Dissolution Properties of 3,4-Dinitrofurazanfuroxan in *N*-Methl-2-pyrrolidone and Dimethyl Sulfoxide

XUE Liang[1,2], ZHAO Feng-qi[1], XING Xiao-ling[1], GAO Hong-xu[1], XU Si-yu[1], HU Rong-zu[1]
(1. Xi'an Modern Chemistry Research Institute, Xi'an 710065, China;
2. Shaanxi Normal University, Xi'an 710062, China)

Abstract: The enthalpies of dissolution of 3,4-dinitrofurazanfuroxan (DNTF) in *N*-methl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO) were measured using a RD496-2000 Calvet microcalorimeter at 298.15K under atmospheric pressure. Differential enthalpies ($\Delta_{dif}H$) and molar enthalpies ($\Delta_{sol}H$) were determined for DNTF in different solvents. The corresponding kinetic equations that describe the two dissolution processes are $d\alpha/dt = 10^{-3.81}(1-\alpha)^{1.19}$ for dissolution process of DNTF in NMP, and $d\alpha/dt = 10^{-3.91}(1-\alpha)^{0.88}$ for dissolution process of DNTF in DMSO.

Key words: physical chemistry; 3,4-dinitrofurazanfuroxan; DNTF; *N*-methl-2-pyrrolidone; dimethyl sulfoxide; dissolution; kinetics
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3,4-二硝基呋咱基氧化呋咱在*N*-甲基-2-吡咯烷酮和二甲基亚砜中的溶解行为

薛　亮[1,2], 赵凤起[1], 邢晓玲[1], 高红旭[1], 徐司雨[1], 胡荣祖[1]
(1. 西安近代化学研究所, 陕西 西安 710065;
2. 陕西师范大学化学与材料科学学院, 陕西 西安 710062)

摘　要:在常压、298.15K条件下,用RD496-2000微热量仪分别测量3,4-二硝基呋咱基氧化呋咱(DNTF)在*N*-甲基-2-吡咯烷酮(NMP)和二甲基亚砜(DMSO)中的溶解焓,得到DNTF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。对于DNTF,在NMP中描述溶解过程的动力学方程为$d\alpha/dt = 10^{-3.81}(1-\alpha)^{1.19}$;在DMSO中,描述溶解过程的动力学方程为$d\alpha/dt = 10^{-3.91}(1-\alpha)^{0.88}$。

关键词:物理化学;3,4-二硝基呋咱基氧化呋咱;DNTF;*N*-甲基-2-吡咯烷酮;二甲基亚砜;溶解;动力学

3,4-dinitrofurazanfuroxan (DNTF) is a novel high energy density material with crystal density of 1.937 g·cm^{-3}. The detonation velocity corresponding to $\rho = 1.937$ g·cm^{-3} is about 9250 m·s^{-1}. Therefore, it has the potential for possible use as an energetic ingredient of propellants and explosives from the point of view of the above-mentioned high performance. There are several reports on the preparation and properties of DNTF[1-6], but the solubility of DNTF in different solvents has not been investigated deeply. In our work, a RD496-2000 Calvet microcalorimeter was employed to measure the enthalpies of DNTF in *N*-methl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO), separately. The kinetic equations of the two dissolution processes were obtained, which provides valuable informations for purification of DNTF in industry.

1 Experimental

1.1 Materials

DNTF was prepared and purified by Xi'an Modern Chemistry Research Institute, and had a

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purity of more than 99.5%. NMP and DMSO 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 298.15K. Two replicates of each sample were tested. The enthalpy of dissolution of KCl (spectrum purity) in distilled water (0.0481g/2.000g) measured at 298.15K was 17.23kJ·mol^{-1}, which was in an excellent accordance with the literature value 17.24kJ·mol^{-1}[7], showing that the device of measuring the enthalpy used in this work was reliable.

