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Dissolution properties of *N*-guanylurea dinitramide (GUDN) in dimethyl sulfoxide and *N*-methyl pyrrolidone

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Abstract The enthalpies of dissolution of *N*-guanylurea dinitramide (GUDN) in dimethyl sulfoxide (DMSO) and *N*-methyl-2-pyrrolidone (NMP) were measured using an RD496-2000 Calvet microcalorimeter at 298.15 K under atmospheric pressure, respectively. Empirical formulae for the calculation of the enthalpy of dissolution ($\Delta_{diss}H$), relative partial molar enthalpy ($\Delta_{diss}H_{partial}$), and relative apparent molar enthalpy ($\Delta_{diss}H_{apparent}$) were obtained from the experimental data of the dissolution processes of GUDN in DMSO and NMP. Furthermore, the corresponding kinetic equations describing the two dissolution processes were $d\alpha/dt = 10^{-3.39}(1-\alpha)^{0.70}$ for the dissolution of GUDN in DMSO, and $d\alpha/dt = 10^{-4.06}(1-\alpha)^{1.11}$ for the dissolution of GUDN in NMP.

Keywords *N*-guanylurea dinitramide · Microcalorimeter · Dimethyl sulfoxide · *N*-methyl pyrrolidone · Dissolution · Kinetics

Introduction

N-guanylurea dinitramide (GUDN) is a new high-energy and low sensitivity oxidizer, and it is a stable salt of dinitramide. In contrast to the more well-known dinitramide, ADN, it does not melt and it is significantly more thermally stable [1, 2]. GUDN has been demonstrated to be an extremely insensitive energetic molecule. It does not react in fall hammer and friction tests [3]. GUDN as a main ingredient has been used in insensitive gun propellants [4, 5]. It has also been used as a gas generation component in compositions for air bags due to its excellent burning characteristics [6–9]. It has been demonstrated that it also has a potential as an high explosive [10].

Quite a lot of properties of GUDN have been measured and studied, including density, detonation velocity, detonation heat, reactivity, thermal stability, compatibility, sensitivity, and so on [1, 11]. But the particular properties of its solution have rarely been reported. In the present study, an RD496-2000 Calvet microcalorimeter is used to measure the enthalpies of dissolution of GUDN in dimethyl sulfoxide (DMSO) and *N*-methyl pyrrolidone (NMP). The relationships for the measured enthalpies of dissolution and amounts of substance are studied, and the relative partial molar enthalpy ($\Delta_{diss}H_{partial}$), and the relative apparent molar enthalpy ($\Delta_{diss}H_{apparent}$) at 298.15 K are obtained. The kinetic equations of the two dissolution processes are also obtained, respectively, which will be useful for purification of GUDN in production, and can provide basic guidance for its applications.

Experimental

Materials

GUDN used in the experiment was prepared and purified by Xi'an Modern Chemistry Research Institute, and had a purity of more than 99.4 %. Both NMP ($\rho = 1.029$–1.035 g cm^3) and DMSO ($\rho = 1.098$–1.102 g cm^3) used as solvents were of analysis reagent grade, and their purities were higher than 99.5 %. Deionized water with an electrical conductivity of 0.8×10^{-4}–1.2×10^{-4} S m^{-1}

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used in the experiments was obtained by purification two times via a sub-boiling distillation device.

Equipment and conditions

All the measurement experiments were performed on an RD496-2000 Calvet microcalorimeter (Mianyang CP Thermal Analysis Instrument Co., Ltd.). The standard molar enthalpy of the dissolution of KCl (spectrum purity) in distilled water measured by RD496-2000 Calvet microcalorimeter at 298.15 K was 17.234 ± 0.041 kJ mol^{-1}, and the relative error was less than 0.04 % compared with the literature value 17.241 ± 0.018 kJ mol^{-1} [12]. This showed that the device for measuring the enthalpy used in this work was reliable. The enthalpies of dissolution were measured at 298.15 ± 0.005 K.

Results and discussion

Thermochemical behaviors of the dissolution of GUDN in DMSO and NMP

The proper molar sample of GUDN was dissolved in DMSO and NMP at 298.15 K to form solutions. The molar enthalpy of the dissolution ($\Delta_{diss}H$) was detected on an RD496-2000 Calvet microcalorimeter [13–16]. Each process was repeated three times to insure the precision of the data [17–19]. The dissolution of GUDN in DMSO was an endothermic process, but the dissolution in NMP was an exothermic process. The thermochemical data obtained, $\Delta_{diss}H$, b (the molality of GUDN), $\Delta_{diss}H_{partial}$ (the relative partial molar enthalpy of dissolution), and $\Delta_{diss}H_{apparent}$ (the relative apparent molar enthalpy of dissolution) were listed in Tables 1 and 2.

