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Thermochemical properties of di(*N*,*N*-di(2,4,6-trinitrophenyl)amino)-ethylenediamine in dimethyl sulfoxide and *N*-methyl pyrrolidone

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Abstract The enthalpies of dissolution for di(*N*,*N*-di(2,4,6,-trinitrophenyl)amino)-ethylenediamine (DTAED) in dimethyl sulfoxide (DMSO) and *N*-methyl pyrrolidone (NMP) were measured using a RD496-2000 Calvet microcalorimeter at 298.15 K. Empirical formulae for the calculation of the enthalpies of dissolution ($\Delta_{diss}H$) were obtained from the experimental data of the dissolution processes of DTAED in DMSO and NMP. The linear relationships between the rate (k) and the amount of substance (a) were found. The corresponding kinetic equations describing the two dissolution processes were $d\alpha/dt = 10^{-2.68}(1-\alpha)^{0.84}$ for the dissolution of DTAED in DMSO, and $d\alpha/dt = 10^{-2.79}(1-\alpha)^{0.87}$ for the dissolution of DTAED in NMP, respectively.

Keywords Di(*N*,*N*-di(2,4,6-trinitrophenyl)amino)-ethylenediamine · Dimethyl sulfoxide · Kinetics · *N*-methyl pyrrolidone · Dissolution

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Introduction

Energetic ionic compound is one of the effective ways to develop new kind of high-energy, low-sensitive, and non-toxic materials. Energetic ionic compounds, which are mainly composed of organic cation and inorganic anion or organic anion, include energetic ionic salts and energetic ionic liquids [1, 2]. To meet the requirement of weapons and equipments for multifunctional energetic materials, many new energetic groups are introduced in the chemical structure of cation and anion of energetic ionic compounds by the molecular design [3–6]. This approach makes energetic ionic compounds possess the various excellent functions, such as high density, insensitivity, stability, environmental friendly, and so on [7–9].

Di(*N*,*N*-di(2,4,6-trinitrophenyl)amino)-ethylenediamine (DTAED) is a novel type of energetic ionic compound which consists of anion of *N*,*N*-di(2,4,6-trinitrophenyl)amine and cation of ethylenediamine, but the solution properties have never been reported so far. Dimethyl sulfoxide (DMSO) and *N*-methyl pyrrolidone (NMP) as solvents have been used extensively in our production and application, so thermochemical properties of its solution have been studied first by means of a RD496-2000 Calvet microcalorimeter. The aim of this work is to study the dissolution properties of DTAED in DMSO and NMP. At the same time, the kinetic equations of the two dissolution processes are obtained, respectively, which provides valuable information for its applications in the future.

Experimental

Materials

DTAED used as crystalloid was prepared and purified by Beijing Institute of Technology, its purity determined by

LC–MS, elemental analysis, and ^{13}C NMR was more than 99.5%. Both DMSO (ρ/g cm^{-3}=1.098–1.102) and NMP (ρ/g cm^{-3}=1.029–1.035) used as solvents were of analysis reagent grade, and their purity was more than 99.5%. The water used in these experiments was deionized with an electrical conductivity of 0.8–1.2 × 10^{-4} Sm^{-1}, and obtained by two times purification using sub-boiling distillation device.

Equipment and conditions

All measurements were made using a RD496-2000 Calvet microcalorimeter (MianYang CP Thermal Analysis Instrument CO., LTD). The enthalpy of 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} [10]. This showed that the device for measuring the enthalpy used in this study was reliable. The enthalpies of dissolution were measured at 298.15 ± 0.005 K.

Results and discussion

Thermochemical behaviors of the dissolution of DTAED in DMSO and NMP

The proper molar sample of DTAED was dissolved in DMSO and NMP at 298.15 K in order to form solution. The enthalpy of the process was detected by the RD496-2000 Calvet microcalorimeter [11–14]. Each process was repeated three times [15, 16]. The dissolution is an exothermic process. The heat flow curves obtained under the same conditions overlap with each other and are shown in Fig. 1, indicating that the reproducibility of test is satisfactory.

The thermochemical data obtained are listed in Tables 1 and 2. In Tables, a is the amount of substance, b is the molality of DTAED, $\Delta_{diss}H$ is the molar enthalpy of dissolution, $\Delta_{diss}H_{partial}$ is the relative partial molar enthalpy of dissolution, and $\Delta_{diss}H_{apparent}$ is the relative apparent molar enthalpy of dissolution.

