell of RDX and amorphous cells of the EtOAc and EtOAc/water

3 Results and discussion

3.1 Determination of solubility

The mole fraction of water in the mixed solvent was defined by Eq.(1) and the saturated mole fraction solubility of RDX in the binary solvent mixtures was calculated by Eq.(2)[17-18].

$$x_0 = \frac{m_3/M_3}{m_2/M_2 + m_3/M_3} \quad (1)$$

$$x = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \quad (2)$$

where m_1, m_2 and m_3 represent the mass of RDX, ethyl acetate and water, respectively, M_1, M_2 and M_3 are the molar mass of RDX, ethyl acetate and water, respectively, x_0 and x are the mole fraction of water and RDX, respectively.

3.2 Correlation of the solubility values

Since solid-liquid equilibrium is usually not available, the correlation and prediction schemes are frequently utilized. The Apelblat equation, CNIBS/R-K and Jouyban-Acree models are used to correlate the experimental values. The root-mean-square deviation(RMSD) of each solvent is used to evaluate the fitting results of the correlation equation. RMSD is defined as Eq.(3)[19-20]:

$$\mathrm{RMSD} = \left[\frac{1}{N}\sum_{i=1}^{N}\left(x^{\mathrm{cal}} - x^{\mathrm{exp}}\right)^2\right]^{\frac{1}{2}} \quad (3)$$

3.2.1 Modified Apelblat model

The relationship between the mole fraction solubility and temperatureis generally modeled by Apelblat equation[21-24] deduced from the Clausius-Clapeyron equation, a semi-empirical equation, which can describe the solid-liquid equilibrium precisely. The equation can be expressed as Eq.(4):

$$\ln x = A + \frac{B}{T} + C\ln T \quad (4)$$

where A, B and C are the model parameters, and T denotes the absolute temperature. The constants A and B represent the variation in the solution activity coefficient and provide an indication of the influence of non-ideal solution on the solubility of solute; the parameter C reflects the effect of temperature on the enthalpy of fusion[25].

The correlated solubility curves are presented in Fig.2. The model parameters, correlation coefficient (R^2) together with RMSD of Apelblat equation are displayed in Table 2. The Apelblat equation obtained from experimental results describes the relationship between the solubility of RDX and the temperature precisely. The R^2 is close to 1 with atiny RMSD, resulting in that each fitting curve passes

through all the experimental points.

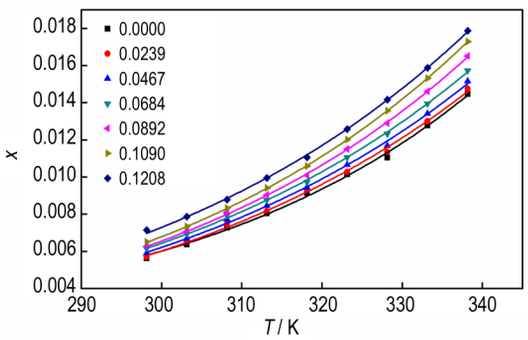

Fig. 2 The mole fraction solubility of RDX in ethyl acetate-water binary mixed solvents correlated by Apelblat equation

Table 2 Model parameters A, B, C, R^2 and RMSD of Apelblat equation

x_0	A	B	C	R^2	10^9×RMSD
0.0000	−158.3574	5253.0600	23.7971	0.9968	8.8363
0.0239	−84.2704	1738.2415	12.8622	0.9973	5.6023
0.0467	−85.4110	1798.6767	13.0323	0.9976	5.5914
0.0684	−87.6660	1894.0214	13.3782	0.9992	2.2630
0.0892	−91.1598	1986.3105	13.9399	0.9996	1.2730
0.1090	−88.3948	1828.0996	13.5538	1.0000	0.1813
0.1280	−81.3346	1591.4042	12.4669	0.9993	2.8186

3.2.2 CNIBS/R-K model

The CNIBS/R-K model is one of the theoretical models used for correlating the relationship between the solute solubility and the concentration of the binary solvents[26−27] as Eq.(5):

$$\ln x = B_0 + B_1 x_0 + B_2 x_0^2 + B_3 x_0^3 + B_4 x_0^4 \quad (5)$$

where B_0, B_1, B_2, B_3 and B_4 are the model parameters.

