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Investigation of the Dilution/Crystallization of CL-20 by Microcalorimetry

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Abstract: It is hard to measure the crystalline heat of CL-20 accurately, not only due to the instrument precision, but also β-polymorph transforming to ε-polymorph can be found easily and frequently in the crystallization progress. This work presents a study of experiments to clarify the crystallization model of ε-CL-20 and α-CL-20 using a solvent/antisolvent method by microcalorimetry without β-polymorph appearing. The results show that the crystallization progresses of ε-CL-20 and α-CL-20 are exothermic and they are fit the theory of Burton-Cabrera-Frank dislocation theory.

Keyword: ε-CL-20; α-CL-20; crystallization dynamics; microcalorimetry; dislocation theory

1. Introduction

2,4,6,8,10,12-hexanitrohexaazaisowurtzitane(HNIW, CL-20) is widely used polycyclic nitramine cage of explosive and energetic ingredient of propellants. Due to the molecule structure, the advantages of high energy and density of CL-20 make it easy to replace the explosives existing(such as cyclotetramethylene tetranitramine (HMX) and cyclotrimethylenetrinitramine (RDX)), where the solid propellants would reach an outstandingly high level[1,2].CL-20 has four stable polymorph modifications, via.,α, β, ε, γ. ε-CL-20 is the most potential polymorph which has high density and thermal stability among all polymorphs[3].

CL-20 can be easily soluble in solvents with carbonyl groups, such as ketones, esters and amides, not easily soluble in non-carbonyl materials such as alcohols, ethers, and nitroalkanes, and insoluble in hydrocarbons halogenated hydrocarbons, and water[4]. But not only dissolution, but also the crystallation, when meet the solvent, the crystal transformation from ε-CL-20 to other polymorphic may occur. Holtz and et al.[4] have studied the solubility of ε-CL-20 in EDNP, ethanol, FEFO, FM-1, and water using lot C-128 from ambient to 347K. The gamma polymorph appeared on the order of 10%. The first discovered β polymorph crystalline is isolated by recrystallization of crude CL-20 from benzene in 1996. And the α polymorph is formed upon precipitation of CL-20 with chloroform from its solutions in sulfolane[5]. 17-50% of α-CL-20 cell is occupied by water. Therefore, if the solvent has a certain amount of water, CL-20 would crystallize in the form of α-CL-20[6]. Jessica H Urbelis and et al. have studied the different phases of CL-20 from slow evaporation at room temperature from different single and mixed solvent systems. When slowly evaporating from CL-20 actone solution, α, β, ε phases were observed. However, when slowly evaporating from CL-20 ethyl acetate solution, only ε phase was observed[7]. Jinjiang Xu and et al have examined a series of CL-20 crystalliziton using solvent/antisolvent precipitation and found that the β-form appears first, which is then transformed into the ε-CL-20 when ethyel acetate(EA) solution is added and saturated with CL-20 using numerous antisovlent, except in water. That means β-CL-20 is initially precipitated from many solution and then transformed into the more stable ε-CL-20 polymorph[8]. Xianfeng Wei and et al have calculated the coherent energy density(CED) equivalent to thermodynamic stability. ε-CL-20 is the most stable crystal, and the β-CL-20 is the most unstable.

So the crystallization of CL-20 is complicated because of solution-mediated phases transformation (SMPT). The heat flow of crystallization would be hard to measure. The aim of this work is to explore the growth process of CL-20 through the expression deduction.

2. Experiment

2.1. Experimental section

Powdered ε-CL-20(purity 99.5%) was obtained from Beijing Institute of Technology, Drying at the time of 4h at 40℃.

All experiments are measured by RD496-2000 Calvet microcalorimenter (Mianyang CAEP Thermal Analysis Instrument Company, China), which has a sensitity of 66.5μVmW-1. The reliable and accurate of the calorimetric system is measured by the enthalpies of solution in deionized water of KCl(spectral purity).

Ethyl acetate as solvent, and the anti-solvents are trichloromethane, cyclohexane, ethyl alcohol ordistilled water. CL-20 ethyl acetate solution and anti-solvent are put into the vessel of instrument. After the instrument is stabilized, mix the solvents up. The dH/dt as the result is recorded. The ratio of solvent and anti-solvent is 1:4. The control test is ethyl acetate and anti-solvent without CL-20.

