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Thermochemical properties of dihydrazidinium bis(tetrazolyl)amine in water and *N*-methyl pyrrolidone

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Abstract The enthalpies of dissolution of dihydrazidinium bis(tetrazolyl)amine (DHBTA) in water and *N*-methyl pyrrolidone (NMP) were measured using a 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 DHBTA in water and NMP. Furthermore, the corresponding kinetic equations describing the two dissolution processes were $d\alpha/dt = 10^{-2.70}(1-\alpha)^{0.82}$ for the dissolution of DHBTA in water, and $d\alpha/dt = 10^{-2.47}(1-\alpha)^{0.66}$ for the dissolution of DHBTA in NMP, respectively.

Keywords Dihydrazidinium bis(tetrazolyl)amine · Thermochemical properties · Water · *N*-methyl pyrrolidone · Dissolution · Kinetics

Introduction

High nitrogen heterocyclic compounds are one of the developing fields in energetic material research because of their positive enthalpy of formation, high thermal stability and low sensitivity to impact and friction. Moreover, the high nitrogen content is able to increase the density and to easily obtain an oxygen balance; the main combustion (decomposition) product is nitrogen. So, high nitrogen heterocyclic compounds are being considered as green energetic materials, which are used in solid propellants, explosives and civil combustible-gas generators [1–6].

Tetrazole has the highest nitrogen content in single heterocyclic compounds. Tetrazole is also the precursor to synthesize other high nitrogen heterocyclic compounds, such as 5-aminotetrazole, azotetrazole and *N*, *N*′-bis[1(2)*H*-tetrazol-5-yl]-amine (BTA). Tetrazole of BTA bears acidity, its isoelectronic character and symmetry (to a degree) of the anion, and by analogy, one might expect interaction of the tetrazolate anion with base containing nitrogen, such as ammonium salt and hydrazium salt. Dihydrazidinium bis(tetrazolyl)amine (DHBTA) has been prepared, and the structure of DHBTA is shown in Scheme 1. It is shown that DHBTA has high heat of formation, large gas production, good thermal stability and high reaction heat, and it has possible application as gas generant, low signature propellants, low-smoke or non-smoke pyrotechnics and high performance explosives [7–11].

In the present study, thermochemical properties of its solution have been studied for the first time. The aim of this work is to study the dissolution properties of DHBTA in water and *N*-methyl pyrrolidone (NMP). The kinetic equations of the two dissolution processes are obtained, respectively, which provide valuable information for its applications in the future.

Experimental

Materials

DHBTA used in the experiments was prepared and purified by Beijing Institute of Technology, and had a purity of

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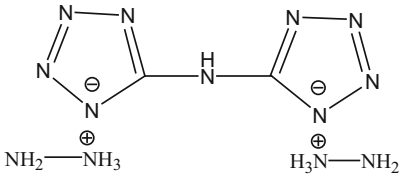

Scheme 1 Structure of DHBTA

more than 99.4 %. The sample was conserved under vacuum. NMP ($\rho = 1.029 - 1.035$ g cm^{-3}) used as solvent was of analysis reagent grade, and their purities were higher than 99.5 %. The water used in the experiments was deionized with an electrical conductivity of $0.8 \times 10^{-4} - 1.2 \times 10^{-4}$ S m^{-1} and obtained by purification two times via a sub-boiling distillation device.

Equipment and conditions

A RD496-2000 Calvet Microcalorimeter (China Academy of Engineering Physics Mianyang CEAP Thermal Analysis Instrument Company) was used to measure the dissolution heat. The standard molar enthalpy of the dissolution of KCl (spectrum purity) in distilled water measured by a 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 DHBTA in water and NMP

The proper molar sample of DHBTA was, respectively, dissolved in water and NMP at 298.15 K in order to form solution. The molar enthalpy of the dissolution ($\Delta_{diss}H$) was detected on a RD496-2000 Calvet microcalorimeter [13, 14]. Each process was repeated three times to ensure the precision of the data [15–17]. The dissolution of DHBTA in water and NMP was all endothermic processes. The thermochemical data obtained, $\Delta_{diss}H$, b (the molality of DHBTA), $\Delta_{diss}H_{partial}$ (the relative partial molar enthalpy of dissolution) and $\Delta_{diss}H_{apparent}$ (the relative apparent molar enthalpy of dissolution), are 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 DHBTA in water describing the b versus $\Delta_{diss}H$ relation is obtained as:

$$\Delta_{diss}H = -126.675 - 1348.48b + 819.754b^{1/2} \quad (1)$$

The empirical formulae of relative apparent molar enthalpy ($\Delta_{diss}H_{apparent}$), relative partial molar enthalpy ($\Delta_{diss}H_{partial}$) and differential molar enthalpy ($\Delta_{dif}H_{1,2}$) calculated by Eq. 1 are, respectively.