With the help of the values of b and $\Delta_{diss}H$ in Table 1, the empirical formula of enthalpy for the dissolution processes of GUDN in DMSO describing the b versus $\Delta_{diss}H$ relation is obtained as:

$$\Delta_{diss}H = 17.00 - 232.47b^{1/2} + 704.08b. \quad (1)$$

The empirical formula of relative molar enthalpy and relative partial molar enthalpy calculated by Eq. (1) are, respectively,

$$\begin{aligned}\Delta_{diss}H_{apparent} &= \Delta_{diss}H(b=b) - \Delta_{diss}H(b=0)\\ &= -232.47b^{1/2} + 704.08b, \end{aligned} \quad (2)$$

$$\begin{aligned}\Delta_{diss}H_{partial} &= b\left(\frac{\partial\Delta_{diss}H}{\partial b}\right) + \Delta_{diss}H_{apparent}\\ &= -348.71b^{1/2} + 1,408.16b. \end{aligned} \quad (3)$$

According to the values of b and $\Delta_{diss}H$ in Table 2, the empirical formula of enthalpy for the dissolution processes of GUDN in NMP describing the b versus $\Delta_{diss}H$ relation is also obtained as:

$$\Delta_{diss}H = 111.19 - 1,211.19b^{1/2} + 3,485.31b. \quad (4)$$

The empirical formula of relative molar enthalpy and relative partial molar enthalpy calculated by Eq. (4) are, respectively,

Table 1 Enthalpies of dissolution of GUDN in DMSO

$a \times 10^5$/mol	$b \times 10^2$/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		
3.4258	1.5572	1.06	1.05	21.59	18.05
3.8708	1.7595	1.42	1.45	21.48	18.45
4.4067	2.0031	1.80	1.80	21.15	18.80
5.9378	2.6989	2.20	2.19	19.28	19.19
7.3339	3.3362	1.97	1.97	16.71	18.97

Table 2 Enthalpies of dissolution of GUDN in NMP

$a \times 10^5$/mol	$b \times 10^2$/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		
4.8756	2.3622	7.35	7.37	114.57	103.82
5.4689	2.6497	6.41	6.38	111.04	104.81
6.0239	2.9186	5.98	5.99	106.94	105.20
6.6794	3.2362	6.07	6.10	101.25	105.10
7.2201	3.4981	6.59	6.58	95.96	104.61

$$\Delta_{\text{diss}}H_{\text{apparent}} = \Delta_{\text{diss}}H(b=b) - \Delta_{\text{diss}}H(b=0) = -1,211.19b^{1/2} + 3,485.31b, \quad (5)$$

$$\Delta_{\text{diss}}H_{\text{partial}} = b\left(\frac{\partial\Delta_{\text{diss}}H}{\partial b}\right) + \Delta_{\text{diss}}H_{\text{apparent}} = -1,816.79b^{1/2} + 6,970.62b. \quad (6)$$

From Tables 1 and 2, we can see that the molality of the solution b can affect the values of $\Delta_{\text{diss}}H$, $\Delta_{\text{diss}}H_{\text{apparent}}$ and $\Delta_{\text{diss}}H_{\text{partial}}$ were calculated. We can also find the two curves for the dissolution processes of GUDN in DMSO or NMP are similar to each other, and the relationships between $\Delta_{\text{diss}}H$ and $b^{1/2}$ are quadratic equation from Figs. 1 and 2.

The kinetics of dissolution process of GUDN in DMSO or NMP.

Equations (7) and (8) are chosen as the model functions [20–22] for describing the dissolution of GUDN in DMSO or NMP.

$$\frac{d\alpha}{dt} = kf(\alpha), \quad (7)$$

$$f(\alpha) = (1-\alpha)^n. \quad (8)$$

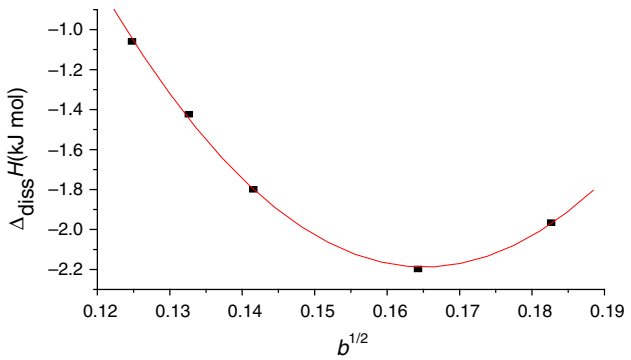

Fig. 1 The relationship between $\Delta_{\text{diss}}H$ and $b^{1/2}$ of GUDN in DMSO