The samples were characterized by micro-attenuated total refraction using Germanium probe over the range of 5-60°and the resolution of 4cm^{-1}.

2.2. Recrystallization Experiment Section

Description the crystal growth process. To describe the crystallization, A(aq)=A(s)+heat

According to kinetic of the dilution/crystallization by Rongzu Hu[9], there are two equations as the model function to describe the crystal growth process.

$$\frac{dH}{dt} = H_{\infty}k(1-\frac{H}{H_{\infty}})^{n} \quad (1)$$

H is quantity of heat production at time t, H_{∞} is total quantity of heat production. *k* is the constant of the rate of heat production, *n* is reaction order.

When *n*=1,it means the crystallization progress in accordance with the regulation of BCF model.

So the Eq.(1) will change into:

$$\frac{dH}{dt} = k_2\left(1-\frac{H}{H_{\infty}}\right) + a \quad (2)$$

k_2 is the constant of the rate of heat production, a is the constant.

$$\frac{dm}{dt} = k_3 m_{\infty}(C - C_{\infty}) + b \quad (3)$$

m is the mass of solid deposited during a certain time t, C is the solute concentration in the solution at time t, the unit is g/100g solvent. C∞ is equilibrium staturation concentration. k is the constant of the rate of heat production, b is the constant.

The equation(1) is equivalent to the equation(2),at this moment:

$$b = \frac{am_{\infty}}{Q_{\infty}} \quad (4)$$

m_{∞} is the mass of crystallization.

3. Results and discussion

3.1. Ethyl acetate-ethanol system

According the origin data we can get the curve of the relationship between *dH/dt* and *1-Ht/H∞* of CL-20 in ethyl acetate-antisolvent solution(Fig.1), we can get the value of the constant(k_2,*a*) So substitute the value of the k_2 and *a* from the Fig.2 into the Eq.(1), and the kinetic of crystallization progress is obtained:

Table 1 Thermokinetic data of the crystal growth processes of ε-CL-20

t	dH/dt	dH/dt(mW)	Ht/H∞	H∞(mJ)	1-Ht/ H∞
314305	2502.472	45.13838	0.1365	19701.57	0.8635
614421	2308.978	41.64823	0.4064	19701.57	0.5936
614537	1618.323	29.19053	0.6163	19701.57	0.3837
614553	1049.816	18.93608	0.7578	19701.57	0.2422
614769	661.0084	11.92295	0.8491	19701.57	0.1509
614885	405.882	7.321104	0.9065	19701.57	0.0935
615001	245.6023	4.430056	0.9424	19701.57	0.0576
615117	144.3412	2.603557	0.9647	19701.57	0.0353
615233	81.7965	1.475406	0.9785	19701.57	0.0215
615349	42.5898	0.768214	0.987	19701.57	0.013
615465	18.2715	0.329573	0.9923	19701.57	0.0077
615581	2.759	0.049766	0.9955	19701.57	0.0045
615697	-6.8509	-0.12357	0.9976	19701.57	0.0024
615813	-12.7209	-0.22945	0.9986	19701.57	0.0014
615929	-16.4393	-0.29652	0.9993	19701.57	0.0007
616045	-18.8844	-0.34063	0.9997	19701.57	0.0003