2 Results and discussion

2.1 Thermochemical behaviors on the dissolution of DNTF in NMP and DMSO

The proper molar sample of DNTF was dissolved in NMP and DMSO at 298.15K. 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 DNTF in NMP was shown in Fig. 1. The dissolution is an exothermic process. The heat flow curves obtained under the same condition overlap with each other, indicating that the reproducibility of test was satisfactory.

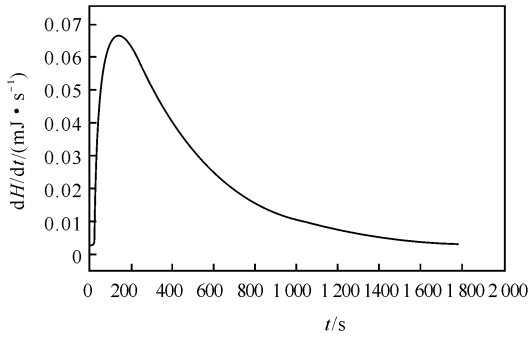

Fig. 1 The heat flow curve of the entire dissolution process of DNTF in NMP

The thermochemical data obtained are listed in Table 1. In Table 1, a is the amount of the substance, b is the concentration of the solution, Q is the heat effect produced during the processes. $\Delta_{sol}H$ is the molar enthalpy. As we can see in Table 1, the value of b almost has little influence on the value of $\Delta_{sol}H$ at 298.15 K. So the average value of $\Delta_{sol}H$ can represent the molar enthalpies of the infinite diluted solution due to very low molal concentration of the solution.

Table 1 The enthalpies of dissolution of DNTF in NMP and DMSO at 298.15K

Solvent	a/10^5 mol	b/(10^2 mol·kg^{-1})	Q/J		$-\Delta_{sol}H$/(kJ·mol^{-1})
			Exp.	Cal.	
NMP	1.81	0.8794	0.5014	0.4727	27.68
	2.10	1.0201	0.5658	0.5446	26.92
	2.75	1.3367	0.7124	0.7064	25.87
	2.93	1.4247	0.7377	0.7514	25.14
	3.37	1.6357	0.8318	0.8592	24.69
Average					26.06
DMSO	5.72	2.6021	0.0838	0.0917	1.46
	6.05	2.7503	0.0915	0.0969	1.51
	6.45	2.9315	0.1005	0.1003	1.56
	6.92	3.1456	0.1125	0.1109	1.63
	7.75	3.5244	0.1351	0.1242	1.74
Average					1.58

The Q vs a relationship of DNTF in different solvents are shown in Fig. 2.

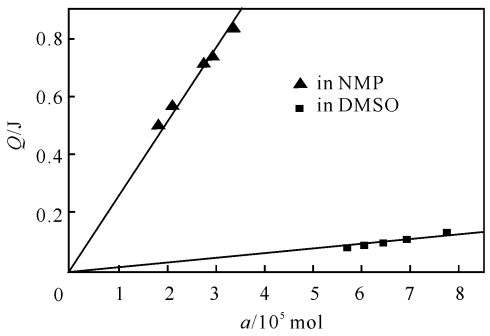

Fig. 2 Relationships of Q vs. a of DNTF in NMP and DMSO

The according linear equations for solvents NMP and DMSO respectively are as follows:

$$Q=24.808a \qquad r=0.999 \qquad (1)$$

$$Q=1.602a \qquad r=0.999 \qquad (2)$$

The differential enthalpies ($\Delta_{dif}H$) are obtained from the slope of the equations. So the differential enthalpies of DNTF in NMP and DMSO are 24.81 and 1.60kJ·mol^{-1}, respectively.