With the help of the values of b and $\Delta_{diss}H$ in Table 1, the empirical formula of enthalpy describing the b versus $\Delta_{diss}H$ relation is obtained

$$\begin{aligned}\Delta_{diss}H &= A + Bb + Cb^{1/2} \\ &= -147.76 + 3589.37b^{1/2} - 29153.46b \end{aligned} \quad (1)$$

where A, B, and C are coefficients for the dissolution equation.

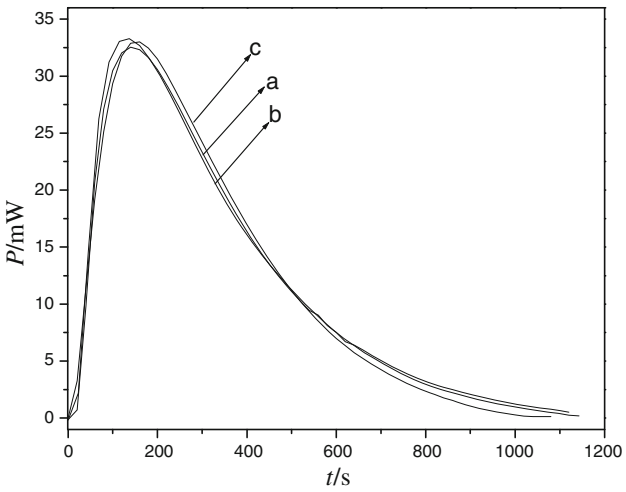

Fig. 1 Curves describing the entire dissolution process of DTAED in DMSO at 298.15 K. (*a*) 10^5a/mol = 0.4721; (*b*) 10^5a/mol = 0.4828; (*c*) 10^5a/mol = 0.4721

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

$$\begin{aligned}\Delta_{diss}H_{apparent} &= \Delta_{diss}H(b=b) - \Delta_{diss}H(b=0) \\ &= 358937b^{1/2} - 2915346b \end{aligned} \quad (2)$$

$$\begin{aligned}\Delta_{diss}H_{partial} &= b\left(\frac{\partial\Delta_{diss}H}{\partial b}\right) + \Delta_{diss}H_{apparent} \\ &= 5384.055b^{1/2} - 58306.92b, \end{aligned} \quad (3)$$

respectively.

According to the values in Table 2, the empirical formula describing the b versus $\Delta_{diss}H$ relation, and the empirical formulae of relative apparent molar enthalpy ($\Delta_{diss}H_{apparent}$) and relative partial molar enthalpy ($\Delta_{diss}H_{partial}$) for DTAED in NMP are

$$\begin{aligned}\Delta_{diss}H &= A + Bb + Cb^{1/2} \\ &= -205.43 + 4483.26b^{1/2} - 33857.7b \end{aligned} \quad (4)$$

$$\begin{aligned}\Delta_{diss}H_{apparent} &= \Delta_{diss}H(b=b) - \Delta_{diss}H(b=0) \\ &= 4483.26b^{1/2} - 33857.7b \end{aligned} \quad (5)$$

$$\begin{aligned}\Delta_{diss}H_{partial} &= b\left(\frac{\partial\Delta_{diss}H}{\partial b}\right) + \Delta_{diss}H_{apparent} \\ &= 672489b^{1/2} - 677154b \end{aligned} \quad (6)$$

respectively.

From Tables 1 and 2, we can see that the values of $\Delta_{diss}H$, the calculated $\Delta_{diss}H_{apparent}$, and $\Delta_{diss}H_{partial}$ change with the values of b. We can find that the relationships between $\Delta_{diss}H$ and $b^{1/2}$ are quadratic equation for DTAED dissolved in DMSO and NMP from Figs. 2 and 3.