The correlated solubility curves are presented in Fig. 3, respectively. The model parameters, R^2, together with RMSD of CNIBS/R-K model are listed in Table 3. The fitting curves pass through every experimental point, which means that the CNIBS/R-K model obtained for experimental results describes the relationship between the solubility of RDX and the concentration of the binary solvents precisely.

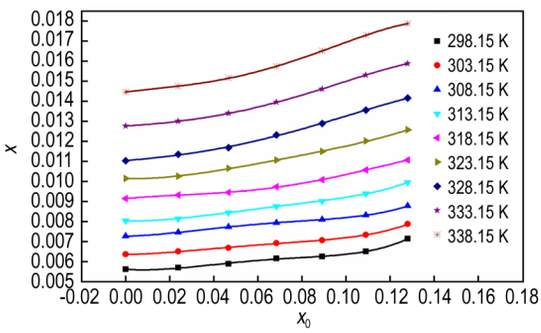

Fig.3 The mole fraction solubility of RDX in ethyl acetate-water binary mixed solvents correlated by CNIBS/R-K equation

3.2.3 Jouyban-Acree Model

Jouyban-Acree model is one of the versatile models to describe the solubility on both solvent compositions and temperature for binary mixed solvents[28−30]. The expression of this model can be described by Eq.(6):

$$\ln x = x_0 \ln(x)_0 + x_1 \ln(x)_1 + x_0 x_1 \sum_{i=1}^{N} \frac{J_i (x_0 - x_1)^i}{T} \quad (6)$$

where J_i is a model constant, T is the absolute temperature, and x_0 and x_1 represent the initial mole fractions of compositions of the binary solvent. When N=2, Eq.(6) can be simplified as Eq.(7):

$$\ln x = A_0 + A_1 \frac{1}{T} + A_2 \ln T + A_3 x_0 + A_4 x_0 \frac{1}{T} + A_5 (x_0)^2 \frac{1}{T} + A_6 (x_0)^3 \frac{1}{T} + A_7 (x_0)^4 \frac{1}{T} + A_8 x_0 \ln T \quad (7)$$

Table 3 Model parameters B_0−B_4, R^2 and RMSD of CNIBS/R-K model

T / K	B_0	B_1	B_2	B_3	B_4	R^2	10^{11}×RMSD
298.15	−5.1807	−1.5317	110.3606	−1437.9065	6116.9144	0.9953	18.8180
303.15	−5.0575	0.1167	45.3821	−635.0569	2925.8635	0.9960	15.7598
308.15	−4.9240	0.3229	45.8469	−665.1202	2944.6574	1.0000	0.0040
313.15	−4.8230	−0.4864	57.4424	−649.1124	2589.3714	0.9993	4.4262
318.15	−4.6947	1.1474	−24.3906	400.4854	−1478.2563	0.9992	5.2310
323.15	−4.5906	−0.3039	42.9317	−380.5694	1297.3967	0.9991	9.9144
328.15	−4.5058	0.7791	9.2411	62.4654	−499.2231	0.9979	40.7612
333.15	−4.3609	0.5747	5.2307	132.9940	−819.1692	0.9999	1.7660
338.15	−4.2360	0.8955	−9.4206	316.0742	−1533.3632	0.9999	2.1997

where A_0–A_8 are empirical model parameters which can be obtained by least-squares analysis. The model parameter values of A_0–A_8, R^2 and RMSD are displayed in Table 4. The three-dimensional diagram of x, x_0 and T is shown in Fig.4. The points represent the experimentalvalues, and the surface represents the results fitted by Jouyban-Acree model. All the experimental values are almost on the surface, indicating that the experimental results are fitted well by the Jouyban-Acree model. In addition, the values of R^2 are very close to 1 and those of RMSD are tiny. Therefore, the Jouyban-Acree model is a suitable equation to correlate the experimental solubility values of RDX in ethyl acetate-water system. Also, the solubility of RDX in ethyl acetate-water system at a random temperature or concentration can be calculated by the simplified Jouyban-Acree model obtained from this study.