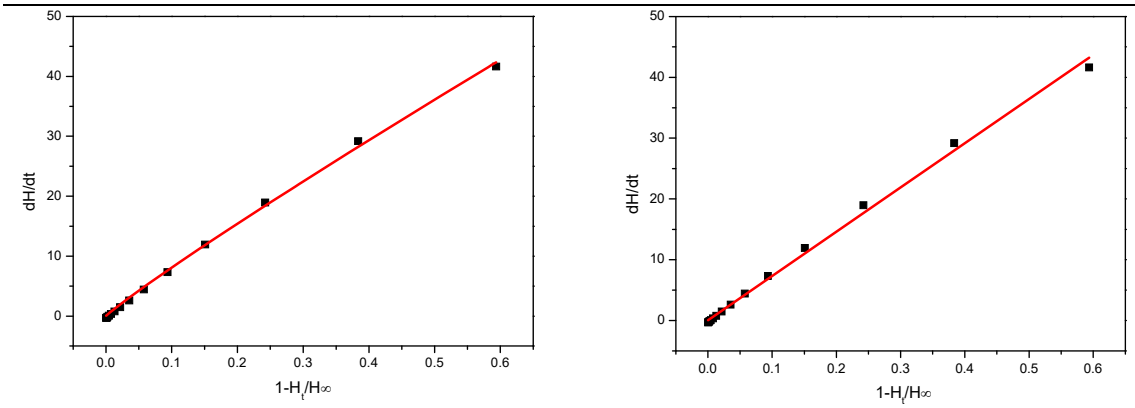

Fig.1 Relationship between *dH/dt* and *1-Ht/H∞* of CL-20 in ethyl acetate-ethanol solution(a.exponential relation b. linear relation)

Table 2 Total heat produced and crystal growth kinetics of ε-CL-20

T/K	CL-20 m_∞/g	Ethyl Acetate /g	ethanol /g	H_∞ /mJ	$\frac{dH}{dt} = H_\infty k(1-\frac{H}{H_\infty})^n$			$\frac{dH}{dt} = k_2\left(1-\frac{H}{H_\infty}\right)+a$			$\frac{dm}{dt} = k_3 m_\infty (C-C_\infty)+b$	
					k_1	n	r	k_2	a	r	k_3	b
298	0.203	0.450	1.580	19701.57	3.489 x10^{-3}	0.929	0.998	72.800	0.0412	0.996	3.695x10^{-4}	4.134 x10^{-7}

The crystal growth process of CL-20 in ethyl acetate-ethanol solution is exothermic, and it fit spiral growth of BCF model.

High performance liquid chromatography (HPLC) was used to measure that the content of CL-20 in the reaction solution was zero. And we use the micro-attenuated total refraction(ATR) to insure the crystalline particles were all ε polymorph(Fig 1). Meanwhile, the recrystallization experiments have been designed to study the crystallization progress and prove the model in the microcalorimetry experiments. When the CL-20 ethyl acetate solution and the ethanol were mixed up, there were no crystalline seed production. As time went on, the crystalline seed appeared in about 20min, Though removing the crystalline particles every 10 min in the crystallization progress it is found that all the particles were ε-CL-20.

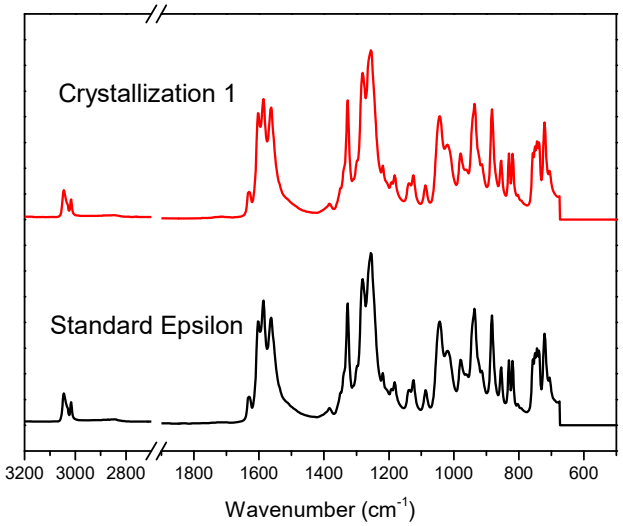

Fig 1 ATR spectra of ε-CL-20 crystal from ethyl acetate- ethanol system

3.2. Ethyl acetate-water system

The same treatment method as CL-20 ethyl acetate-ethanol system has been dealed with CL-20 ethyl acetate-water system. We can get the kinetic equation of crystal growth progress from the thermokinetic data as the table below:

