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Dissolution properties of ammonium dinitramide in *N*-methyl pyrrolidone

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Abstract The dissolution properties of ammonium dinitramide (ADN) in *N*-methyl pyrrolidone (NMP) were studied with a RD496-2000 Calvet microcalorimeter at four different temperatures under atmospheric pressure. The heat effects were determined for ADN in NMP. The molar enthalpies and the differential molar enthalpies for ADN in NMP were also obtained at the same time. The corresponding kinetic equations that describe the four dissolution processes are discussed.

Keywords Ammonium dinitramide · Thermochemical properties · *N*-Methyl pyrrolidone · Kinetics

Introduction

Ammonium dinitramide (ADN) as an energetic material has been extensively studied in propellants [1–7]. ADN does not contain any chlorine; no hydrochloric acid is produced during combustion compared to ammonium perchlorate (AP). In addition, it also has high-temperature stability, high-energy density, low sensitivity, and positive oxygen balance. So, it can be widely used as a replacement for AP in environmentally benign propellant systems. Earlier work have mostly focused on synthesis, thermal stability, combustion mechanism, detonation properties, sensitivity, compatibility with main compositions of propellant, and its use in propellants [8–18]. However, the thermochemical properties of its solution at different temperatures have never been reported until now.

In the present paper, we investigate the dissolution behaviors for ADN in NMP using a RD496-2000 Calvet microcalorimeter. The relationships between the measured heat effects and amounts of substance were studied, the molar enthalpies ($\Delta_{diss}H$) and the differential molar enthalpies ($\Delta_{dif}H$) for ADN in NMP at different temperatures were obtained, and the kinetic behaviors were also studied at the same time. The resulting data can provide basic guidance for its further applications.

Experimental

Materials

The ADN used in this work was prepared and purified by Xi'an Modern Chemistry Research Institute, and its purity was more than 99.8 %. The sample was stored under vacuum before the experimental measurements. NMP (ρ/g cm^{-3}=1.029–1.035) used as solvent was of analytical reagent grade, their purity was more than 99.5 %, and made by Tianjin Baishi Chemical Industry Co. Ltd., China. The water used in these experiments was deionized with an electrical conductivity of 0.8–1.2 × 10^{-4} S m^{-1} and obtained by purification for two times using sub-boiling distillation device.

Equipment and conditions

All measurements were made by a RD496-2000 Calvet microcalorimeter (Mianyang CP Thermal Analysis Instrument CO., LTD). The enthalpy of dissolution of KCl (spectrum purity) in distilled water at 298.15 K was

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Table 1 The enthalpies of dissolution of ADN in NMP

T/K	$10^5 \times a$/mol	$10^2 \times b$/mol kg^{-1}	Q/J		$-\Delta_{diss}h$/J g^{-1}	$-\Delta_{diss}H$/kJ mol^{-1}
			Experimental	Calculated		
298.15	6.60	3.20	1.3892	1.3864	169.82	21.06
	9.51	4.61	2.0488	2.0344	173.77	21.55
	11.87	5.75	2.5115	2.5603	170.62	21.16
	13.70	6.63	3.0121	2.9660	177.39	22.00
	17.98	8.71	3.8881	3.9192	174.43	21.63
	19.65	9.52	4.3122	4.2925	176.95	21.94
Average					173.83 ± 3.14	21.56 ± 0.39
303.15	7.77	3.76	1.6730	1.7002	173.73	21.54
	10.08	4.88	2.2547	2.2051	180.38	22.37
	11.98	5.81	2.6316	2.6203	177.10	21.96
	14.06	6.81	3.0066	3.0749	172.50	21.39
	17.38	8.42	3.8542	3.8004	178.85	22.18
	19.98	9.68	4.3479	4.3686	175.53	21.77
Average					176.35 ± 3.01	22.33 ± 0.38
308.15	8.35	0.3249	1.8727	1.8776	180.94	22.44
	10.77	0.4874	2.4090	2.4302	180.31	22.36
	13.12	0.8123	2.9793	2.9669	183.11	22.71
	14.97	0.9938	3.4504	3.3894	185.91	23.05
	17.42	1.1563	3.8927	3.9489	180.22	22.35
	19.27		4.3805	4.3714	183.28	22.73
Average					182.30 ± 2.23	22.61 ± 0.27
313.15	8.27	4.01	1.8736	1.87166	180.61	22.64
	10.8	5.23	2.5042	2.4563	187.02	23.19
	14.29	6.92	3.2011	3.2629	180.65	22.40
	14.80	7.17	3.3834	3.3808	184.38	22.86
	17.14	8.31	3.8778	3.9216	182.39	22.62
	20.02	9.70	4.6401	4.5872	186.95	23.18
Average					183.67 ± 2.92	22.82 ± 0.32