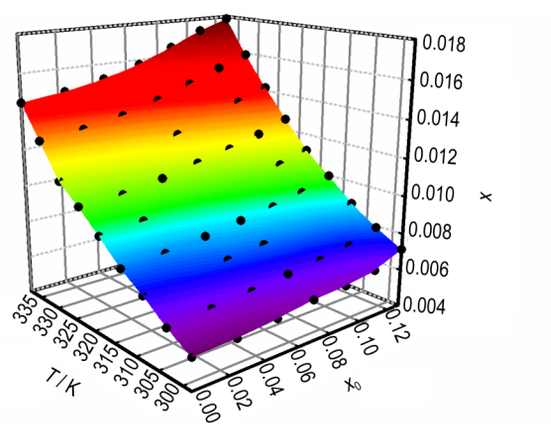

Fig.4 The mole fraction solubility of RDX in ethyl acetate-water binary mixed solvents correlated by Jouyban-Acree model

Table 4 Model parameters A_0–A_8, R^2 and RMSD of Jouyban-Acree model

parameters	values	parameters	values
A_0	−110.1876	A_6	−10000.8545
A_1	479.4046	A_7	6578.7368
A_2	16.6790	A_8	3.4612
A_3	−19.4866	R^2	0.9989
A_4	149.8984	10^4×RMSD	1.0516
A_5	4113.8900		

3.3 Thermodynamic properties of the solution

Some thermodynamic properties such as the standard enthalpy of dissolution ($\Delta_{\text{dissln}}H$, kJ·mol^{-1}), standard entropy of dissolution ($\Delta_{\text{dissln}}S$, J·K^{-1}·mol^{-1}) and the standard Gibbs free energy($\Delta_{\text{dissln}}G$, kJ·mol^{-1}) can be calculated when the solubility of RDX in ethyl acetate-water mixed solvents at different temperatures is confirmed. According to the Van't Hoff analysis, the apparent enthalpy change of solution can be related to the temperature and the solubility as Eq.(8)[31]:

$$\frac{\Delta_{\text{dissln}}H}{R} = -\left(\frac{\partial \ln x}{\partial (1/T)}\right)_P \tag{8}$$

Over a limited temperature interval (298.15 K to 338.15 K), the heat capacity change of solution may be assumed to be constant. Hence, the values of$H$ and S would be valid for the mean temperature, T_{mean}(318.15 K). Thus, combined with the Apelblat model, the $\Delta_{\text{dissln}}H$, $\Delta_{\text{dissln}}S$, $\Delta_{\text{dissln}}G$ can be calculated by Eq.(9)–Eq.(11), respectively[32].

$$\Delta_{\text{dissln}}H = -R\left(B - CT_{\text{mean}}\right) \tag{9}$$

$$\Delta_{\text{dissln}}S = R\left(\frac{\partial \ln x}{\partial \ln T} + \ln x\right) = R\left[A + C\left(1 + \ln T_{\text{mean}}\right)\right] \tag{10}$$

$$\Delta_{\text{dissln}}G = \Delta_{\text{dissln}}H - T_{\text{mean}}\Delta_{\text{dissln}}S \tag{11}$$

The results of the standard Gibbs energy, enthalpy, of dissolution and entropy of dissolution are shown in Table 5, together with $\%\xi_H$ and $\%\xi_S$. $\%\xi_H$ and $\%\xi_S$ represent the relative contribution to the standard Gibbs energy made by enthalpy and entropy in the dissolution process[33-34], as Eq.(12)–Eq.(13).

$$\%\xi_H = \frac{\left|\Delta_{\text{dissln}}H\right|}{\left|\Delta_{\text{dissln}}H\right| + \left|T\Delta_{\text{dissln}}S\right|} \times 100 \tag{12}$$

Table 5 Standard enthalpy of dissolution ($\Delta_{\text{dissln}}H$), entropy of dissolution ($\Delta_{\text{dissln}}S$), and Gibbs energy ($\Delta_{\text{dissln}}G$) at the mean temperature (318.15 K) together with $\%\xi_H$ and $\%\xi_S$

x_0	$\Delta_{\text{dissln}}H$ /kJ·mol^{-1}	$\Delta_{\text{dissln}}S$ /J·K^{-1}·mol^{-1}	$\Delta_{\text{dissln}}G$ /kJ·mol^{-1}	$\%\xi_H$	$\%\xi_S$
0.0000	19.2718	21.3766	12.4708	73.92	26.08
0.0239	19.5701	22.5353	12.4005	73.19	26.81
0.0467	19.5175	22.6161	12.3222	73.06	26.94
0.0684	19.6398	23.3159	12.2218	72.58	27.42
0.0892	20.3583	25.8496	12.1342	71.23	28.77
0.1090	20.6523	27.1295	12.0211	70.53	29.47
0.1280	19.7452	24.7177	11.8813	71.52	28.48

$$\%\xi_S = \frac{\left|T\Delta_{dissln}S\right|}{\left|\Delta_{dissln}H\right| + \left|T\Delta_{dissln}S\right|} \times 100 \quad (13)$$