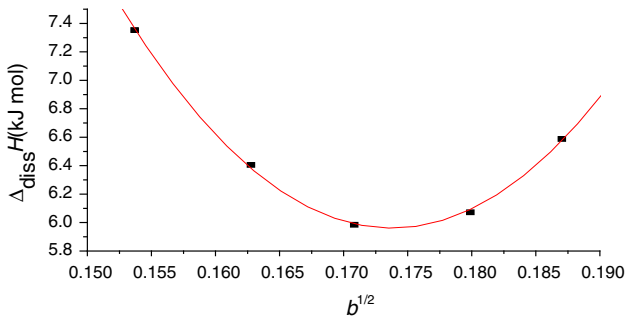

Fig. 2 The relationship between $\Delta_{\text{diss}}H$ and $b^{1/2}$ of GUDN in NMP

Table 3 Original data of the dissolution process of GUDN in DMSO at 298.15 K

m_{GUDN}/g	m_{DMSO}/g	t/s	$-(dH/dt)_i$/mJ s^{-1}	$(H/H_0)_i$	$-H_\infty$/kJ mol^{-1}
0.00716	2.2	90	0.0139	0.288651	1.06
		120	0.0121	0.442598	
		150	0.0108	0.581426	
		180	0.0086	0.69936	
		210	0.0069	0.795302	
		240	0.0051	0.870077	
		270	0.0036	0.926432	
		300	0.0023	0.965194	
		330	0.0012	0.988561	
0.00809	2.2	120	0.0129	0.387887	1.42
		150	0.0117	0.495754	
		180	0.0096	0.586189	
		210	0.0081	0.662095	
		240	0.0070	0.725835	
		270	0.0058	0.779406	
		300	0.0049	0.824441	
		330	0.0041	0.862031	
		360	0.0034	0.893266	
0.00921	2.2	90	0.0297	0.393765	1.80
		120	0.0241	0.553440	
		150	0.0188	0.680827	
		180	0.0142	0.779332	
		210	0.0105	0.853620	
		240	0.0077	0.908232	
		270	0.0058	0.947331	
		300	0.0038	0.973565	
		330	0.0019	0.990214	
0.01241	2.2	120	0.034	0.359866	2.21
		150	0.0298	0.472596	
		180	0.0253	0.569756	
		210	0.0212	0.651651	
		240	0.0176	0.720037	
		270	0.0146	0.776822	
		300	0.0121	0.823761	
		330	0.0101	0.862839	
		360	0.0083	0.895276	
0.01534	2.2	120	0.0381	0.320492	1.96
		150	0.0344	0.436058	
		180	0.0303	0.539699	
		210	0.0262	0.630169	
		240	0.0223	0.707883	
		270	0.0188	0.773604	
		300	0.0157	0.828787	
		330	0.0128	0.874542	
		360	0.0101	0.91170	

Table 4 Original data of the dissolution process of GUDN in NMP at 298.15 K

m_{GUDN}/g	m_{NMP}/g	t/s	$(dH/dt)_i$/mJ s^{-1}	$(H/H_0)_i$	$-H_\infty$/kJ mol^{-1}
0.01019	2.064	300	0.0205	0.223031	7.35
		400	0.0177	0.308405	
		500	0.0152	0.383065	
		600	0.0131	0.447932	
		700	0.0115	0.504094	
		800	0.0103	0.552054	
		900	0.0093	0.592509	
		1000	0.0082	0.627077	
		1100	0.0073	0.657516	
		1200	0.0065	0.685025	
0.01143	2.064	400	0.0209	0.437108	6.41
		500	0.0171	0.548719	
		600	0.0140	0.636346	
		700	0.0107	0.703444	
		800	0.0087	0.755409	
		900	0.0068	0.796353	
		1000	0.0056	0.829531	
		1100	0.0049	0.857398	
		1200	0.0038	0.88153	
		1300	0.0031	0.903025	
0.01259	2.064	500	0.0196	0.408556	5.99
		600	0.0175	0.485751	
		700	0.0155	0.554633	
		800	0.0136	0.615065	
		900	0.0117	0.667572	
		1000	0.0100	0.713262	
		1100	0.0086	0.753855	
		1200	0.0075	0.790180	
		1300	0.0063	0.823153	
		1400	0.0052	0.852967	
0.01396	2.064	400	0.0221	0.279393	6.06
		500	0.0198	0.355142	
		600	0.0179	0.423575	
		700	0.0158	0.484965	
		800	0.0141	0.540053	
		900	0.0124	0.589481	
		1000	0.0111	0.633324	
		1100	0.0099	0.672842	
		1200	0.0087	0.708381	
		1300	0.0078	0.739842	
0.01509	2.064	400	0.0258	0.297389	6.59
		500	0.0222	0.378181	
		600	0.0195	0.446924	
		700	0.0165	0.505006	
		800	0.0146	0.554781	
		900	0.0129	0.598626	
		1000	0.0115	0.637655	
		1100	0.0103	0.672752	
		1200	0.0093	0.704632	
		1300	0.0082	0.732726	