2.2 Kinetics of dissolution process of DNTF in NMP and DMSO

Eq. (3) and Eq. (4)[7-8] is chosen as the model

function describing the process of DNTF dissolved in NMP or DMSO.

$$\frac{d\alpha}{dt}=kf(\alpha) \tag{3}$$

$$f(\alpha)=(1-\alpha)^n \tag{4}$$

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

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

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

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

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

Table 2　Original data of the dissolution process of DNTF in NMP at 298.15K

m_{DNTF}/g	m_{NMP}/g	t/s	$(dH/dt)_i$/(mJ·s^{-1})	$(H/H_\infty)_i$	H_∞/(kJ·mol^{-1})
0.0050	2.06	160	0.0325	0.3162	27.68
		200	0.0298	0.3544	
		240	0.0271	0.3893	
		280	0.0247	0.4211	
		320	0.0225	0.4501	
		360	0.0206	0.4765	
		400	0.0189	0.5008	
		440	0.0173	0.5230	
		480	0.0160	0.5435	
		520	0.0149	0.5624	
		560	0.0137	0.5799	
		600	0.0128	0.5962	
		640	0.0120	0.6114	
		680	0.0112	0.6256	
		720	0.0106	0.6390	
		760	0.0100	0.6517	
0.0058	2.06	160	0.0582	0.3533	26.92
		200	0.0536	0.4140	
		240	0.0489	0.4697	
		280	0.0444	0.5203	
		320	0.0402	0.5663	
		360	0.0364	0.6079	
		400	0.0329	0.6455	
		440	0.0298	0.6796	
		480	0.0269	0.7104	
		520	0.0245	0.7383	
		560	0.0223	0.7637	
		600	0.0203	0.7868	
		640	0.0185	0.8079	
		680	0.0170	0.8272	
0.0076	2.06	160	0.0577	0.4416	25.87
		200	0.0527	0.4890	
		240	0.0479	0.5322	
		280	0.0435	0.5714	
		320	0.0395	0.6070	
		360	0.036	0.6394	
		400	0.0329	0.6690	
		440	0.0301	0.6960	
		480	0.0276	0.7208	
		520	0.0253	0.7435	
		560	0.0233	0.7644	
		600	0.0215	0.7836	
		640	0.0199	0.8013	
		680	0.0183	0.8176	
0.0081	2.06	360	0.0486	0.5120	25.14
		400	0.0441	0.5506	
		440	0.0399	0.5857	
		480	0.0362	0.6174	
		520	0.0328	0.6462	
		560	0.0297	0.6722	
		600	0.027	0.6958	
		640	0.0246	0.7173	
		680	0.0224	0.7369	
		720	0.0204	0.7548	
		760	0.0187	0.7711	
		800	0.0171	0.7860	
		840	0.0157	0.7997	
		880	0.0145	0.8122	
		920	0.0133	0.8238	
0.0093	2.06	440	0.0455	0.5636	24.69
		480	0.0411	0.5956	
		520	0.0372	0.6245	
		560	0.0336	0.6507	
		600	0.0305	0.6744	
		640	0.0277	0.6959	
		680	0.0252	0.7154	
		720	0.0230	0.7332	
		760	0.0210	0.7494	
		800	0.0192	0.7643	
		840	0.0175	0.7778	
		880	0.0161	0.7903	
		920	0.0149	0.8017	
		960	0.0137	0.8123	
		1000	0.0127	0.8220	
		1040	0.0118	0.8311	

