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## Thermochemistry and Thermodynamics of Solution of Styphnic Acid in DMF at 298.15 K

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**Abstract:** The enthalpies of solution and the thermodynamics of styphnic acid 2,4,6-trinitroresorcinol (TNR) the solution solved in DMF were studied. The enthalpies of TNR solution with different concentrations were measured by a SETARAM C80 II calorimeter at 298.15 K and the empirical formula for enthalpies of TNR solution is calculated by polynomial simulation on the computer. The results show that the formula is  $\Delta_{\text{sol}}H = -14.392 - 988.6b + 34.992b^{1/2}$ . The standard molar enthalpy of solution is determined to be  $\Delta_{\text{sol}}H_m^{\ominus} = -14.392 \text{ kJ} \cdot \text{mol}^{-1}$ . The relative apparent molar enthalpies of solution ( $\Phi L_i$ ), the relative partial molar enthalpies ( $L_i$ ), enthalpies of dilution ( $\Delta_{\text{dil}}H_{1,2}$ ) are also stretched respectively. The thermodynamics of TNR solution was studied by analyzing heat-flux to time curves, the rate constant of reaction and the reaction order were determined to be  $1.632 \times 10^{-3} \text{ s}^{-1}$  and 0.6158, respectively.

**Key words:** physical chemistry; thermochemistry; thermodynamics; 2,4,6-trinitroresorcinol (TNR); microcalorimetry

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### 1 Introduction

2,4,6-Trinitroresorcinol (TNR) was widely used as materials for dynamite such as Lead Styphnate<sup>[1,2]</sup>, etc., while its properties, as well as the thermochemical properties and the thermodynamics for the solution action, have been rarely reported. In this paper, a lot of efforts had been put on this aspect. At 298.15 K, the empirical formula of enthalpies for solution, the standard molar enthalpies for solution, the relative apparent molar enthalpies for solution, the relative partial molar enthalpies, enthalpies for dilution, the reaction velocity constant and the reaction progression of TNR in the solvent of *N,N*-dimethylformamide (DMF) were all calculated respectively.

### 2 Experimental

#### 2.1 Preparation of reagents and compounds

*N,N*-dimethylformamide (DMF) is of A. R. grade. The electrical conductivity of de-ionized water is  $6.25 \times 10^{-8} \text{ s} \cdot \text{cm}^{-1}$ . Alcohol using for cleaning equip-

ments is industrial. The compound TNR is refined, the obtained fulvous crystal is purified, dried, sifted through a 200-mesh sifter and then stocked in the dryer.

#### 2.2 Equipment and conditions

The calorimetric experiment was carried out by using a Calvet microcalorimeter, type C80 II from Setaram, France and operated at  $(298.15 \pm 0.01) \text{ K}$ . The microcalorimeter was calibrated by Joule effect before experiment, and the sensitivity was obtained to be  $30.501 \mu\text{V} \cdot \text{mW}^{-1}$  at 298.15 K. The reaction solution/solvent were put into the stainless steel mixing with membrane vessel, which was made of PTFE (0.05 mm thick), separately. The working temperature is required to be constant. After thermal equilibration for about 1 h, the containers of sample and reference were pushed down simultaneously. The enthalpy-change process was recorded for about 45 minutes, and the thermogram was obtained.

The accuracy of the calorimeter was checked by performing test measurements of the enthalpies of solution for KCl (special purity) in de-ionized water. The experimental value herein  $\Delta_{\text{sol}}H_m^{\ominus} = (17.201 \pm 0.058) \text{ kJ} \cdot \text{mol}^{-1}$  is in good agreement with that  $\Delta_{\text{sol}}H_m^{\ominus} = (17.241 \pm 0.018) \text{ kJ} \cdot \text{mol}^{-1}$  reported in the literature<sup>[3]</sup>, which indicated that the device used in this work is reliable. The veracity of the measurements is within 0.23%.

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### 3 Results and discussion

#### 3.1 Thermochemistry of the TNR solution

The TNR has a good solubility in DMF. The quantity of DMF solvent was definite to be 3 mL, and the quantity of TNR was changeable from time to time. Large numbers of experiments had been done, then six experiments with good performance and average mass distribution were picked up. The experimental and calculated values of enthalpies of solution in DMF for TNR were given in Table 1. It also included the calculated values of the relative apparent molar enthalpies of solution ( $\Phi L_i$ ) and the relative partial molar enthalpies ( $L_i$ ).