Table 1 The enthalpies of dissolution of DTAED in DMSO

$a \times 10^5$/mol	$b \times 10^2$/mol kg^{-1}	$-\Delta_{diss}H$/kJ mol^{-1}		$\Delta_{diss}H_{apparent}$/kJ mol^{-1}	$\Delta_{diss}H_{partial}$/kJ mol^{-1}
		Found	Calculated		
0.4721	0.2287	42.92	42.78	104.98	124.13
0.6009	0.2911	38.73	38.96	108.79	120.76
0.9335	0.4523	38.38	38.22	109.54	98.38
1.1373	0.5510	41.91	41.96	105.80	78.38
1.2232	0.5926	44.29	44.21	103.55	68.93
1.3412	0.6498	47.79	47.86	99.90	55.13

Table 2 The enthalpies of dissolution of DTAED in NMP

$a \times 10^5$/mol	$b \times 10^2$/mol kg^{-1}	$-\Delta_{diss}H$/kJ mol^{-1}		$\Delta_{diss}H_{apparent}$/kJ mol^{-1}	$\Delta_{diss}H_{partial}$/kJ mol^{-1}
		Found	Calculated		
0.3541	0.1715	77.95	77.82	127.61	162.37
0.5365	0.2599	64.83	64.87	140.56	166.84
0.6974	0.3379	58.78	59.23	146.20	162.10
0.9013	0.4367	57.27	57.02	148.41	148.69
1.0837	0.5250	58.63	58.34	147.09	131.75
1.3841	0.6706	65.15	65.34	140.08	96.60

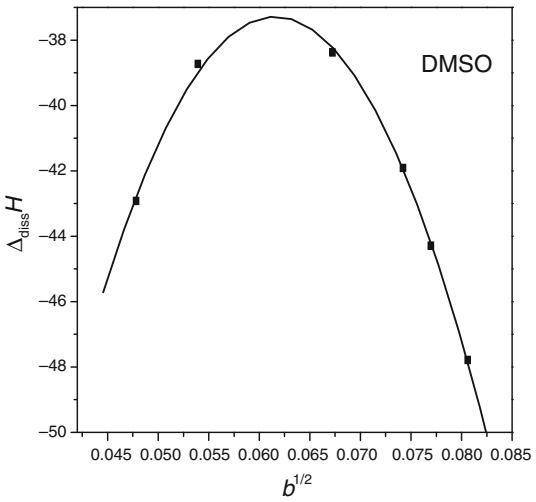

Fig. 2 The relationship between $\Delta_{diss}H$ and $b^{1/2}$ of DTAED in DMSO

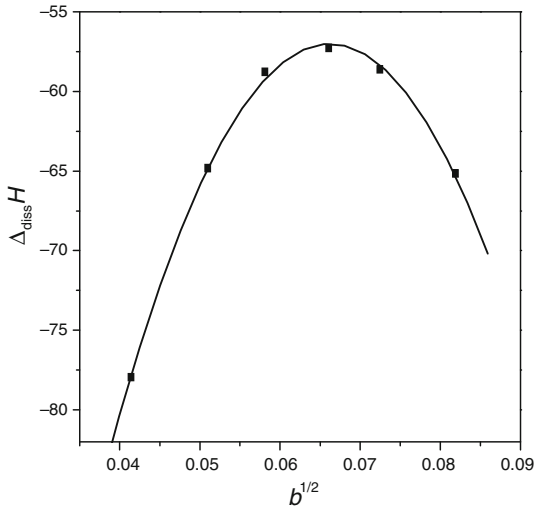

Fig. 3 The relationship between $\Delta_{diss}H$ and $b^{1/2}$ of DTAED in NMP

The kinetics of dissolution process of DTAED in DMSO and NMP

The kinetic equations describing the dissolution of DTAED in DMSO and NMP are Eqs. 7 and 8 [17–21] which are chosen as the model function describing the dissolution process.

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

$$f(\alpha) = (1-\alpha)^n \tag{8}$$

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

Table 3 The original data of the dissolution process of DTAED in DMSO at 298.15 K

