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Dissolution properties of hexanitrohexaazaisowurtzitane (CL-20) in ethyl acetate and acetone

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Abstract The enthalpies of dissolution in ethyl acetate and acetone of hexanitrohexaazaisowurtzitane (CL-20) were measured by means of a RD496-2000 Calvet microcalorimeter at 298.15 K, respectively. Empirical formulae for the calculation of the enthalpy of dissolution ($\Delta_{diss}H$), relative partial molar enthalpy ($\Delta_{diss}H_{partial}$), relative apparent molar enthalpy ($\Delta_{diss}H_{apparent}$), and the enthalpy of dilution ($\Delta_{dil}H_{1,2}$) of each process were obtained from the experimental data of the enthalpy of dissolution of CL-20. The corresponding kinetic equations describing the two dissolution processes were $\frac{d\alpha}{dt} = 1.60 \times 10^{-2}(1-\alpha)^{0.84}$ for dissolution process of CL-20 in ethyl acetate, and $\frac{d\alpha}{dt} = 2.15 \times 10^{-2}(1-\alpha)^{0.89}$ for dissolution process of CL-20 in acetone.

Keywords Enthalpy · Dissolution · Ethyl acetate · Acetone · CL-20

Introduction

Hexanitrohexaazaisowurtzitane (CL-20) is a novel high energetic density material (HEDM) [1]. Its crystal density is 2.10 g cm^{-3}, and the detonation velocity corresponding to $\rho = 2.10$ g cm^{-3} is about 9,400 m s^{-1}. It can be expected that CL-20 has a good potential application in increasing the impulses and density of solid propellant field. And it can be regarded as a deputy of the next generation propellant raw material replacing energetic compounds such as RDX and HMX. Its preparation [2, 3], properties [4, 5], and thermal behavior [6, 7] have been reported widely.

In the present article, we reported its enthalpy of dissolution in ethyl acetate and acetone, and four kinds of empirical formulae describing the concentration b versus the enthalpy of dissolution ($\Delta_{diss}H$), relative partial molar enthalpy ($\Delta_{diss}H_{partial}$), relative apparent molar enthalpy ($\Delta_{diss}H_{apparent}$), and the enthalpy of dilution ($\Delta_{dil}H_{1,2}$) relations. It provides more information for the purification of CL-20 and the thermochemical database of energetic materials.

Experimental

Materials

CL-20 was prepared by Beijing Institute of Technology, and had a purity of more than 99.5%. Ethyl acetate and acetone used as solvents were of analytical purity.

Equipment and conditions

All measurements were made using a RD496-2000 Calvet microcalorimeter and operated at 298.15 ± 0.005 K. Two replicates of each sample were tested. The enthalpy of dissolution of KCl (spectrum purity) in distilled water measured at 298.15 K was 17.234 kJ/mol, which was an excellent accord with the literature value 17.241 kJ/mol [8], showing that the device of measuring the enthalpy used in this study was reliable.

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Results and discussion

The enthalpy of dissolution in ethyl acetate

The experimental and calculated values of enthalpy of dissolution [9, 10] in ethyl acetate for CL-20 are given in the Table 1. The calculated relative apparent molar enthalpy and relative partial molar enthalpy of CL-20 are also given in Table 1.

With the help of the values of b and $\Delta_{diss}H$ in Table 1, the empirical formula describing the b versus $\Delta_{diss}H$ relation is obtained:

$$\Delta_{diss}H = A + Bb + Cb^{1/2} = 4.2294 - 103.35b + 62.509b^{1/2} \quad (1)$$

where, $\Delta_{diss}H$ is enthalpy of dissolution in ethyl acetate. A, B, and C are coefficients for the dissolution equation.

