1,3,3-三硝基氮杂环丁烷在乙酸乙酯和 *N,N*-二甲基甲酰胺中的溶解行为

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摘要: 在常压、298.15 K 条件下, 用 RD496-2000 微热量仪分别测量了 1,3,3-三硝基氮杂环丁烷(TNAZ)在乙酸乙酯(EA)和 *N,N*-二甲基甲酰胺(DMF)中的溶解焓. 得到了 TNAZ 在不同溶剂中的微分溶解热和积分溶解热. 建立了热量与溶质的量之间的关系式. 对 TNAZ, 得到了在乙酸乙酯中描述溶解过程的动力学方程为 $d\alpha/dt = 10^{-7.26}(1-\alpha)^{0.88}$, 在 *N,N*-二甲基甲酰胺中, 描述溶解过程的动力学方程为 $d\alpha/dt = 10^{-7.21}(1-\alpha)^{0.66}$.

关键词: 动力学; 溶解; 乙酸乙酯; *N,N*-二甲基甲酰胺; 1,3,3-三硝基氮杂环丁烷

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Dissolution Properties of 1,3,3-Trinitroazetidine in Ethyl Acetate and *N,N*-Dimethylformamide

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Abstract: The enthalpies of dissolution for 1,3,3-trinitroazetidine (TNAZ) in ethyl acetate (EA) and *N,N*-dimethylformamide (DMF) were measured using a RD496-2000 Calvet Microcalorimeter at 298.15 K under atmospheric pressure. Differential enthalpies ($\Delta_{\text{diff}}H$) and molar enthalpies ($\Delta_{\text{sol}}H$) were determined for TNAZ in different solvents. The corresponding kinetic equations that describe the two dissolution processes are $d\alpha/dt = 10^{-7.26}(1-\alpha)^{0.88}$ for the dissolution of TNAZ in ethyl acetate and $d\alpha/dt = 10^{-7.21}(1-\alpha)^{0.66}$ for the dissolution of TNAZ in *N,N*-dimethylformamide.

Key Words: Kinetics; Dissolution; Ethyl acetate; *N,N*-dimethylformamide; 1,3,3-Trinitroazetidine

1,3,3-Trinitroazetidine is a high performance and melt castable explosive that has been proposed as potential replacement for trinitrotoluene (TNT). The low melting point (101 °C) and good thermal stability (>180 °C) of TNAZ enables its applications as energetic component whilst its performance is approximately 30% greater than TNT's^[1-5]. It is reported that TNAZ is highly energetic material and more powerful than cyclotrimethylenetrinitramine (RDX), and it is less vulnerable than most other nitramines. TNAZ is a steam-castable material which is attrac-

tive as an explosive or as a near-term candidate component for explosives/propellants with low sensitivity, good stability, and enhanced performance over existing military formulations^[6-10].

There are several reports on the properties of TNAZ, mainly about its stabilities^[7,8], thermal behaviors^[9-14], sensitivities^[15,16] and so on, but the solubility of TNAZ in different solvents has not been investigated deeply. In our work, a RD496-2000 Calvet Microcalorimeter was employed to measure the enthalpies of TNAZ in ethyl acetate and *N,N*-dimethylformamide, separately.

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The kinetic equations of the two dissolution processes were obtained, which provides valuable informations for purification of TNAZ in industry.

1 Experimental

1.1 Materials

TNAZ was prepared and purified in Xi'an Modern Chemistry Research Institute, and had a purity of more than 99.5%. Ethyl acetate and *N,N*-dimethylformamide used as solvents were of analytical purity.

1.2 Equipment and conditions

All measurements were made using a RD496-2000 Calvet Microcalorimeter (Mianyang CAEP Thermal Analysis Instrument Company, China) and operated at 298.15 K. Two replicates of each sample were tested. The enthalpy of dissolution of KCl (spectrum purity) in distilled water (0.0481 g/2.000 g) measured at 298.15 K was 17.23 kJ·mol⁻¹, which was in an excellent accordance with the literature value 17.241 kJ·mol⁻¹ [17,18], showing that the device of measuring the enthalpy used in this work was reliable.