$$\begin{aligned}\Delta_{diss}H_{apparent} &= \Delta_{diss}H(b=b) - \Delta_{diss}H(b=0) \\ &= -1348.48b + 819.754b^{1/2}\end{aligned} \quad (2)$$

$$\begin{aligned}\Delta_{diss}H_{partial} &= b\left(\frac{\partial\Delta_{diss}H}{\partial b}\right) + \Delta_{diss}H_{apparent} \\ &= -2696.96b + 1229.63b^{1/2}\end{aligned} \quad (3)$$

$$\begin{aligned}\Delta_{dif}H_{1,2} &= \Delta_{diss}H(b=b_2)\,\Delta_{diss}H(b=b_1) \\ &= -1348.48(b_2 - b_1) + 819.75\,(b_2^{1/2} - b_1^{1/2})\end{aligned} \quad (4)$$

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

$$\Delta_{diss}H = -33.68 - 1021.38b + 340.88b^{1/2} \quad (5)$$

The empirical formulae of relative apparent molar enthalpy ($\Delta_{diss}H_{apparent}$), relative partial molar enthalpy ($\Delta_{diss}H_{partial}$) and differential molar enthalpy ($\Delta_{dif}H_{1,2}$) calculated by Eq. 5 are, respectively.

$$\begin{aligned}\Delta_{diss}H_{apparent} &= \Delta_{diss}H(b=b) - \Delta_{diss}H(b=0) \\ &= -1021.38b + 340.88b^{1/2}\end{aligned} \quad (6)$$

$$\begin{aligned}\Delta_{diss}H_{partial} &= b\left(\frac{\partial\Delta_{diss}H}{\partial b}\right) + \Delta_{diss}H_{apparent} \\ &= -2042.75b + 511.31b^{1/2}\end{aligned} \quad (7)$$

$$\begin{aligned}\Delta_{dif}H_{1,2} &= \Delta_{diss}H(b=b_2) - \Delta_{diss}H(b=b_1) \\ &= -1021.38(b_2 - b_1) + 340.88(b_2^{1/2} - b_1^{1/2})\end{aligned} \quad (8)$$

Table 1 Enthalpies of dissolution of DHBTA in water

10^5a/mol	10^2b/mol kg^{-1}	$-\Delta_{diss}H$/kJ mol^{-1}	
		Found	Calculated
3.0157	1.5078	46.29	46.13
3.6096	1.8048	41.05	41.03
3.8858	1.9429	38.59	38.81
4.4567	2.2284	34.18	34.44
4.9632	2.4816	31.09	30.80

Table 2 Enthalpies of dissolution of DHBTA in NMP

$10^5 a$/mol	$10^2 b$/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		
3.7063	1.7957	6.34	6.34	31.33	26.89
4.2035	2.0366	5.85	5.84	30.88	27.39
5.0460	2.4448	5.37	5.36	29.55	27.87
5.7413	2.7816	5.22	5.25	28.04	27.98
6.5700	3.1831	5.39	5.37	25.84	27.86

From Tables 1 and 2, we can see that the molality of the solution b can affect the values of $\Delta_{diss}H$, the calculated $\Delta_{diss}H_{apparent}$ and $\Delta_{diss}H_{partial}$. In Table 1, the values of $\Delta_{diss}H$ decrease with values of b increasing during the dissolution processes of DHBTA in water. One can also find that the relationships between $\Delta_{diss}H$ and $b^{1/2}$ for the dissolution processes of DHBTA in water is linear equation from Fig. 1, and at the same time, the relationship between $\Delta_{diss}H$ and $b^{1/2}$ for the dissolution processes of DHBTA in NMP is quadratic equation from Fig. 2.

The kinetics of dissolution process of DHBTA in water or NMP

Equations 9 and 10 are chosen as the model function describing the dissolution of DHBTA in water or NMP [18–20].

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{9}$$

$$\ln\left[\frac{1}{H_0}\left(\frac{dH}{dt}\right)_i\right] = \ln k + n\ln\left[1-\left(\frac{H}{H_0}\right)_i\right] \quad i = 1, 2, \ldots, L \tag{10}$$

By putting the original data in Tables 3 and 4, $-(dH/dt)_i$, $(H/H_0)_i$, H_∞, i = 1, 2, …, L, into Eq. 10, the values of n and ln k are obtained and listed in Table 5, where n is the reaction order and k the reaction rate constant.