The empirical formulae of relative apparent molar enthalpy ($\Delta_{diss}H_{apparen}$) and relative partial molar enthalpy ($\Delta_{diss}H_{partial}$) calculated by formula above are

$$\Delta_{diss}H_{apparent} = \Delta_{diss}H(b=b) - \Delta_{diss}H(b=0) = -103.35b + 62.509b^{1/2} \quad (2)$$

and

$$\Delta_{diss}H_{partial} = b\left(\frac{\partial \Delta_{diss}H}{\partial b}\right) + \Delta_{diss}H_{apparent} = -206.7b + 93.764b^{1/2}, \quad (3)$$

respectively.The empirical formula of dilution enthalpy ($\Delta_{dil}H_{1,2}$) for CL-20 is

$$\Delta_{dil}H_{1,2} = \Delta_{diss}H_2 - \Delta_{diss}H_1 = -103.35(b_2 - b_1) + 62.509\left(b_2^{1/2} - b_1^{1/2}\right) \quad (4)$$

where b_1 and b_2 represent different concentrations of the solutions after dissolving.

The enthalpy of dissolution of CL-20 in acetone

The experimental and calculated values of enthalpy of dissolution in acetone for CL-20 are given in the Table 2.

Table 1 The enthalpy of dissolution of CL-20 in ethyl acetate

$b/\times 10^2$ mol kg^{-1}	$\Delta_{diss}H$/kJ mol^{-1}		$\Delta_{diss}H_{partial}$/ kJ mol^{-1}	$\Delta_{diss}H_{apparent}$/ kJ mol^{-1}
	Found	Calculated		
3.6416	12.33	12.39	10.37	8.16
4.4256	12.83	12.81	10.58	8.58
4.5268	12.95	12.85	10.59	8.62
6.3223	13.35	13.41	10.51	9.18
6.5120	13.43	13.45	10.47	9.22
8.7500	13.70	13.69	9.65	9.45

b concentration

Table 2 The enthalpy of dissolution of CL-20 in acetone

$b/\times 10^2$ mol kg^{-1}	$\Delta_{diss}H$/kJ mol^{-1}		$\Delta_{diss}H_{partial}$/ kJ mol^{-1}	$\Delta_{diss}H_{apparent}$/ kJ mol^{-1}
	Found	Calculated		
2.924	21.32	21.27	−125.09	−103.67
4.264	14.23	13.73	−110.50	−111.21
5.474	15.30	15.37	−94.37	−109.57
6.569	13.46	13.74	−109.91	−111.20
6.728	14.79	14.99	−120.57	−109.94

The calculated relative apparent molar enthalpy and relative partial molar enthalpy of CL-20 in acetone are also given in Table 2.

According to the values in Table 2, the empirical formula describing the b versus $\Delta_{diss}H$ relation, the empirical formulae of relative apparent molar enthalpy, relative partial molar enthalpy, and the empirical formula of dilution enthalpy for CL-20 in acetone are

$$\Delta_{diss}H = A + Bb + Cb^{1/2} = 124.94 + 2080b - 961.94b^{1/2} \quad (5)$$

$$\Delta_{diss}H_{apparent} = \Delta_{diss}H(b=b) - \Delta_{diss}H(b=0) = 2080b - 961.94b^{1/2} \quad (6)$$

$$\Delta_{diss}H_{partial} = b\left(\frac{\partial \Delta_{diss}H}{\partial b}\right) + \Delta_{diss}H_{apparent} = 4160b - 1442.91b^{1/2} \quad (7)$$

and

$$\Delta_{dil}H_{1,2} = \Delta_{diss}H_2 - \Delta_{diss}H_1 = 2080(b_2 - b_1) - 961.94\left(b_2^{1/2} - b_1^{1/2}\right), \quad (8)$$

respectively.

The kinetics of dissolution processes of CL-20 in ethyl acetate and acetone

The proper molar sample of CL-20 was dissolved in ethyl acetate and acetone at 298.15 K. The enthalpy of the process was determined by the RD496-2000 Calvet microcalorimeter. Each process was repeated twice. The heat flow curves obtained under the same conditions overlap with each other, indicating that the reproducibility of test is satisfactory.

The kinetic Eq. 9 was selected to describe the dissolution process [11, 12].

$$\ln\left[\frac{1}{H_\infty}\left(\frac{dH}{dt}\right)_i\right] = \ln k + n\ln\left[1 - \left(\frac{H}{H_\infty}\right)_i\right] \quad i = 1, 2, \ldots, L \quad (9)$$

where H is the enthalpy at time of t, i is any time during the process, H_∞ is the enthalpy of the whole process, k is the reaction rate constant, and n is the reaction order [13].