2 Results and discussion

2.1 Thermochemical behaviors of the dissolution of TNAZ in ethyl acetate and *N,N*-dimethylformamide

The proper molar sample of TNAZ was dissolved in ethyl acetate and *N,N*-dimethylformamide at 298.15 K. The enthalpy of the process was detected by the RD496-2000 Calvet Microcalorimeter. The entire process was repeated two times. The curve describing the entire dissolution process of TNAZ in ethyl acetate is showed in Fig.1. The dissolution is an endothermal process. The heat flow curves obtained under the same conditions overlap with each other, indicating that the reproducibility of test is satisfactory.

The thermochemical data obtained are listed in Table 1. As we can see in Table 1, the concentration of the solution (*b*) almost has little influence on the values of the molar enthalpies ($\Delta_{\text{sol}}H$) at 298.15 K. So the average value of $\Delta_{\text{sol}}H$ can represent the molar enthalpies of the infinite diluted solution due to very

Fig.1 Heating rate (dH/dt) of the entire dissolution process of TNAZ in ethyl acetate

Table 1 The enthalpies of dissolution of TNAZ in ethyl acetate and *N,N*-dimethylformamide

	$10^4 a/\text{mol}$	$b/(\text{mol} \cdot \text{kg}^{-1})$	Q/J		$\Delta_{\text{sol}}H$ (kJ·mol ⁻¹)
			Experimental	Calculated	
ethyl acetate	2.02	0.1002	-1.2343	-1.2601	6.10
	2.59	0.1281	-1.5775	-1.6157	6.10
	3.17	0.1567	-1.9762	-1.9775	6.24
	3.00	0.1487	-1.8928	-1.8715	6.30
	1.82	0.0899	-1.1390	-1.1354	6.27
average					6.20±0.10
<i>N,N</i> -dimethylformamide	1.90	0.0941	-0.2290	-0.2205	1.21
	1.09	0.0539	-0.1132	-0.1054	1.04
	3.02	0.1497	-0.2838	-0.2846	1.21
	2.35	0.1165	-0.1388	-0.1504	0.99
	1.41	0.0696	-0.1804	-0.1843	1.10
average					1.11±0.10

a: the amount of the substance; *b*: the concentration of the solution;

Q: the heat effect of each process, the calculated *Q* obtained from Eqs.(1, 2);

$\Delta_{\text{sol}}H$: the molar enthalpy

low molalities of the solution.

The heat effect *vs* the amount of the substance relationships of TNAZ in different solvents are shown in Fig.2.

The according linear equations for solvents ethyl acetate and *N,N*-dimethylformamide respectively are as follows:

$$Q = -6238.4a, r = 0.998 \quad (1)$$

$$Q = -1187.1a, r = 0.994 \quad (2)$$

where, *r* is correlation coefficient.

The differential enthalpies ($\Delta_{\text{diff}}H$) are obtained from the slope of the equations. So the differential enthalpies of TNAZ in ethyl acetate and *N,N*-dimethylformamide are about 6.24 and 1.19 kJ·mol⁻¹, respectively.

2.2 Kinetics of dissolution processes of TNAZ in ethyl acetate and *N,N*-dimethylformamide

The kinetic equation describing the dissolution of TNAZ in ethyl acetate and *N,N*-dimethylformamide is Eq.(3), and Eq.(4) [19-25] is chosen as the model function describing the process:

$$\frac{d\alpha}{dt} = k f(\alpha) \quad (3)$$

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

Fig.2 Relationships of *Q vs a* of TNAZ in ethyl acetate and *N,N*-dimethylformamide