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} [19, 20]. This showed that the device of measuring the enthalpy used in this work was reliable.

The heat effects were measured at 298.15, 303.15, 308.15, and 313.15 K. Each process was repeated three times to ensure the precision of the data.

Results and discussion

Thermochemical behaviors

The experimental and calculated values of heat effect of ADN dissolved in NMP at different temperatures are given in Table 1. Each process was repeated three times [21–25]. The molar enthalpies ($\Delta_{diss}H$) and the specific enthalpies ($\Delta_{diss}h$) for dissolution processes are obtained and also listed in Table 1, where a is the amount of the substance, b is the molality of ADN, and Q is the heat effect produced during the processes.

It is seen from Table 1 that the values of $\Delta_{diss}H$ and $\Delta_{diss}h$ decrease as the experimental temperatures are increased. This means that the temperature is one of the important factors that influences the dissolution processes. The molality of solution (b) almost has little effect on the values of $\Delta_{diss}H$ and $\Delta_{diss}h$ at each temperature. Thus, the average value of $\Delta_{diss}H$ at each temperature can represent the molar enthalpies of the infinite diluted solution due to their very low molalities of solution.

The relationships between Q and a of ADN dissolved in NMP at different temperatures are shown in Fig. 1. The relationships are represented with linear equations at each different temperature. The linear equations are given in Table 2. The differential molar enthalpy ($\Delta_{dif}H$) is

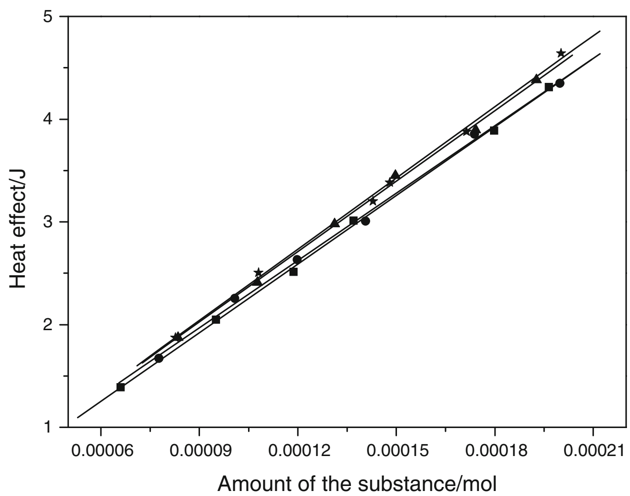

Fig. 1 The relationships between heat effect and amount of the substance at different temperatures (*filled square* $T = 298.15$ K, *filled circle* $T = 303.15$ K, *filled triangle* $T = 308.15$ K, *open square* $T = 313.15$ K)

produced when a molar amount of solute is added to an infinite amount of solution having the same solute already in it. These values can be obtained from the slope of the equations. The results are also shown in Table 2.

The kinetic behaviors

Equations 1–4 [26–28] are chosen as the model function describing the dissolution process of ADN in NMP.

