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# Dissolution Properties of Trinitrophloroglucinol Dissolved in Deionized Water

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**Abstract**: A SETARAM C80 calorimeter was used in the experiment to measure the enthalpy of dissolution and thermodynamic properties of trinitrophloroglucinol (TNPG) dissolved in deionized water ($H_2O$) at 298.15 K. The empirical formula for the enthalpy of dissolution was calculated by polynomial expressions. The fomula is: $\Delta_{diss}H_m = 106.799266 - 2352.19194b^{1/2} + 15538.58581b$. The standard molar enthalpy of dissolution, the relative apparent molar dissolution enthalpy and the relative partial molar enthalpy also were obtained from the experimental data of the enthalpy of dissolution of TNPG in water. The kinetic formula was obtained. From the formula the rate constant and reaction order are deduced.

**Key words**: physical chemistry; microcalorimeter; trinitrophloroglucinol (TNPG); enthalpy of solution; thermochemistry; thermodynamics

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## 1 Introduction

2,4,6-trinitro-1,3,5-trihydroxybenzene (trinitrophloroglucinol, TNPG) belongs to the polynitro hydroxybenzenes. It has three nitrogroups and three phenolic hydroxyl groups conjugated with the ring[1-7]. It is an important explosive. It has been used in the chemical industry as an ingredient for making dyes and in explosive industry as an ingredient for primer compositions, percussion caps, and detonator for mulations[8]. TNPG is a strong acidic organic compound so it can form a large number of salts with metals which are efficient primary explosives and used in important applications in the military and commercial industry. Alkalina and alkali-earth metal salts of TNPG as well as Zn, Cd, Pb, Mn, Ag and ammonium salts have been synthesized and extensively studied[9-11]. Till now, the enthalpy of dissolution of TNPG dissolved in *N*,*N*-dimethylformamide (DMF) and alcohol (EtOH) are studied in our research group[12], but enthalpy of solution of TNPG dissolved in deionized water and the thermodynamic properties of the solutions have rarely been reported.

In this paper, the process of dissolution of TNPG dissolved $H_2O$ and thermochemistry and thermodynamic properties are studied at different concentrations by a SETARAMC 80 calorimeter at 298.15 K. The empirical formulas of enthalpy of dissolution, the values of standard molar enthalpy of dissolution, relative apparent molar enthalpy of dissolution and relative partial molar dissolution enthalpy are all determined. The kinetic formula was calculated. From the formulas we can deduce the rate constant and order of the reaction.

## 2 Experiment

### 2.1 Preparation of reagents and compounds

The compound TNPG is synthesized according to the reported paper[5]. The molecular structure and the thermal decomposition mechanism of TNPG have been studied by using differential scanning calorimetry(DSC), thermogravimetry-derivative thermogravimetry (TG-DTG), and FTIR technologies. It was purified and dried. Before the experiment it was sifted through a 200-mesh sieve, and then kept in a dryer for 24 h. The solvent, $H_2O$ used in the experiment was deionized with an electrical conductivity of $6.25\times10^{-8}$ S·cm$^{-1}$.

### 2.2 Equipment and conditions

A microcalorimetry, SETARAM C80 calorimeter (Setaram Instrumentation, Caluire, France) was used in the experiment at (298.15 ±0.01) K. It has two cells, one for reaction cell, the other for reference cell to cancel out the effect of residual deviation. Both the cells are made of stainless steel. The temperature is measured by 100 pairs of 100 Ω thermocouples located around the two vessels and it is held constant to within 0.01 K during each measurement. The microcalorimeter was calibrated by Joule effect and the sensitivity was obtained to be 30.501 μV·mW$^{-1}$. The solution and solvent which are separated with a membrane made by polytetrafluoroethylene (PTEF, 0.05 mm thick) are put into the reaction cell.

The enthalpy of dissolution of KCl (special purity) in deionized water was tested for checking the accuracy of the calorimeter. The experimental result of the enthalpy of dissolution for KCl is 17.2225 kJ·mol$^{-1}$ while the reported result is (17.241 ±0.018) kJ·mol$^{-1}$[13]. The data from the calorimeter is reliable.

## 3 Results and discussions

### 3.1 Thermochemistry of TNPG dissolved in $H_2O$

Six times measurements with different concentrations were picked up in the experiment. The quantity of the solvent $H_2O$ was definite to be 3.0 mL while the quantity of TNPG was varied. The molalities and their molar dissolution enthalpy ($\Delta_{diss}H_m$) are shown in Table1. The relationship between the concentration and the $\Delta_{diss}H_m$ are shown in Fig.1.