Table 5 Values of n, ln$k$, and the correlative coefficient (r) for the dissolution process at 298.15 K

Solvents	n	ln$k$	r
DMSO	0.601	−7.638	0.9998
	0.779	−7.962	0.9991
	0.658	−7.602	0.9989
	0.793	−7.895	0.9999
	0.656	−7.968	0.9992
Average	0.697	−7.813	
NMP	1.252	−9.458	0.9998
	1.107	−9.054	0.9991
	0.961	−9.290	0.9995
	1.031	−9.469	0.9989
	1.184	−9.415	0.9992
Average	1.107	−9.337	

Combining Eqs. (7) and (8), yields

$$\frac{d\alpha}{dt} = k(1-\alpha)^n. \tag{9}$$

Substituting $\alpha = H/H_\infty$ into the Eq. (9), we get

$$\ln\left[\frac{1}{H_\infty}\left(\frac{dH}{dt}\right)_i\right] = \ln k + n\ln\left[1-\left(\frac{H}{H_\infty}\right)_i\right] \quad i = 1, 2, \ldots, L. \tag{10}$$

In these equations, α is conversion degree, $f(\alpha)$ is the kinetic model function, H represents the enthalpy at time of t, i is any time during the process, H_∞ is the enthalpy of the whole process, k is the rate of GUDN in DMSO or NMP, n is the reaction order, and L is counting number.

The data needed for Eq. (10) are summarized in Tables 3 and 4.

Substituting the original data in Tables 3 and 4, $-(dH/dt)_i$, $(H/H_\infty)_i$, H_∞, $i = 1, 2, \ldots, L$, into the kinetic Eq. (8) yields the values of n and ln$k$ that are listed in Table 5.

Substituting the values of n and k in Table 5 into Eq. (9), we can get

$$\frac{d\alpha}{dt} = 10^{-3.39}(1-\alpha)^{0.70}, \tag{11}$$

for dissolution process of GUDN in DMSO, and

$$\frac{d\alpha}{dt} = 10^{-4.06}(1-\alpha)^{1.11}, \tag{12}$$

for dissolution process of GUDN in NMP.

Conclusions

(1) The dissolution process of GUDN in DMSO and NMP were investigated by RD496-2000 Calvet microcalorimeter at 298.15 K. The relationship

between $\Delta_{diss}H$ and $b^{1/2}$ of GUDN dissolved in DMSO and NMP are quadratic equation.

(2) The expressions describing values of $\Delta_{diss}H$, $\Delta_{diss}H_{apparent}$, and $\Delta_{diss}H_{partial}$ versus the molality (b) of GUDN in DMSO are $\Delta_{diss}H = 17.00 - 232.47b^{1/2} + 704.08b$, $\Delta_{diss}H_{apparent} = -232.47b^{1/2} + 704.08b$, $\Delta_{diss}H_{partial} = -348.71b^{1/2} + 1{,}408.16b$. The expressions describing values of $\Delta_{diss}H$, $\Delta_{diss}H_{apparent}$ and $\Delta_{diss}H_{partial}$ versus the concentration (b) of GUDN in NMP are $\Delta_{diss}H = 111.19 - 1{,}211.19b^{1/2} + 3{,}485.31b$, $\Delta_{diss}H_{apparent} = -1{,}211.19b^{1/2} + 3{,}485.31b$, $\Delta_{diss}H_{partial} = -1{,}816.79b^{1/2} + 6{,}970.62b$, respectively.

(3) The kinetics equations of dissolution processes for GUDN are $d\alpha/dt = 10^{-3.39}(1 - \alpha)^{0.70}$ in DMSO, and $d\alpha/dt = 10^{-4.06}(1 - \alpha)^{1.11}$ in NMP.

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