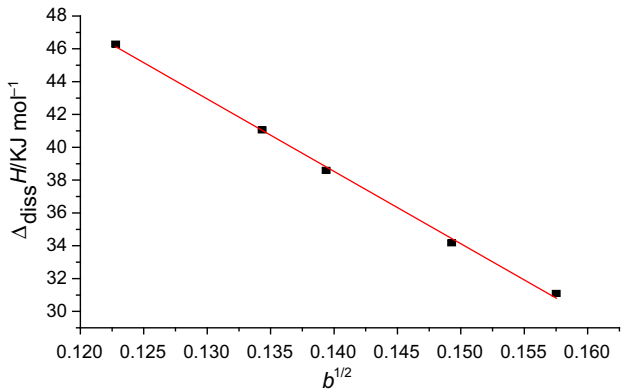

Fig. 1 Relationship between $\Delta_{diss}H$ and $b^{1/2}$ of DHBTA in water

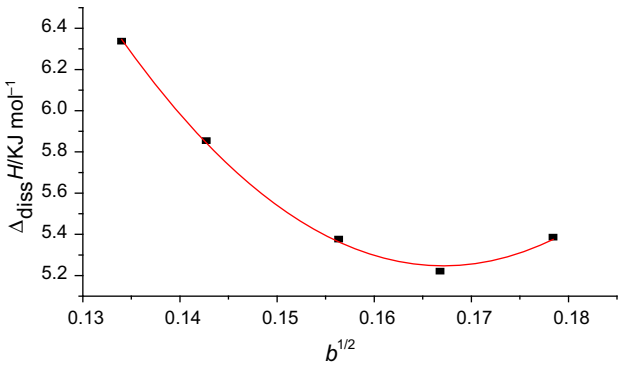

Fig. 2 Relationship between $\Delta_{diss}H$ and $b^{1/2}$ of DHBTA in NMP

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

$$\frac{d\alpha}{dt} = 10^{-2.70}(1-\alpha)^{0.82} \tag{11}$$

for dissolution process of DHBTA in water, and

$$\frac{d\alpha}{dt} = 10^{-2.47}(1-\alpha)^{0.66} \tag{12}$$

for dissolution process of DHBTA in NMP.

Conclusions

The dissolution processes of DHBTA in water and NMP were investigated by RD496-2000 Calvet microcalorimeter at 298.15 K, respectively. The relationship between $\Delta_{diss}H$ and $b^{1/2}$ of DHBTA dissolved in water is linear equation, and the relationship between $\Delta_{diss}H$ and $b^{1/2}$ of DHBTA dissolved in NMP is quadratic equation.

The expressions describing values of $\Delta_{diss}H$, $\Delta_{diss}H_{apparent}$, $\Delta_{diss}H_{partial}$ and $\Delta_{dif}H_{1,2}$ versus the molality (b) for DHBTA dissolved in water are $\Delta_{diss}H = -126.68 - 1{,}348.48b + 819.75b^{1/2}$, $\Delta_{diss}H_{apparent} = -1{,}348.48b + 819.75b^{1/2}$, $\Delta_{diss}H_{partial} = -2{,}696.96b + 1{,}229.63b^{1/2}$, $\Delta_{dif}H_{1,2} = -1{,}348.48(b_2 - b_1) + 819.75\,(b_2^{1/2} - b_1^{1/2})$. The expressions describing values of $\Delta_{diss}H$, $\Delta_{diss}H_{apparent}$, $\Delta_{diss}H_{partial}$ and $\Delta_{dif}H_{1,2}$ versus the molality (b) of DHBTA in NMP are $\Delta_{diss}H = -33.69 - 1{,}021.38b + 340.88b^{1/2}$, $\Delta_{diss}H_{apparent} =$