**Table 1** Enthalpies of solution in DMF for the TNR at 298.15 K

No.	$m$ /mg	$b$ / $\times 10^{-3} \text{ mol} \cdot \text{kg}^{-1}$	$\Delta_{\text{sol}} H_m^0 / \text{kJ} \cdot \text{mol}^{-1}$		$\Phi L_i$ / $\text{kJ} \cdot \text{mol}^{-1}$	$L_i$ / $\text{kJ} \cdot \text{mol}^{-1}$
			found	cal.		
blank	0.00	0.00	-	-14.39	0.00	0.00
1	2.74	3.93	-16.10	-16.08	-1.69	-25.58
2	3.07	4.40	-16.40	-16.42	-2.03	-30.31
3	3.56	5.11	-16.94	-16.94	-2.55	-37.85
4	3.99	5.72	-17.42	-17.40	-3.01	-44.94
5	4.24	6.08	-17.67	-17.68	-3.28	-49.24
6	4.72	6.77	-18.20	-18.21	-3.81	-57.83

Note:  $m$ , mass of sample;  $b$ , molality of sample in the solution;  $\Delta_{\text{sol}} H$ , the molar enthalpies for solution of sample. The results of calcd. were the simulation results from obtained equation ( $\Delta_{\text{sol}} H = -14.392 - 988.6b + 34.992b^{1/2}$ ).

From the data of Table 1, it can be seen that the value of  $\Delta_{\text{sol}} H$  is descending as the concentrations rising, but the  $|\Delta_{\text{sol}} H|$  is ascending as the concentration ascending. The enthalpies of solution in DMF with different concentrations of TNR and the values of concentration are simulated through the empirical formula (1) [4]:

$$\Delta_{\text{sol}} H = A + Bb + Cb^{1/2} \quad (1)$$

$A$ ,  $B$ ,  $C$  in Equation (1) mean the regression coefficients. After a polynomial simulation on the computer, the chart is in Fig 1.

The empirical formula of enthalpies of solution  $\Delta_{\text{sol}} H(b)$  in DMF and the standard enthalpies of solution  $\Delta_{\text{sol}} H_m^0(b=0)$  in DMF for the coordination compound TNR are calculated as:

$$\Delta_{\text{sol}} H = -14.392 - 988.6b + 34.992b^{1/2} \quad (2)$$

$$\Delta_{\text{sol}} H_m^0 = -14.392 \text{ kJ} \cdot \text{mol}^{-1} \quad (3)$$

According to the relationship as shown in Eq. (4) [4]

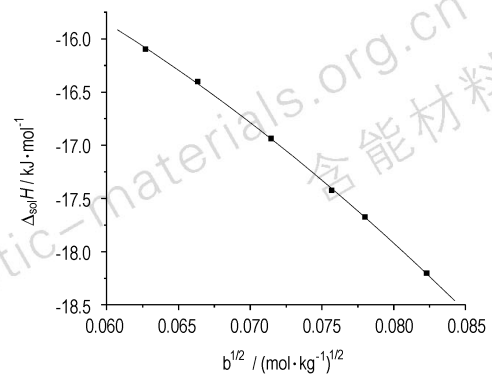


Fig. 1 Measured  $\Delta_{\text{sol}} H$  for TNR as a function of molality  $b$  at 298.15 K

$$\Phi L_i = \Delta_{\text{sol}} H(b = b) - \Delta_{\text{sol}} H(b = 0) \quad (4)$$

Bringing Eq. (2) and Eq. (3) into Eq. (4), the empirical formula of relative apparent molar enthalpy  $\Phi L_i$  for the coordination compound is obtained:

$$\Phi L_i = -988.6b + 34.992b^{1/2} \quad (5)$$

According to the empirical formula as presented in Eq. (6) [4]

$$L_i = b \left[ \frac{\partial \Delta_{\text{sol}} H}{\partial b} \right] + \Phi L_i \quad (6)$$

From Eq. (2) and Eq. (5), the following empirical formulae of the relative partial molar enthalpy  $L_i$  for the title coordination compound was determined:

$$L_i = -1977.2b + 52.488b^{1/2} \quad (7)$$

$$\Delta_{\text{dil}} H_{1,2} = \sum_1^2 A_i [(b_2^{1/2})^i - (b_1^{1/2})^i] \quad (8)$$

According to the empirical formula described in Eq. (8) [4], the following empirical formulae of dilution enthalpies  $\Delta_{\text{dil}} H_{1,2}$  for the coordination compound between different concentrations is obtained, where  $A_1 = -988.6$ ,  $A_2 = 34.992$ . From the Equation (9), the alterant quantity of the enthalpies from some concentration to another could be concluded.

$$\Delta_{\text{dil}} H_{1,2} = -988.6(b_2^{1/2} - b_1^{1/2}) + 34.992(b_2 - b_1) \quad (9)$$

#### 3.2 Thermodynamics of the TNR solution

Since the thermodynamics (TD) curves recorded by using a microcalorimeter at 298.15 K with different concentrations are similar in tendency and the solution processes are of some specific characters with different concentrations, a typical thermodynamics (TD) curves shown in Fig. 2 was picked up to study.