Based on the reported empirical formula Eq. (1)[14].

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

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Where, $b$ is the molality of solution, mol · kg$^{-1}$; $A$, $B$ and $C$ are the regression coefficients.

The empirical formula of TNPG dissolved in $H_2O$ are obtained by fitted the experimental data in Fig.1.

$$\Delta_{diss}H_m = 106.79926 + 15538.58581b - 2352.19194b^{1/2} \quad (2)$$

The standard enthalpy of dissolution $\Delta_{diss}H_m^\theta$ ($b = 0$) are calculated:

$$\Delta_{diss}H_m^\theta = 106.799 \text{ kJ} \cdot \text{mol}^{-1} \quad (3)$$

The formulas of the relative apparent molar enthalpy of dissolution ($\Phi L_i$) and the relative partial molar enthalpy ($L_i$) were also identified according to the reported empirical formulas Eq. (4) and Eq. (5)[14].

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

$$L_i = b\left[\frac{\partial \Delta_{diss}H}{\partial b}\right] + \Phi L_i \quad (5)$$

The formulas of $\Phi L_i$ and $L_i$ are as follows:

$$\Phi L_i = 15538.5858b - 2352.19194b^{1/2} \quad (6)$$

$$L_i = 62154.34324b - 2328.28791b^{1/2} \quad (7)$$

**Table 1** Enthalpy of dissolution of TNPG in $H_2O$ at 298.15 K

| No. | $m$/mg | $b/10^{-3}$ mol · kg$^{-1}$ | $\Delta_{diss}H_m$/kJ · mol$^{-1}$ | | $\Phi L_i$/kJ · mol$^{-1}$ | $L_i$/kJ · mol$^{-1}$ |
|---|---|---|---|---|---|---|
| | | | calcd. | found | | |
| blank | 0.00 | 0.00 | 106.80 | | 0.00 | 0.00 |
| 1 | 1.69 | 2.16 | 31.07 | 31.0 | −75.73 | −29.79 |
| 2 | 1.96 | 2.50 | 28.02 | 28.07 | −78.78 | −20.96 |
| 3 | 2.33 | 2.97 | 24.73 | 24.95 | −82.07 | −7.55 |
| 4 | 2.60 | 3.32 | 22.86 | 22.66 | −83.94 | 3.03 |
| 5 | 2.92 | 3.72 | 21.11 | 21.03 | −85.69 | 16.28 |
| 6 | 3.32 | 4.24 | 19.52 | 19.60 | −87.28 | 33.74 |

Note: $m$ is mass of sample; $b$ is molality of sample in the solution; $\Delta_{diss}H_m$ is the molar enthalpy for dissolution.

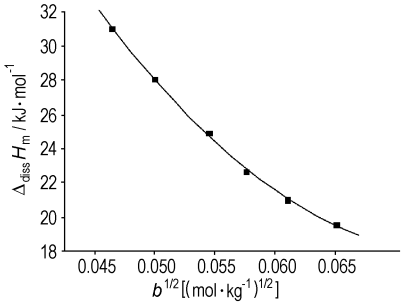


**Fig.1** The relationship between the concentration and the $\Delta_{diss}H_m$ of TNPG in $H_2O$ at 298.15 K

It can be deduced that the process of TNPG dissolving in $H_2O$ is endothermal. It is because that the interaction among the molecules of solute is stronger than the interaction between the molecules of solute and solvent. And as the concentration increases, the quantity of heat reduces in the process. The maximum is in the infinite dilution, which is known as the standard enthalpy of dissolution, the value $\Delta_{diss}H_m^\theta = 106.799$ kJ · mol$^{-1}$.

## 3.2 Thermodynamics of TNPG dissolved in $H_2O$

The heat flow curves with different concentrations recorded by using a microcalorimeter at 298.15 K are similar in tendency of TNPG dissolved in $H_2O$. The reactions are endothermal. The rate constant ($k$) and the reaction order ($n$) are irrelevant with concentrations. The original data from the curve were shown in Table 2.