m/g	m_{DMSO}/g	t/s	$(dH/dt)_i$/ mJ s^{-1}	$(H/H_0)_i$	$-H_\infty$/ kJ mol^{-1}
0.0044	2.2	210	0.0297	0.384110	42.87
		280	0.0246	0.528774	
		350	0.0194	0.645546	
		420	0.0150	0.736576	
		490	0.0114	0.806223	
		560	0.0086	0.859047	
		630	0.0065	0.899228	
		700	0.0050	0.929823	
		770	0.0036	0.952491	
		840	0.0026	0.969032	
0.0056	2.2	140	0.0440	0.271080	38.66
		210	0.0377	0.461993	
		280	0.0289	0.616764	
		350	0.0213	0.732031	
		420	0.0155	0.816763	
		490	0.0111	0.877759	
		560	0.0079	0.921289	
		630	0.0055	0.952054	
		700	0.0037	0.973134	
		770	0.0023	0.986931	
0.0087	2.2	140	0.0654	0.260159	38.49
		210	0.0552	0.442109	
		280	0.0437	0.589808	
		350	0.0334	0.705593	
		420	0.0254	0.793545	
		490	0.0183	0.858435	
		560	0.0134	0.905621	
		630	0.0095	0.939492	
		700	0.0067	0.963518	
		770	0.0045	0.980261	
0.0106	2.2	350	0.0479	0.613038	41.98
		420	0.0378	0.709575	
		490	0.0292	0.784916	
		560	0.0222	0.842623	
		630	0.0167	0.886262	
		700	0.0124	0.918908	
		770	0.0091	0.943097	
		840	0.0067	0.960826	
		910	0.0048	0.973646	
		980	0.0034	0.982751	
0.0114	2.2	210	0.0735	0.389387	43.78
		280	0.0602	0.523849	
		350	0.0477	0.632197	
		420	0.0372	0.717243	
		490	0.0287	0.783151	
		560	0.0220	0.833849	
		630	0.0169	0.872754	
		700	0.0129	0.902572	
		770	0.0100	0.925414	
		840	0.0077	0.943063	
0.0125	2.2	280	0.0932	0.390296	42.92
		350	0.0759	0.535018	
		420	0.0592	0.650254	
		490	0.0452	0.739087	
		560	0.0343	0.806608	
		630	0.0258	0.857673	
		700	0.0195	0.896165	
		770	0.0146	0.925199	
		840	0.0109	0.946771	
		910	0.0081	0.962788	

Table 4 The original data of the dissolution process of DTAED in NMP at 298.15 K

m/g	m_{DMSO}/ g	t/s	$(dH/dt)_i$/ mJ s^{-1}	$(H/H_0)_i$	$-H_\infty$/ kJ mol^{-1}
0.0033	2.064	140	0.0445	0.257503	75.97
		210	0.0371	0.421426	
		280	0.0295	0.554329	
		350	0.0230	0.658802	
		420	0.0178	0.740037	
		490	0.0137	0.802925	
		560	0.0107	0.851608	
		630	0.0083	0.889469	
		700	0.0066	0.919240	
		770	0.0052	0.942784	
0.0050	2.064	280	0.0343	0.506569	62.45
		350	0.0284	0.607377	
		420	0.0229	0.689787	
		490	0.0182	0.755713	
		560	0.0142	0.807554	
		630	0.0111	0.847967	
		700	0.0087	0.879583	
		770	0.0070	0.904685	
		840	0.0058	0.925083	
		910	0.0048	0.941899	
0.0065	2.064	420	0.0480	0.542744	58.76
		490	0.0380	0.655566	
		560	0.0296	0.744092	
		630	0.0227	0.812435	
		700	0.0171	0.864486	
		770	0.0128	0.903635	
		840	0.0095	0.932873	
		910	0.0071	0.95451	

Table 4 continued

m/g	m_{DMSO}/g	*t*/s	$(dH/dt)_i$/mJ s^{-1}	$(H/H_0)_i$	$-H_\infty$/kJ mol^{-1}
		980	0.0051	0.970376	
		1050	0.0036	0.981703	
0.0084	2.064	210	0.0655	0.38737	57.25
		280	0.0535	0.511321	
		350	0.0431	0.611843	
		420	0.0346	0.692721	
		490	0.0277	0.757581	
		560	0.0220	0.809309	
		630	0.0174	0.850199	
		700	0.0136	0.882307	
		770	0.0106	0.907321	
		840	0.0085	0.926974	
0.0101	2.064	350	0.0978	0.414944	58.62
		420	0.0787	0.564704	
		490	0.0606	0.682512	
		560	0.0456	0.772174	
		630	0.0337	0.839030	
		700	0.0250	0.888386	
		770	0.0187	0.925238	
		840	0.0135	0.952400	
		910	0.0093	0.971561	
		980	0.0062	0.984639	
0.0129	2.064	630	0.0673	0.717818	65.14
		700	0.0519	0.788677	
		770	0.0397	0.843095	
		840	0.0300	0.884487	
		910	0.0225	0.915686	
		980	0.0168	0.939043	
		1050	0.0125	0.956468	
		1120	0.0093	0.969417	
		1190	0.0068	0.978961	
		1260	0.0049	0.985877	

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

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 DTAED dissolved in DMSO and NMP, n is the reaction order, and L is counting number.