Table 2 Original data of the dissolution process of TNAZ in ethyl acetate (EA) at 298.15 K

m_{TNAZ}/g	m_{EA}/g	t/s	$-(\text{d}H/\text{d}t)/(\text{mJ}\cdot\text{s}^{-1})$	$(H/H_{\infty})_t$	$-H_{\infty}/(\text{kJ}\cdot\text{mol}^{-1})$	m_{TNAZ}/g	m_{EA}/g	t/s	$-(\text{d}H/\text{d}t)/(\text{mJ}\cdot\text{s}^{-1})$	$(H/H_{\infty})_t$	$-H_{\infty}/(\text{kJ}\cdot\text{mol}^{-1})$							
0.0349	2.20	120	0.2010	0.2899	6.09	0.0435	2.20	360	0.1044	0.7639	6.26							
		160	0.1788	0.3935				400	0.0886	0.8045								
		200	0.1560	0.4847				440	0.0748	0.8388								
		240	0.1347	0.5638				480	0.0630	0.8677								
		280	0.1165	0.6322				520	0.0531	0.8922								
		320	0.0998	0.6911		0.0497	2.20	120	0.2273	0.3692								
		360	0.0847	0.7413				160	0.2046	0.4534								
		400	0.0721	0.7839				200	0.1818	0.5289								
		440	0.0613	0.8202				240	0.1601	0.5956								
		480	0.0521	0.8510				280	0.1398	0.6541								
520	0.0444	0.8772	320	0.1213	0.7050	0.0389	2.20	120	0.2085	0.3777		6.10	0.0608	2.20	120	0.2918	0.3307	6.21
160	0.1826	0.4752	400	0.0901	0.7870													
200	0.1575	0.5599	120	0.0772	0.8196													
240	0.1346	0.6327	160	0.0660	0.8475													
280	0.1145	0.6947	200	0.0564	0.8713													
320	0.0969	0.7474	160	0.2652	0.4171													
360	0.0819	0.7920	200	0.2368	0.4948													
400	0.0690	0.8296	240	0.2088	0.5638													
440	0.0578	0.8612	280	0.1829	0.6245													
480	0.0486	0.8876	320	0.1589	0.6774													
0.0435	2.20	120	0.2543	0.3310	6.46	360	0.1379	0.7232										
		160	0.2234	0.4316		400	0.1196	0.7631										
		200	0.1938	0.5194		440	0.1035	0.7976										
		240	0.1668	0.5952		480	0.0893	0.8274										
		280	0.1432	0.6604		520	0.0768	0.8531										
		320	0.1223	0.7162		520	0.0768	0.8531										

Table 3 Original data of the dissolution process of TNAZ in *N,N*-dimethylformamide (DMF) at 298.15 K

m_{TNAZ}/g	m_{DMF}/g	t/s	$-(\text{d}H/\text{d}t)/(\text{mJ}\cdot\text{s}^{-1})$	$(H/H_{\infty})_t$	$-H_{\infty}/(\text{kJ}\cdot\text{mol}^{-1})$	m_{TNAZ}/g	m_{DMF}/g	t/s	$-(\text{d}H/\text{d}t)/(\text{mJ}\cdot\text{s}^{-1})$	$(H/H_{\infty})_t$	$-H_{\infty}/(\text{kJ}\cdot\text{mol}^{-1})$	
0.0209	1.895	80	0.0367	0.3203	1.04	0.0316	1.895	360	0.0143	0.8247	1.21	
		120	0.0330	0.5077				400	0.0118	0.8692		
		160	0.0269	0.6682				440	0.0096	0.9057		
		200	0.0200	0.7937				480	0.0077	0.9352		
		240	0.0133	0.8823		0.0452	1.895	40	0.0854	0.1465		
		280	0.0082	0.9392				80	0.0796	0.3288		
		320	0.0047	0.9732				120	0.0671	0.4885		
0.0270	1.895	360	0.0022	0.9910	0.99	0.0581	1.895	160	0.0543	0.6202		1.14
		80	0.0367	0.3203				200	0.0429	0.7255		
		120	0.0330	0.5077				240	0.0329	0.8076		
		160	0.0269	0.6682				280	0.0247	0.8700		
		200	0.0200	0.7937				320	0.0182	0.9163		
		240	0.0133	0.8823				360	0.0131	0.9501		
		280	0.0082	0.9392				400	0.0092	0.9741		
0.0316	1.895	320	0.0047	0.9732	1.10	0.0581	1.895	40	0.1177	0.2158	1.14	
		360	0.0022	0.9910				80	0.0988	0.4109		
		40	0.0394	0.0834				120	0.0769	0.5673		
		80	0.0366	0.2152				160	0.0584	0.6873		
		120	0.0334	0.3340				200	0.0437	0.7781		
		160	0.0308	0.4436				240	0.0327	0.8457		
		200	0.0275	0.5432				280	0.0247	0.8968		
		240	0.0240	0.6312				320	0.0183	0.9349		
		280	0.0204	0.7070					360	0.0131	0.9628	
		320	0.0172	0.7711					400	0.0087	0.9821	