**Table 2** Thermokinetic data of TNPG dissolved in $H_2O$ at 298.15 K

| $t$/s | $H_i$/J | ($dH_i/dt$)/J · s$^{-1}$ | $H_i/H_\infty$ | $\ln[1 - H_i/H_\infty]$ | $\ln[1/H_\infty \cdot dH_i/dt]$ |
|---|---|---|---|---|---|
| 1284 | 0.0564 | 0.000353 | 0.2263 | −0.2566 | −6.5584 |
| 1383.6 | 0.0877 | 0.000314 | 0.3519 | −0.4338 | −6.6758 |
| 1484.4 | 0.1151 | 0.000272 | 0.4619 | −0.6197 | −6.8209 |
| 1584 | 0.1385 | 0.000235 | 0.5558 | −0.8114 | −6.9667 |
| 1683.6 | 0.1591 | 0.000207 | 0.6384 | −1.0173 | −7.0941 |
| 1784.4 | 0.1771 | 0.000179 | 0.7107 | −1.2402 | −7.2410 |
| 1884 | 0.1919 | 0.000149 | 0.7701 | −1.4700 | −7.4248 |
| 1983.6 | 0.2036 | 0.000117 | 0.8170 | −1.6983 | −7.6598 |
| 2084.4 | 0.2138 | 0.000101 | 0.8579 | −1.9515 | −7.8090 |
| 2184 | 0.2215 | 0.000077 | 0.8888 | −2.1968 | −8.0782 |
| 2283.6 | 0.2276 | 0.000061 | 0.9133 | −2.4456 | −8.3111 |
| 2484 | 0.2365 | 0.000044 | 0.9491 | −2.9767 | −8.6378 |

Based on Equation (8) derived from the literature[15], the experimental data are fitted by a linear least squares method.

$$\ln\left[\frac{1}{H_\infty}\frac{dH_i}{dt}\right] = \ln k + n\ln\left[1 - \frac{H_i}{H_\infty}\right] \quad (8)$$

Where, $H_\infty$ is the total reaction enthalpy, kJ · mol$^{-1}$; $H_i$ is the reaction heat in a certain time, kJ · mol$^{-1}$; $k$ is the rate constant of reaction; $n$ is the reaction order. The fitting results are shown in Fig.2.

The curve shown in Fig. 2 can be received. From the data of Table 2 the kinetic formula of TNPG dissolved in $H_2O$ is obtained:

$$\ln\left[\frac{1}{H_\infty}\frac{dH_i}{dt}\right] = -6.32176 + 0.78377\ln\left[1 - \frac{H_i}{H_\infty}\right], \quad R^* = 0.9967 \quad (9)$$

Where, $R^*$ is correlation coefficient.

From the parameters of the kinetic formula the rate constant of reaction ($k$) and the reaction order ($n$) can be calculated: $n=0.78377$, $k=1.80\times10^{-3}\ s^{-1}$.

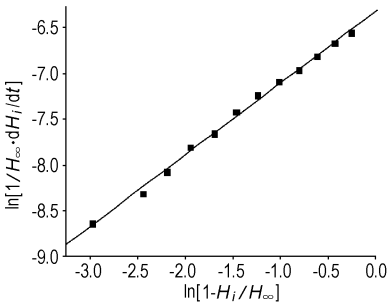


**Fig. 2** The kinetic curve of TNPG dissolved in $H_2O$

## 4 Conclusions

(1) The empirical formula for the dissolution enthalpy of TNPG dissolved in $H_2O$ at 298.15 K is determined, as well as the standard molar enthalpy of dissolution ($\Delta_{diss}H_m^\theta$), the relative apparent molar enthalpy of dissolution ($\Phi L_i$) and the relative partialmolar enthalpy ($L_i$) are calculated respectively. The value $\Delta_{diss}H_m^\theta=106.799\ kJ\cdot mol^{-1}$.

(2) The process of TNPG dissolving in $H_2O$ is endothermal. It is because that the the interaction among the molecules of solute is stronger than interaction between the molecules of solute and solvent. And as the concentration increases, the quantity of heat reduces in the processes. The maximum is in the infinite dilution, which is known as the standard enthalpy of dissolution $\Delta_{diss}H_m^\theta(b=0)$.

(3) On the basis of the experimental data and calculated results, the rate constant of reaction ($k$) and the reaction order ($n$) are also determined: $n=0.78377$, $k=1.80\times10^{-3}\ s^{-1}$.

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# 三硝基间苯三酚在去离子水中的溶解性质

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**摘 要:** 在温度 298.15 K,采用 C80 微热量热仪测定了三硝基间苯三酚(TNPG)在去离子水($H_2O$)的溶解焓及热力学参数。由多项式拟合得到该物质溶解焓($\Delta_{diss}H$)的经验公式 $\Delta_{diss}H_m=106.799266+15538.58581-2352.19194b^{1/2}b$,并计算获得标准摩尔溶解焓、相对表观摩尔焓和相对偏摩尔焓。同时,对溶液反应的动力学进行研究,获得了动力学方程以及相应的反应速率常数和反应级数。

**关键词:** 物理化学; 微热量热仪; 三硝基间苯三酚(TNPG); 溶解焓; 热力学; 动力学
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