Table 3 Thermokinetic data of the crystal growth processes of α-CL-20

t	dH/dt	dH/dt(mW)	Ht/ H_∞	H_∞(mJ)	1-Ht/ H_∞
550547	246.8334	4.452262	0.1059	5992.172	0.8941
550787	245.3083	4.424753	0.3057	5992.172	0.6943
551027	185.25	3.34145	0.4754	5992.172	0.5246
551267	132.1481	2.383624	0.6021	5992.172	0.3979
551507	93.9202	1.694087	0.6959	5992.172	0.3041
551747	66.7107	1.203295	0.7663	5992.172	0.2337
551987	47.6614	0.859693	0.8201	5992.172	0.1799
552227	32.572	0.587518	0.8616	5992.172	0.1384
552467	21.4641	0.387159	0.8937	5992.172	0.1063
552707	13.2953	0.239814	0.9187	5992.172	0.0813
552947	6.7569	0.121878	0.9385	5992.172	0.0615
553187	1.9349	0.034901	0.9541	5992.172	0.0459
553427	-1.3039	-0.02352	0.9666	5992.172	0.0334
553667	-4.5516	-0.0821	0.977	5992.172	0.023
553907	-7.5914	-0.13693	0.9849	5992.172	0.0151
554147	-10.0521	-0.18131	0.9908	5992.172	0.0092
554387	-12.0419	-0.21721	0.995	5992.172	0.005
554627	-13.9231	-0.24753	0.9979	5992.172	0.0021

Table 4 Total heat produced and crystal growth kinetics of α-CL-20

T/K	CL-20 m_∞/g	EA /g	H_2O /g	H_∞ /mJ	$\frac{dH}{dt} = H_\infty k(1-\frac{H}{H_\infty})^n$			$\frac{dH}{dt} = k_2\left(1-\frac{H}{H_\infty}\right)+a$			$\frac{dm}{dt} = k_3 m_\infty (C - C_\infty) + b$	
					k_1	n	r	k_2	a	r	k_3 x10^{-4}	b x10^{-6}
298	0.203	0.450	1.580	5992.172	1.348	1.340	0.9845	6.740	-0.286	0.998	1.358	-9.682

Because the reaction order of *n* is close to 1, we use Eq.(2) and Eq.(3) to describe the progress, $k_2>a$ and $k_3>b$,it means the CL-20 crystal progress in ethyl acetate-water system can use BCF model to describe.

micro-ATR measure insure that the crystalline particles were all α polymorph(Fig 2).Though removing the crystalline particles every 10min in the crystallization progress and we found all the particles were α polymorph. Also, the recrystallization experiments have been designed to study the crystallization progress and prove the model in the microcalorimetry experiments. When the CL-20 ethyl acetate solution and the ethanol were mixed up, there were no crystalline seed production. As time went on, the crystalline seed appeared in about 20min, Though removing the crystalline particles every 10 min in the crystallization progress it is found that all the particles were ε-CL-20.

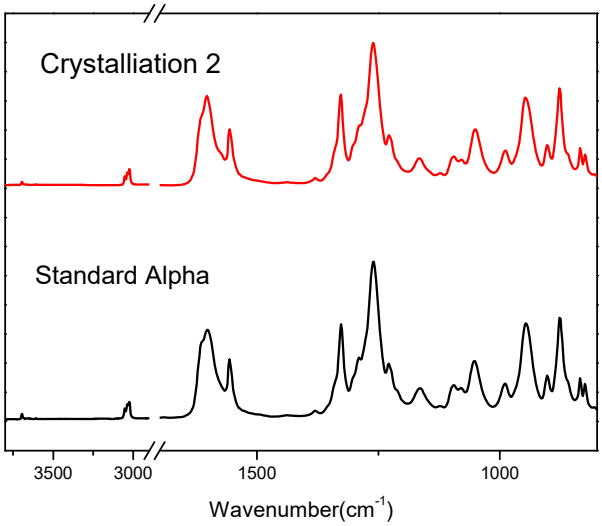

Fig 2 ATR spectra of α-CL-20 crystal from ethyl acetate-water system

4. Conclusions

In summary, we discussed the effects of solvent on the polymorphs and their cystal pogress from ethyl acetate-water system and ethyl acetate-ethanol system using experiments. The crystal growth process of CL-20 in ethyl acetate-ethanol solution is exothermic, and it fit spiral growth of BCF model. The crystal growth process of CL-20 in ethyl acetate-water solution is exothermic, and it fit spiral growth of BCF model.

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