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

m_{DNTF}/g	m_{NMP}/g	t/s	$(dH/dt)_i$/(mJ·s^{-1})	$(H/H_\infty)_i$	H_∞/(kJ·mol^{-1})
0.0158	2.20	120	0.0114	0.2505	1.46
		160	0.0110	0.3328	
		200	0.0102	0.4109	
		240	0.0093	0.4825	
		280	0.0084	0.5476	
		320	0.0075	0.6061	
		360	0.0067	0.6582	
		400	0.0060	0.7048	
		440	0.0054	0.7464	
		480	0.0047	0.7834	
		520	0.0041	0.8158	
		560	0.0036	0.8442	
		600	0.0032	0.8689	
		640	0.0028	0.8908	
		680	0.0026	0.9105	
		720	0.0023	0.9284	
0.0167	2.20	120	0.0082	0.2881	1.51
		160	0.0077	0.3415	
		200	0.0073	0.3919	
		240	0.0067	0.4390	
		280	0.0063	0.4828	
		320	0.0058	0.5234	
		360	0.0054	0.5610	
		400	0.0049	0.5955	
		440	0.0046	0.6274	
		480	0.0043	0.6570	
		520	0.0040	0.6846	
		560	0.0037	0.7105	
		600	0.0035	0.7348	
		640	0.0033	0.7575	
		680	0.0030	0.7789	
0.0178	2.20	80	0.0126	0.2312	1.56
		120	0.0120	0.3065	
		160	0.0112	0.3774	
		200	0.0103	0.4428	
		240	0.0093	0.5027	
		280	0.0084	0.5568	
		320	0.0076	0.6057	
		360	0.0068	0.6496	
		400	0.0062	0.6892	
		440	0.0055	0.7248	
		480	0.0050	0.7569	
		520	0.0045	0.7858	
		560	0.0041	0.8121	
		600	0.0037	0.8358	
		640	0.0034	0.8575	
0.0191	2.20	120	0.0100	0.1933	1.63
		160	0.0094	0.2450	
		200	0.0089	0.2938	
		240	0.0084	0.3397	
		280	0.0078	0.3825	
		320	0.0072	0.4224	
		360	0.0067	0.4596	
		400	0.0063	0.4939	
		440	0.0058	0.5260	
		480	0.0054	0.5558	
		520	0.0050	0.5835	
		560	0.0047	0.6093	
		600	0.0044	0.6334	
		640	0.0041	0.6561	
		680	0.0038	0.6772	
		720	0.0036	0.6970	
0.0214	2.20	80	0.0091	0.1086	1.74
		120	0.0089	0.1497	
		160	0.0085	0.1893	
		200	0.0081	0.2272	
		240	0.0077	0.2631	
		280	0.0073	0.2973	
		320	0.0070	0.3299	
		360	0.0066	0.3610	
		400	0.0064	0.3905	
		440	0.0061	0.4188	
		480	0.0058	0.4457	
		520	0.0056	0.4715	
		560	0.0053	0.4963	
		600	0.0051	0.5201	
		640	0.0049	0.5429	
		680	0.0047	0.5648	
		720	0.0045	0.5858	

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

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

Solvent	$\ln(k/s^{-1})$	n	r
NMP	−8.9516	1.2747	0.999
	−8.7610	0.9521	0.999
	−8.8379	1.0142	0.999
	−8.6986	1.2783	0.999
	−8.6120	1.4323	0.999
average	−8.7722	1.1903	
DMSO	−8.6632	0.7203	0.998
	−9.0213	0.8714	0.999
	−8.7363	0.8124	0.999
	−9.0854	1.0118	0.999
	−9.4788	0.9710	0.999
average	−8.9970	0.8774	

Substituting the values of n and k in table 4

into Eq. (5), we can get Eq. (7) for dissolution process of DNTF in NMP, and Eq(8) in DMSO.

$$\frac{d\alpha}{dt}=1.55\times10^{-4}(1-\alpha)^{1.19} \quad (7)$$

$$\frac{d\alpha}{dt}=1.24\times10^{-4}(1-\alpha)^{0.88} \quad (8)$$

3 Conclusions

(1) The enthalpies of DNTF in NMP and DMSO were investigated by RD496-2000 Calvet microcalorimeter at 298.15 K.

(2) The concentration of the solution (b) almost has little influence on the values of the molar enthalpies. The differential enthalpies of DNTF in NMP and DMSO are 24.81 and 1.60 kJ·mol^{-1}.

(3) The kinetic equations of the dissolution processes of DNTF are $d\alpha/dt=1.55\times10^{-4}(1-\alpha)^{1.19}$ in NMP, and $d\alpha/dt=1.24\times10^{-4}(1-\alpha)^{0.88}$ in DMSO.

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