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

$$f(\alpha) = (1-\alpha)^{n} \tag{2}$$

Combining Eqs. 1 and 2 yields

$$\frac{d\alpha}{dt} = k(1-\alpha)^{n} \tag{3}$$

Substituting $\alpha = Q/Q_\infty$ into Eq. 3, we get

$$\ln\left[\frac{1}{Q_\infty}\left(\frac{dQ}{dt}\right)_i\right] = \ln k + n\ln\left[1-\left(\frac{Q}{Q_\infty}\right)_i\right] \quad i = 1, 2, \ldots\ldots L \tag{4}$$

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

The data needed for Eq. 4 are summarized in Table 3. By substituting the data taken from Table 3 into the kinetic Eq. 4, the values of n and ln$k$ at different temperatures are obtained and listed in Table 4.

From Table 4, one can see that the values of n and ln$k$ show that the reaction order and the dissolved rate of ADN dissolved in NMP vary during the experimental temperatures; the values of n and ln$k$ increase with the increasing experimental temperature. So, the dissolution process becomes much quicker as the temperature rises.

Substituting the values of n and k from Table 4 into Eq. 3, the kinetic equations of the dissolution processes of ADN dissolved in NMP can be described as

$$\frac{d\alpha}{dt} = 10^{-2.50}(1-\alpha)^{1.08} \quad (T = 298.15\ \text{K}) \tag{5}$$

$$\frac{d\alpha}{dt} = 10^{-2.44}(1-\alpha)^{1.18} \quad (T = 303.15\ \text{K}) \tag{6}$$

$$\frac{d\alpha}{dt} = 10^{-2.38}(1-\alpha)^{1.47} \quad (T = 308.15\ \text{K}) \tag{7}$$

$$\frac{d\alpha}{dt} = 10^{-2.33}(1-\alpha)^{1.75} \quad (T = 313.15\ \text{K}) \tag{8}$$

Equation 9 is applied to calculate the values of activation energy (E) and pre-exponential factor (A) by the slope and the intercept of the linear equation. The value of E is 20.68 kJ mol^{-1} and that of A is $10^{1.12}$ s^{-1}; the correlative coefficient is 0.9992. The relationship of ln$k$ versus $1/T$ for the dissolution of ADN dissolved in NMP is shown in Fig. 2. From the values of E and A, we can see that dipicrylamine imidazolium can easily dissolve in NMP. This is very consistent with the fact that NMP is an excellent solvent for dipicrylamine imidazolium.

$$\ln k = \ln A - \frac{E_a}{RT} \tag{9}$$

Table 2 Thermochemical equations and differential enthalpies ($\Delta_{dif}H$) of dissolution process of ADN in NMP

T/K	Thermochemical equation	$\Delta_{dif}H$/kJ mol^{-1}	r	SD
298.15	Q/J = 22258 a − 0.0819	−22.26	0.9995	0.0387
303.15	Q/J = 21854 a − 0.0022	−21.85	0.9988	0.0536
308.15	Q/J = 22837 a − 0.0293	−22.84	0.9991	0.0436
313.15	Q/J = 23112 a − 0.0398	−23.11	0.9988	0.0521

Table 3 The original data of the dissolution process of ADN in NMP at different temperatures

T/K	m/g	t/s	$(dQ/dt)_i$/J s^{-1}	$(Q/Q_\infty)_i$	Q_∞/J
298.15	0.01698	450	0.005506	0.367739	3.0121
		500	0.004856	0.455841	
		550	0.004218	0.529083	
		600	0.003633	0.594191	
		650	0.003115	0.650137	
		700	0.002660	0.698006	
		750	0.002268	0.738867	
		800	0.001932	0.773686	
		850	0.001638	0.803272	
		900	0.001385	0.828325	
		950	0.001169	0.849487	
303.15	0.01743	400	0.004253	0.539542	3.0066
		450	0.003630	0.605105	
		500	0.003079	0.660889	
		550	0.002608	0.708169	
		600	0.002204	0.748154	
		650	0.001862	0.781943	
		700	0.001573	0.810491	
		750	0.001331	0.834619	
		800	0.001125	0.855034	
		850	0.000956	0.872339	
		900	0.000813	0.887043	
308.15	0.01856	350	0.003767	0.588369	3.4504
		400	0.003192	0.638765	
		450	0.002703	0.681450	
		500	0.002289	0.717594	
		550	0.001944	0.748239	
		600	0.001654	0.774281	
		650	0.001413	0.796490	
		700	0.001213	0.815501	
		750	0.001046	0.831851	
		800	0.000906	0.845987	
		850	0.000793	0.858284	
313.15	0.02482	400	0.004571	0.579109	4.6401
		450	0.003902	0.621118	
		500	0.003323	0.660022	
		550	0.002828	0.693147	
		600	0.002413	0.721359	
		650	0.002061	0.745447	
		700	0.001764	0.766042	
		750	0.001513	0.783686	
		800	0.001303	0.798855	
		850	0.001127	0.812929	
		900	0.000978	0.826570	