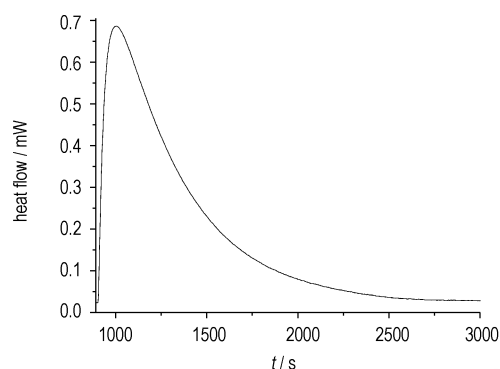


Fig. 2 Heat flow curve of solution at 298.15 K

It can be seen that the reaction is an exothermic one which attributed to the annectent effects between molecules of solutes (or ions) and DMF molecules.

The original data obtained from the TD curves were shown in Table 2. Eq. (10) which is derived from the literature [5] was non-reversible thermodynamics equation under isothermal and isotonic condition. The rate constant of reaction ( $k$ ) and the reaction order ( $n$ ) of the solution reaction could be calculated from this equation. These experimental data in Table 2 were put into Eq. (10) by linear least-squares method.

$$\ln \left| \frac{1}{H} \frac{dH_i}{dt} \right| = \ln k + n \ln \left| 1 - \frac{H_i}{H_0} \right| \quad (10)$$

where  $H_0$  is the total reaction enthalpy (corresponding to the global area under the TD curve),  $H_i$  is the reaction heat in a certain time (corresponding to the partial area under the curve),  $dH_i/dt$  is the rate of reaction at time  $t$ ,  $k$  is the rate constant of reaction,  $n$  is the reaction order.

According to the data of Table 2, the values of  $k$  and  $n$  [5] were obtained. The rate constant of reaction  $k = 1.632 \times 10^{-3} \text{ s}^{-1}$ , the reaction order  $n = 0.6158$ , and the correlation coefficient  $R^* = 0.9882$ .

#### 4 Conclusions

The enthalpies of solution in DMF of the coordination compound of TNR are measured by using a Calvet micro-calorimeter. Empirical formula for the calculation of the enthalpies for solution ( $\Delta_{\text{sol}}H$ ), relative apparent molar enthalpies ( $\Phi L_i$ ), relative partial molar enthalpies ( $L_i$ ) and enthalpies of dilution ( $\Delta_{\text{dil}}H_{1,2}$ ) are calculated from the experimental data of the enthalpies of solution.  $\Delta_{\text{sol}}H = -14.392 - 988.6b + 34.992b^{1/2}$ ,  $\Phi L_i = -988.6b +$

$$34.992b^{1/2}, L_i = -1977.2b + 52.488b^{1/2} \text{ and } \Delta_{\text{dil}}H_{1,2} = -988.6[b_2^{1/2} - b_1^{1/2}] + 34.992[b_2 - b_1].$$

Table 2 Thermodynamics data of the solution reaction at 298.15 K

$t$ /s	$H_i$ /J	$10^4(dH_i/dt)$ /J · s <sup>-1</sup>	$H_i/H_\infty$	$\ln[1 - H_i/H_\infty]$	$\ln[1/H_\infty \cdot dH_i/dt]$
150	-0.0345	-	-	-	-
200	-0.0548	-4.06	0.179	-0.198	-6.62
250	-0.0753	-4.1	0.246	-0.283	-6.61
300	-0.0954	-4.02	0.312	-0.374	-6.63
350	-0.115	-3.84	0.375	-0.470	-6.68
400	-0.133	-3.66	0.435	-0.570	-6.73
450	-0.150	-3.42	0.491	-0.675	-6.80
500	-0.166	-3.24	0.544	-0.785	-6.85
550	-0.181	-2.9	0.591	-0.894	-6.96
600	-0.195	-2.76	0.636	-1.01	-7.01
650	-0.208	-2.24	0.679	-1.14	-7.22
700	-0.219	-2.32	0.717	-1.26	-7.18
750	-0.230	-2.08	0.751	-1.39	-7.29
800	-0.239	-1.98	0.783	-1.53	-7.34
850	-0.248	-1.76	0.812	-1.67	-7.46

Note:  $H_0 = -0.3057 \text{ J}$ .