Table 3 The original data of the dissolution process of CL-20 in ethyl acetate at 298.15 K

m/g	$m_{\text{eth.ace.}}$/g	t/s	$-(\mathrm{d}H/\mathrm{d}t)_i$/ mJ s^{-1}	$(H/H_0)_i$	$-H_\infty$/ kJ mol^{-1}
0.0288	1.80	80	0.1042	0.4428	12.33
		160	0.0813	0.5836	
		240	0.0603	0.6904	
		320	0.0452	0.7698	
		400	0.0342	0.8296	
		480	0.0260	0.8750	
		560	0.0195	0.9094	
		640	0.0143	0.9349	
		720	0.0105	0.9535	
		800	0.0081	0.9670	
		880	0.0060	0.9780	
		960	0.0043	0.9859	
		1040	0.0030	0.9913	
0.0350	1.80	50	0.1381	0.1045	12.83
		100	0.1282	0.2084	
		150	0.1156	0.3086	
		200	0.1030	0.4000	
		250	0.0913	0.4821	
		300	0.0800	0.5549	
		350	0.0695	0.6192	
		400	0.0599	0.6752	
		450	0.0508	0.7237	
		500	0.0439	0.7651	
		550	0.0383	0.8005	
		600	0.0333	0.8314	
		650	0.0289	0.8582	
		700	0.0247	0.8815	
		750	0.0210	0.9016	
		800	0.0176	0.9187	
		850	0.0149	0.9332	
		900	0.0127	0.9453	
0.0358	1.80	80	0.1424	0.2224	12.95
		160	0.1249	0.3750	
		240	0.1035	0.5051	
		320	0.0841	0.6115	
		400	0.0677	0.6976	
		480	0.0540	0.7666	
		560	0.0429	0.8215	
		640	0.0336	0.8649	
		720	0.0258	0.8986	
		800	0.0196	0.9243	
		880	0.0149	0.9438	
		960	0.0114	0.9587	
		1040	0.0088	0.9702	
		1120	0.0068	0.9791	
		1200	0.0049	0.9857	
		1280	0.0035	0.9904	
0.0500	1.80	80	0.2014	0.2353	13.35
		160	0.1668	0.3848	
		240	0.1392	0.5055	
		320	0.1063	0.6017	
		400	0.0861	0.6792	
		480	0.0693	0.7418	
		560	0.0556	0.7921	
		640	0.0445	0.8323	
		720	0.0356	0.8646	
		800	0.0287	0.8905	
		880	0.0231	0.9114	
		960	0.0180	0.9279	
		1040	0.0143	0.9409	
		1120	0.0114	0.9513	
		1200	0.0093	0.9596	
		1280	0.0076	0.9664	
0.515	1.80	80	0.1942	0.1860	13.43
		160	0.1668	0.3236	
		240	0.1370	0.4387	
		320	0.1102	0.5322	
		400	0.0892	0.6075	
		480	0.0725	0.6687	
		560	0.0594	0.7185	
		640	0.0495	0.7596	
		720	0.0417	0.7941	
		800	0.0355	0.8233	
		880	0.0303	0.8482	
		960	0.0258	0.8695	
		1040	0.0219	0.8875	
		1120	0.0188	0.9029	
		1200	0.0162	0.9161	
		1280	0.0139	0.9275	

The original data of the dissolution process of CL-20 in the different solvent were listed in Tables 3 and 4.