Table 5 shows that the values of $\Delta_{dissln}H$ are positive in the binary solvent mixtures, indicating that the dissolution of RDX is an endothermic process. What's more, $\%\xi_H$ is larger than $\%\xi_S$ for each solvent, indicating that the main contributor to the standard molar Gibbs energy of dissolution is the enthalpy rather than the entropy.

3.4 Computational parameters

The solubility parameter (δ) of RDX and EtOAc/water is calculated by MD method to research why RDX solubility increases with the increasing water ratio of EtOAc /water binary system. The calculated solubility parameter of RDX and EtOAc /water is displayed in Table 6.

The solubility parameters of RDX and ethyl acetate are 30.208 $(J\cdot cm^{-3})^{1/2}$ and 18.317 $(J\cdot cm^{-3})^{1/2}$ respectively. The simulation results agree with the reported results of 31.8 $(J\cdot cm^{-3})^{1/2}$ and 18.6$(J\cdot cm^{-3})^{1/2}$[12], demonstrating that this method of computation is valid and reliable. From the calculation results we can deduce that with the increase of water, the solubility parameter of solvent is increasing and the difference of solubility parameter between RDX and solvent is decreasing. This phenomenon demonstrates that RDX solubility should increase with the mole fraction water in ethyl acetate-water binary system theoretically, which has a good agreement with the experimental results.

Table 6 The solubility parameters of RDX and solvent

	RDX	solvent						
		0.0000	0.0239	0.0467	0.0684	0.0892	0.1090	0.1280
solubility parameter/$(J\cdot cm^{-3})^{1/2}$	30.208	18.317	18.511	18.588	18.681	18.784	19.009	19.330

4 Conclusions

(1) The solubility values of RDX increase with an increase of water concentration and temperature as a nonlinear function.

(2) Three equations (Apelblat, CNIBS / R-K, and Jouyban-Acree) are used for the correlation of the experimental data, and all the models agree well with the experimental values.

(3) Some important thermodynamic properties such as the standard enthalpy of dissolution, standard entropy of dissolution and standard Gibbs free energy of dissolution have been calculated. It can be deduced that the dissolution process of RDX in ethyl acetate-water binary system is endothermic because of the positive value of $\Delta_{dissln}H$.

(4) The solubility parameter is calculated by MD simulations to verify the reliability of the experimental results. The difference of the solubility parameter between RDX and mixed solvents decreases with an increase of the mole fraction of water. So, RDX prefer to dissolve into ethyl acetate-water binary system with increasing the mole fraction of water, which reflects a good consistency with the experimental results.

References:

[1] CAO Xin-mao, LI Fu-ping. HMX and its application[M]. Beijing:Weapon Industry Press,1993:104-106.

[2] CAO Duan-lin, WANG Jian-long. A study on the recovery of small quantity of RDX in the producing of HMX with acetic anhydride[J]. *Journal of North China Institute of Technology*, 1996, 17(3): 279-282.

[3] YE Ling, WU Yu-zhong, LI Zhi-hua. Study on transformation of α-HMX into β-HMX with spent acetic acid[J]. *Chinese Journal of Explosives & Propellants*, 2000, 23(1): 38-39, 42.

[4] LI Qiao-ling, YE Yu-peng. A novel process for the refining of HMX[J]. *Acta Armamentarii*, 2002, 23(4): 555-557.

[5] ZHAO Rui-xian, LI Guang-ming, GAO Tian-ping, et al. Study on RDX granulate stage process[J]. *Chinese Journal of Explosives & Propellants*, 2003, 26(4): 67-70.

[6] ZHANG Min-hua, DOU Mao-bin, WANG Meng-yan, et al. Study on the solubility parameter of supercritical carbon dioxide system by molecular dynamics simulation[J]. *Journal of Molecular Liquids*, 2017, 248: 322-329.