The reactions of TNR dissolved in DMF are exothermic. It is probably because the annectent effects between the molecules of solutes and DMF solvent.

On the basis of experimental and calculated results, the rate constant of reaction are found to be  $1.632 \times 10^{-3} \text{ s}^{-1}$  and the reaction order are determined to be 0.6158.

The experimental results can provide new content to the thermochemical properties, thermodynamics and function mechanism of the title coordination compound.

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## Deformation Analysis of Free Loading Propellant in Storage

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**Abstract:** Three-dimensional viscoelastic large deformation incremental constitutive equation was derived based on Total Lagrangian method. From materials property testing of composite modified double base (CMDB) propellant by dynamic mechanical analyzer (DMA), deformation, equivalent von mises stress and strain of free loading propellant in storage were obtained. The results show that the subsidence magnitude of solid propellant in the axis direction is about 0.16 mm. Outer diameter increases 0.04 mm and inner diameter is nearly unchanged. Stress between solid propellant and binder is about 11.8 kPa, which will not lead to dewetting. Balanceable time of the free loading propellant in long-term storage is about half a year. Thus the deformation of the free loading propellant grains in storage can be deduced by that of propellant stored for more than half a year.

**Key words:** aerospace propulsion theory and engineering; free loading propellant; storage; viscoelasticity; dynamic mechanical analyzer (DMA)

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## The Hydrus Enthalpy of $\text{NTO}^-$

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**Abstract:** Based on the literature data of the enthalpies of solution in water,  $\Delta_{\text{sol}}H_m^0$ , lattice enthalpy,  $\Delta H_L^0$ , lattice energy,  $\Delta U_L^0$  for the complexes of the lanthanide metals with 3-nitro-1,2,4-triazol-5-one (NTO),  $\text{M}(\text{NTO})_n \cdot m\text{H}_2\text{O}$  ( $\text{M} = \text{La}, \text{Ce}, \text{Pr}, \text{Eu}, \text{Sm}, \text{Gd}$ ,  $n = 3, m = 7$ ;  $\text{M} = \text{Y}, \text{Yb}$ ,  $n = 3, m = 6$ ;  $\text{M} = \text{Dy}, \text{Tb}$ ,  $n = 3, m = 5$ ;  $\text{M} = \text{Nd}$ ,  $n = 3, m = 8$ ), standard enthalpies of formation,  $\Delta_f H_m^0(\text{M}^{n+}, \text{aq}, \infty)$ ,  $\Delta_f H_m^0(\text{M}^{n+}, \text{g})$ ,  $\Delta_f H_m^0(\text{H}_2\text{O}, \text{g})$ ,  $\Delta_f H_m^0(\text{H}_2\text{O}, \text{l})$ ,  $\Delta_f H_m^0(\text{NTO}^-, \text{aq}, \infty)$ ,  $\Delta_f H_m^0(\text{NTO}^-, \text{g})$  and hydrus enthalpy of  $\text{M}^{n+}$ ,  $\Delta_h H_m^0(\text{M}^{n+})$ , the hydrus enthalpy of  $\text{NTO}^-$ ,  $\Delta_h H_m^0(\text{NTO}^-)$  was estimated as  $-(153.73 \pm 0.21) \text{ kJ} \cdot \text{mol}^{-1}$ .

**Key words:** physical chemistry;  $\text{NTO}^-$ ; hydrus enthalpy

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## 斯蒂芬酸在 DMF 中的热化学和热动力学性质研究

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**摘要:** 应用微热量热仪测定了斯蒂芬酸(TNR)在溶剂  $N,N$ -二甲基甲酰胺(DMF)中不同浓度( $b$ )时的溶解焓, 用计算机拟合的方法求得计算该物质溶解焓( $\Delta_{\text{sol}}H$ )的经验公式( $\Delta_{\text{sol}}H = -14.392 - 988.6b + 34.992b^{1/2}$ )。由此得到了该物质的标准摩尔溶解焓( $\Delta_{\text{sol}}H_m^0 = -14.392 \text{ kJ} \cdot \text{mol}^{-1}$ ), 并分别推导出了 TNR 的相对表观摩尔焓、相对偏摩尔焓以及配合物的稀释焓的经验公式。同时, 对 TNR 溶液反应的动力学进行了研究, 通过分析热流对时间的曲线图, 确定了该溶解反应的速率常数为  $1.632 \times 10^{-3} \text{ s}^{-1}$ , 反应级数为 0.6158。

**关键词:** 物理化学; 热化学性质; 热动力学性质; 斯蒂芬酸 (TNR); 微热量热法

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