Table 4 Values of n, ln$k$, and the correlative coefficient r for the dissolution process at different temperatures

T/K	n	ln(k/s^{-1})	r
298.15	1.0819	−5.7618	0.9987
303.15	1.1788	−5.6132	0.9994
308.15	1.4689	−5.4792	0.9992
313.15	1.7487	−5.3628	0.9982

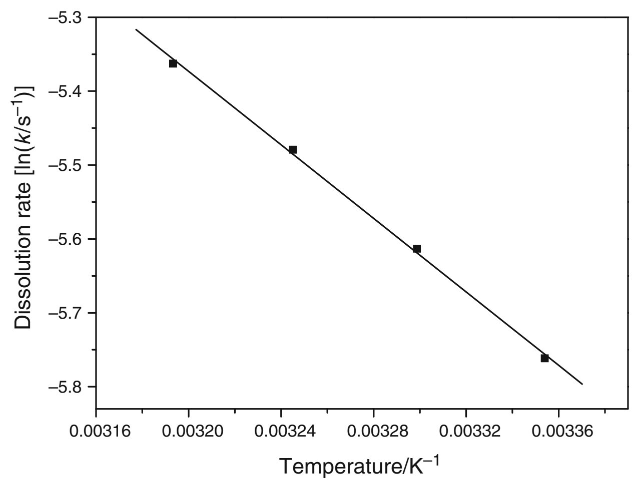

Fig. 2 The relationship between reaction rate constant (k) and temperature (T) for ADN dissolved in NMP

Conclusions

(1) The values of heat effect of ADN dissolved in NMP are determined at different temperatures. It is found that the molality has little effect on the values of the molar enthalpy at each temperature. And the obtained enthalpies can be regarded as the enthalpies at infinite dilution because of its very low molalities.

(2) The molar enthalpies ($\Delta_{diss}H$) are −21.56, −22.33, −22.61, and −22.82 kJ mol^{-1} and the differential enthalpies ($\Delta_{dif}H$) are −22.26, −21.85, −22.84, and −23.11 kJ mol^{-1} for ADN in NMP at 298.15, 303.15, 308.15, and 313.15 K, respectively. The molar enthalpies ($\Delta_{diss}H$) decrease with the increasing temperatures.

(3) The kinetic equations describing the dissolution processes for ADN in NMP at different temperatures are $d\alpha/dt = 10^{-2.50}(1-\alpha)^{1.08}$ (T = 298.15 K), $d\alpha/dt = 10^{-2.44}(1-\alpha)^{1.18}$ (T = 303.15 K), $d\alpha/dt = 10^{-2.38}(1-\alpha)^{1.47}$ (T = 308.15 K), and $d\alpha/dt = 10^{-2.33}(1-\alpha)^{1.75}$ (T = 313.15 K), respectively.

(4) In the dissolution processes of ADN dissolved in NMP, the reaction order and the dissolution rate vary with the experimental temperatures, and the relationships between the dissolution rate and experimental temperature are linear. The kinetic parameters E and A are obtained as 20.68 kJ mol^{-1} and $10^{1.12}$ s^{-1}.

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