[7] LUO Yan-long, WANG Run-guo, WANG Wei, et al. Molecular dynamics simulation insight into two-component solubility

parameters of graphene and thermodynamic compatibility of graphene and styrene butadiene rubber[J]. *Journal of Physical Chemistry C*, 2017, 121(18): 10163-10173.

[8] Goharshadi E K, Akhlamadi G, Mahdizaeh S J. Investigation of graphene oxide nanosheets dispersion in water based on solubility parameters: a molecular dynamics simulation study[J]. *RSC Advance*, 2015, 5(129): 106421-106430.

[9] Leach A R. Molecular modelling: principles and applications [M]. Beijing: World Book Inc, 2003.

[10] Choi C S, Bennema P. The crystal structure of cyclotrimethylenetrinitramine[J]. *Acta Crystallogr B*, 1972, 28: 2857-2862.

[11] Barton A F M. Solubility parameters [J]. *Chemical Reviews*, 1975, 75(6): 731-753.

[12] SUN Ye-bin, HUI Jun-ming, CAOXin-mao. Military Use Blended Explosives [M]. Beijing: Weapon Industry Press, 1995: 242-251.

[13] LI Jing, JIN Shao-hua, LAN Guan-chao, et al. Morphology control of 3-nitro-1, 2, 4-triazole-5-one (NTO) by molecular dynamics simulation[J]. *Crystengcomm*, 20(40): 6252-6260.

[14] LAN Guan-chao, JIN Shao-hua, LI Jing, et al.The study of external growth environments on the crystal morphology of epsilon-HNIW by molecular dynamics simulation [J]. *Journal of Materials Science*, 2018, 53(18): 12921-12936.

[15] LI Jing, JIN Shao-hua, LAN Guan-chao, et al. Molecular dynamics simulations on miscibility, glass transition temperature and mechanical properties of PMMA/DBP binary system [J]. *Journal of Molecular Graphics & Modelling*, 2018, 84: 182-188.

[16] LAN Guan-chao, JIN Shao-hua, LI Jing, et al. Miscibility, glass transition temperature and mechanical properties of NC/DBP binary systems by molecular dynamics [J]. *Propellants, Explosives, Pyrotechnics*, 2018, 43(6): 559-567.

[17] Almarri F, Haq N, Alanazi F K, et al. Solubilityand thermodynamic function of vitamin D3 in different mono solvent [J]. *Journal of molecular liquids*, 2017, 229: 477-481.

[18] Shakeel F, Imran M, Abida, Haq N, et al. Solubility and thermodynamic/solvation behavior of 6-phenyl-4, 5-dihydropyridazin-3 (2H)-one in different (Transcutol-water) mixtures [J]. *Journal of molecular liquids*, 2017, 230: 511-517.

[19] CHEN Li-zhen, ZHANG Tian-bei, LI Man, et al. Solubility of 2,2′,4,4′,6,6′-hexanitrostilbene in binary solvent of N, N-dimethylformamide and acetonitrile [J]. *Journal of Chemical Thermodynamics*, 2016, 99: 99-104.

[20] LAN Guan-chao, WANG Jian-long, CHEN Li-zhen, et al. Measurement and correlation of the solubility of 3, 4-bis(3-nitrofurazan-4-yl) furoxan (DNTF) in different solvents [J]. *Journal of Chemical Thermodynamics*, 2015, 89: 264-269.

[21] Apelblat A, Manzurola E. Solubilities of manganese, cadmium, mercury and lead acetates in water from *T*=278.15 K to *T*=340.15 K[J]. *Journal of Chemical Thermodynamics*, 2001, 33(2): 147-153.

[22] Apelblat A, Manzurola E. Solubilities of L-aspartic, DL-aspartic, DL-glutamic, *p*-hydroxybenzoic, *o*-anisic, *p*-anisic, and itaconic acids in water from *T*=278 K to *T*=345 K[J]. *Journal of Chemical Thermodynamics*, 1997, 29(12): 1527-1533.

[23] Apelblat A, Manzurola E. Solubilities of *o*-acetylsalicylic, 4-aminosalicylic, 3, 5-dinitrosalicylic, and *p*-toluic acid, and magnesium-DL-aspartate in water from *T*=(278 to 348) K[J]. *Journal of Chemical Thermodynamics*, 1999, 31(1): 85-91.