Table 4 Values of n , $\ln k$ and the correlative coefficient r for the dissolution process at 298.15 K

Solvent	n	$\ln(k/s^{-1})$	r
ethyl acetate	0.8732	-16.90	0.9997
	0.8553	-16.77	0.9999
	0.8643	-16.69	0.9999
	0.8934	-16.72	0.9995
	0.8981	-16.51	0.9995
average	0.8767±0.0214	-16.72±0.21	
<i>N,N</i> -dimethylformamide	0.6310	-16.85	0.9958
	0.6674	-16.78	0.9991
	0.6333	-17.04	0.9989
	0.6806	-16.27	0.9988
	0.7031	-16.06	0.9981
average	0.6631±0.0400	-16.60±0.44	

Combining Eqs.(3) and (4), yields

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (5)$$

Substituting $\alpha = H/H_\infty$ into the Eq.(5), we get

$$\ln \left[\frac{1}{H_\infty} \left(\frac{dH}{dt} \right)_i \right] = \ln k + n \ln \left[1 - \left(\frac{H}{H_\infty} \right)_i \right] \quad i=1, 2, \dots, L \quad (6)$$

In these equations, α is the conversion degree, $f(\alpha)$ is the kinetic model function, H represents the heat at time of t , i is the any time during the process, H_∞ is the heat of the whole process, k is the rate of TNAZ dissolved in ethyl acetate and *N,N*-dimethylformamide, and n is the reaction order, L is counting number.

By substituting the data taken from Tables 2 and 3, $(dH/dt)_i$, $(H/H_\infty)_i$, H_∞ , $i=1, 2, \dots, L$, into the kinetic Eq.(6), the obtained values of n and $\ln k$ are listed in Table 4.

Substituting the values of n and k in Table 4 into Eq.(5), we can get

$$d\alpha/dt = 10^{-7.26}(1-\alpha)^{0.88} \quad (7)$$

for dissolution process of TNAZ in ethyl acetate, and

$$d\alpha/dt = 10^{-7.21}(1-\alpha)^{0.66} \quad (8)$$

for dissolution process of TNAZ in *N,N*-dimethylformamide.

The values of k indicate that the reaction rates of TNAZ dissolved in ethyl acetate and *N,N*-dimethylformamide are at the same level, the value of n in ethyl acetate is larger than that in *N,N*-dimethylformamide.

3 Conclusions

(1) The enthalpies of TNAZ in ethyl acetate and *N,N*-dimethylformamide were investigated by RD496-2000 Calvet Microcalorimeter at 298.15 K. The concentration of the solution (b) almost has little influence on the values of the molar enthalpies. The differential enthalpies of TNAZ in ethyl acetate and *N,N*-dimethylformamide are about 6.24 and 1.19 kJ·mol⁻¹.

(2) The kinetics equations of dissolution processes of TNAZ are $d\alpha/dt = 10^{-7.26}(1-\alpha)^{0.88}$ in ethyl acetate, and $d\alpha/dt = 10^{-7.21}(1-\alpha)^{0.66}$ in *N,N*-dimethylformamide.

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