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

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

Solvent	n	ln$k$	r
DMSO	0.8360	−6.8569	0.9998
	0.7566	−6.5186	0.9990
	0.7596	−6.1328	0.9993
	0.8565	−5.9564	0.9999
	0.9637	−5.8747	0.9997
	0.8875	−5.7634	0.9998
Mean	0.8433	−6.1838	
NMP	0.8637	−7.1817	0.9990
	0.9512	−6.8217	0.9990
	0.8127	−6.4969	0.9995
	0.9651	−6.2802	0.9998
	0.7688	−6.0151	0.9990
	0.8323	−5.7808	0.9998
Mean	0.8656	−6.4294	

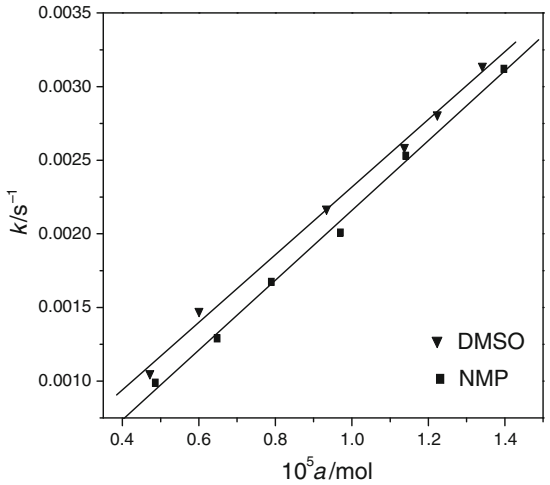

Fig. 4 The relationship between k and a for the dissolution of DTAED in DMSO and NMP

By 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 equation (10), the values of n and ln$k$ are obtained and listed in Table 5.

Substituting the values of n and k from Table 5 into Eq. 7, we can get

$$d\alpha/dt = 10^{-2.68}(1-\alpha)^{0.84} \tag{11}$$

for dissolution process of DTAED in DMSO, and

$$d\alpha/dt = 10^{-2.79}(1-\alpha)^{0.87} \tag{12}$$

for dissolution process of DTAED in NMP.

The relationships between k and a are shown in Fig. 4. One can see that the rate (k) for the dissolution processes of

DTAED in DMSO and NMP increase with the amount of substance (a) increasing from Fig. 4, the linear relationships exist obviously, and the correlative coefficients (r) are 0.9981 and 0.9978, respectively.

Conclusions

(1) The dissolution process of DTAED in DMSO 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 DTAED dissolved in DMSO and NMP are quadratic equations.

(2) The expressions describing values of $\Delta_{diss}H$, $\Delta_{diss}H_{apparent}$, and $\Delta_{diss}H_{partial}$ versus the molality (b) of DTAED in DMSO are $\Delta_{diss}H = -147.76 + 3589.37b^{1/2} - 29153.46b$, $\Delta_{diss}H_{apparent} = 3589.37b^{1/2} - 29153.46b$, and $\Delta_{diss}H_{partial} = 5384.055b^{1/2} - 58306.92b$. The expressions describing values of $\Delta_{diss}H$, $\Delta_{diss}H_{apparent}$, and $\Delta_{diss}H_{partial}$ versus the molality (b) of DTAED in NMP are $\Delta_{diss}H = -205.43+4483.26b^{1/2} - 33857.7b$, $\Delta_{diss}H_{apparent} = 4483.26b^{1/2} - 33857.7b$, and $\Delta_{diss}H_{partial} = 6724.89b^{1/2} - 67715.4b$, respectively.

(3) The kinetics equations of dissolution processes for DTAED are $d\alpha/dt = 10^{-2.68}(1-\alpha)^{0.84}$ in DMSO, and $d\alpha/dt = 10^{-2.79}(1-\alpha)^{0.87}$ in NMP.

(4) The relationships between k and a are obtained, and the linear relationships exist obviously.

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