By substituting the data taken from Tables 3 and 4, $(\mathrm{d}H/\mathrm{d}t)_i$, $(H/H_\infty)_i$, H_∞, $i = 1,2,\ldots,L$, into the kinetic equation, the values of n and $\ln k$ listed in Table 5 are obtained. Substituting the values of n and k in Table 5 into Eq. 10

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-\alpha)^n \tag{10}$$

yields

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = 1.60 \times 10^{-2}(1-\alpha)^{0.84} \tag{11}$$

for dissolution process of CL-20 in ethyl acetate, and

Table 4 The original data of the dissolution process of CL-20 in acetone at 298.15 K

m/g	$m_{acetone}$/g	t/s	$-(dH/dt)_i$/ mJ s^{-1}	$(H/H_0)_i$	$-H_\infty$/ kJ mol^{-1}
0.0296	1.44	50	0.1863	0.2022	14.23
		100	0.1695	0.3403	
		150	0.1455	0.4617	
		200	0.1218	0.5646	
		250	0.1000	0.6500	
		300	0.0811	0.7196	
		350	0.0654	0.7759	
		400	0.0528	0.8213	
		450	0.0424	0.8579	
		500	0.0338	0.8872	
		550	0.0268	0.9105	
		600	0.0215	0.9290	
		650	0.0172	0.9438	
		700	0.0138	0.9558	
		750	0.0106	0.2022	
		800	0.0076	0.3403	
		850	0.0065	0.4617	
		900	0.0054	0.5647	
0.0380	1.44	50	0.1927	0.1592	15.30
		100	0.1860	0.2852	
		150	0.1665	0.4016	
		200	0.1448	0.5043	
		250	0.1231	0.5926	
		300	0.1029	0.6670	
		350	0.0850	0.7289	
		400	0.0701	0.7799	
		450	0.0574	0.8218	
		500	0.0468	0.8561	
		550	0.0381	0.8840	
		600	0.0309	0.9067	
		650	0.0250	0.9251	
		700	0.0200	0.9399	
		750	0.0161	0.9517	
		800	0.0130	0.9613	
		850	0.0105	0.9689	
		900	0.0086	0.9752	
0.0456	1.44	150	0.2690	0.4212	13.46
		200	0.2369	0.4954	
		250	0.2009	0.5627	
		300	0.1662	0.6228	
		350	0.1373	0.6761	
		400	0.1132	0.7231	
		450	0.0939	0.7642	
		500	0.0784	0.8001	
		550	0.0650	0.8302	
		600	0.0543	0.8585	
		650	0.0465	0.8821	
		700	0.0405	0.9025	
		750	0.0352	0.9201	
		800	0.0311	0.9354	
		850	0.0271	0.9486	
		900	0.0237	0.9601	
0.0467	1.44	150	0.2445	0.2669	14.79
		200	0.2197	0.3767	
		250	0.1900	0.4735	
		300	0.1589	0.5557	
		350	0.1331	0.6244	
		400	0.1118	0.6820	
		450	0.0942	0.7304	
		500	0.0788	0.7712	
		550	0.0659	0.8052	
		600	0.0549	0.8337	
		650	0.0459	0.8574	
		700	0.0383	0.8772	
		750	0.0310	0.8936	
		800	0.0250	0.9067	
		850	0.0217	0.9177	
		900	0.0187	0.9272	

Table 5 The values of n, ln k, and the linear correlative coefficient r for the dissolution process

Solvent	n	ln k	r
Ethyl acetate	0.8626	−4.33	0.997
	0.8493	−4.28	0.999
	0.8595	−4.25	0.999
	1.0557	−3.85	0.999
	1.1139	−3.98	0.999
Acetone	0.8626	−4.07	0.995
	0.8576	−4.08	0.997
	0.9938	−3.57	0.996
	1.1314	−3.63	0.995

$$\frac{d\alpha}{dt} = 2.15 \times 10^{-2}(1-\alpha)^{0.89} \quad (12)$$

for dissolution process of CL-20 in acetone, indicating that the reaction rates of CL-20 dissolved in ethyl acetate and acetone are similar, and the reaction orders can be considered the same.

Summaries

(1) The enthalpies of dissolution of CL-20 in ethyl acetate and acetone were investigated by RD496-2000 Calvet microcalorimeter at 298.15 K. The results were analyzed with mathematics formulae to get the expression of $\Delta_{diss}H$, $\Delta_{diss}H_{apparent}$, $\Delta_{diss}H_{partial}$, and $\Delta_{dil}H_{1,2}$ of CL-20 in different solvents.

(2) The reaction orders of the dissolution processes of CL-20 in ethyl acetate and acetone at 298.15 K were

similar, and the progressions of the reaction rates were at the same level.

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