Table 3 Original data of the dissolution process of DHBTA in water at 298.15 K

m_{DHBTA}/g	m_{water}/g	t/s	$-(dH/dt)_i$/mJ s^{-1}	$(H/H_0)_i$	$-H_0$/kJ mol^{-1}
0.00655	2.00	400	1.9332	0.5178	46.29
		480	1.6701	0.6177	
		560	1.3993	0.7019	
		640	1.1493	0.7710	
		720	0.9327	0.8267	
		800	0.7548	0.8709	
		880	0.6069	0.9056	
		960	0.4883	0.9326	
		1,040	0.3936	0.9533	
0.00784	2.00	360	1.9509	0.4213	41.05
		480	1.5972	0.5966	
		600	1.2550	0.6887	
		720	0.9335	0.7961	
		840	0.7608	0.8434	
		960	0.6433	0.8725	
		1,080	0.5473	0.9002	
		1,200	0.4717	0.9226	
		1,320	0.3310	0.9492	
0.00844	2.00	400	1.7532	0.5128	38.59
		500	1.4819	0.6218	
		600	1.1913	0.7108	
		700	0.9302	0.7806	
		800	0.7156	0.8337	
		900	0.5683	0.8737	
		1,000	0.4730	0.9048	
		1,100	0.3823	0.9294	
		1,200	0.2910	0.9487	
0.00968	2.00	360	1.9124	0.4153	34.18
		480	1.5840	0.5596	
		600	1.1941	0.6687	
		720	0.9307	0.7470	
		840	0.7527	0.8024	
		960	0.6139	0.8425	
		1,080	0.5158	0.8728	
		1,200	0.4192	0.8972	
		1,320	0.3429	0.9182	
0.01078	2.00	240	1.8567	0.2531	31.09
		360	1.4797	0.4052	
		480	1.1729	0.5221	
		600	0.9665	0.6052	
		720	0.8349	0.6625	
		840	0.7206	0.7039	
		960	0.6343	0.7464	
		1,080	0.5394	0.7832	
		1,200	0.4950	0.8112	

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

m_{DHBTA}/g	m_{NMP}/g	t/s	$-(dH/dt)_i$/mJ s^{-1}	$(H/H_0)_i$	$-H_0$/kJ mol^{-1}
0.00805	2.064	210	0.5325	0.4040	6.34
		280	0.4383	0.5449	
		350	0.3476	0.6577	
		420	0.2704	0.7452	
		490	0.2088	0.8119	
		560	0.1598	0.8622	
		630	0.1242	0.9000	
		700	0.0961	0.9282	
		770	0.0752	0.9492	
		840	0.0603	0.9647	
0.00913	2.064	180	0.6021	0.3236	5.85
		240	0.5331	0.4571	
		300	0.4502	0.5718	
		360	0.3697	0.6668	
		420	0.2994	0.7436	
		480	0.2413	0.8047	
		540	0.1925	0.8531	
		600	0.1541	0.8908	
		660	0.1228	0.9202	
		720	0.0989	0.9429	
0.01096	2.064	200	0.6429	0.3923	5.37
		250	0.4946	0.5989	
		300	0.4216	0.6800	
		350	0.3575	0.7477	
		400	0.3022	0.8036	
		450	0.2555	0.8495	
		500	0.2159	0.8867	
		550	0.1831	0.9165	
		600	0.1469	0.9402	
		650	0.1164	0.9587	
0.01247	2.064	240	0.8165	0.4761	5.22
		280	0.7484	0.5620	
		320	0.6605	0.6392	
		360	0.5867	0.7072	
		400	0.5240	0.7664	
		440	0.4645	0.8173	
		480	0.3927	0.8603	
		520	0.3258	0.8963	
		560	0.2642	0.9259	
		600	0.2246	0.9496	
0.01427	2.064	200	0.8003	0.3851	5.39
		250	0.7192	0.4966	
		300	0.6227	0.5942	
		350	0.5305	0.6770	
		400	0.4467	0.7461	
		450	0.3740	0.8031	
		500	0.3118	0.8496	
		550	0.2584	0.8869	
		600	0.2161	0.9168	
		650	0.1816	0.9404	

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

Solvent	n	ln$k$	r
Water	0.6961	−6.0755	0.9998
	0.7338	−6.2078	0.9991
	0.8078	−6.1610	0.9989
	0.8860	−6.1760	0.9999
	0.9784	−6.4527	0.9992
Average	0.8204	−6.2146	
NMP	0.7913	−5.6869	0.9998
	0.7531	−5.6895	0.9991
	0.6331	−5.7468	0.9995
	1.0310	−5.5365	0.9989
	0.5630	−5.7690	0.9992
Average	0.6553	−5.6857	

$-\ 1{,}021.38b + 340.88b^{1/2}$, $\Delta_{\mathrm{diss}}H_{\mathrm{partial}} = -\ 2{,}042.75b + 511.31b^{1/2}$, $\Delta_{\mathrm{dif}}H_{1,2} = -\ 1{,}021.38\quad(b_2 - b_1) + 340.88\ (b_2^{1/2} - b_1^{1/2})$.

The kinetics equations of dissolution processes for DHBTA are $\mathrm{d}\alpha/\mathrm{d}t = 10^{-2.70}(1-\alpha)^{0.82}$ in water, and $\mathrm{d}\alpha/\mathrm{d}t = 10^{-2.47}(1-\alpha)^{0.66}$ in NMP.

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