[24] ZHOU Li, ZHANG Pei-pei, YANG Guang-de, et al.Solubility of chrysin in ethanol and water mixtures[J]. *Journal of Chemical and Engineering Data*, 2014, 59(7): 2215-2220.

[25] CHEN Zhao-guo, YANG Wen-ge, HU Yong-hong, et al. Measurement and correlation for the solubility of dimethyl 1, 4-cyclohexanedione-2, 5-dicarboxylate in different solvents at temperatures from (278.15 to 323.15) K[J]. *Journal of Chemical and Engineering Data*, 2011, 56(5):2726-2729.

[26] AcreeJr W E .Comments concerning 'model for solubility estimation in mixed solvent system' [J]. *International Journal of Pharmaceutics*, 1996, 127(1): 27-30.

[27] Jouyban-Gharamaleki A, Hanaee J. A general model from theoretical cosolvency models[J].*International Journal of Pharmaceutics*, 1997, 152(2): 247-250.

[28] LIU Bao-shu, SUN Hua, WANG Jing-kang, et al. Solubility of disodium 5′-guanylate heptahydrate in aqueous methanol mixtures[J].*Food Chemistry*, 2011, 128(1): 218-221.

[29] Jouyban A. Review of the cosolvency models for predicting solubility of drugs in water-cosolvent mixtures[J].*Journal of Pharmacy and Pharmaceutical Sciences*, 2008, 11(1): 32-57.

[30] WANG Shui, QIN Li-ying, ZHOU Zhi-mao, et al. Solubility and solution thermodynamics of betaine in different pure solvents and binary mixtures [J]. *Journal of Chemical and Engineering Data*, 2012, 57(8): 2128-2135.

[31] WANG Guan, WANG Yong-li, MA You-guang, et al. Determination and correlation of cefuroxime acid solubility in (acetonitrile-water) mixtures [J]. *Journal of Chemical Thermodynamics*, 2014, 77: 144-150.

[32] ZHANG Hui, YIN Qiu-xiang, LIU Zeng-kun, et al. Measurement and correlation of solubility of dodecanedioic acid in different pure solvents from *T*=(288.15 to 323.15) K[J]. *Journal of Chemical Thermodynamics*, 2014, 68: 270-274.

[33] Delgado D R, Holguin A R, Almanza O, et al. Solubility and preferential solvation of meloxicam in ethanol-water mixtures [J]. *Fluid Phase Equilibria*, 2011, 305(1): 80-85.

[34] Holguin A R, Delgado D R, Martinez F, et al. Solution thermodynamics and preferential solvation of meloxicam in propylene glycol-water mixtures [J]. *Journal of Solution Chemistry*, 2011, 40(12):1987-1999.

黑索今在乙酸乙酯-水二元混合溶剂中的溶解特性的模拟

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摘　要: 为了研究黑索今(RDX)在乙酸乙酯-水二元体系中的溶解特性,测定了RDX在298.15~338.15 K温度下的溶解度。分别采用Apelblat方程、CNIBS/R-K模型及Jouyban-Acree方程对实验数据进行拟合。算出了标准溶解焓、标准溶解熵及吉布斯自由能。为了研究溶解机理,采用分子动力学模拟方法计算了RDX在二元混合溶剂中的溶度参数。结果表明,RDX的溶解度随着温度和水含量的升高而增大。经验方程拟合值与实验值基本保持一致。实验所得的溶解度数据,模型参数、热力学性质、溶度参数都为RDX和HMX的回收过程提供了基础数据和模型。

关键词: 黑索今(RDX);溶解度;溶度参数;热力学性质
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含能共晶是不同含能分子通过氢键等相互作用力形成的具有稳定结构和性能的分子晶体。含能共晶充分组合了单质含能分子的优点,呈现出感度低,综合性能优良的特点,具有潜在的应用前景,共晶研究已经引起国内外含能材料学界的高度关注。为推动含能共晶的研究和交流,本刊特推出"含能共晶"专栏,主要征稿范围包括含能共晶晶体设计与性能预测、含能共晶的制备、结构解析、性能等。来稿请注明"含能共晶"专栏。

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