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Solubility of 3,7-Dinitro-1,3,5,7-tetraazabicyclo [3.3.1] Nonane in Ethanenitrile, Methanol, 1,1-Dichloroethane, Dimethyl Sulfoxide, Acetone, and Mixed Solvents

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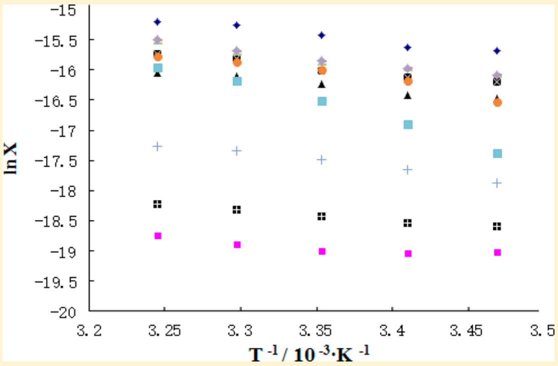
ABSTRACT: The solubility of 3,7-dinitro-1,3,5,7-tetraazabicyclo [3.3.1] nonane (DPT) was measured in ethanenitrile, methanol, 1,1-dichloroethane, dimethyl sulfoxide (DMSO), acetone, ethyl acetate, ethyl acetate and methanol mixture, and acetonitrile and water mixture from 288.15 K to 308.15 K. In this paper, the determination method of DPT was first established by high-performance liquid chromatography (HPLC) with optimized chromatographic conditions. The solubility of DPT in all solvents was measured upon this chromatographic method. Experimental results show that the order of solubility can be represented as DMSO > acetonitrile > ethyl acetate > ethyl acetate/methanol (9:1, v/v) > ethyl acetate/methanol (7:3, v/v) > acetone > acetonitrile/water (9:1, v/v) > ethyl acetate/methanol (5:5, v/v) > acetonitrile/water (7:3, v/v) > 1,1 - dichloroethane > methanol. Moreover, its solubility increased with raising the temperature. The thermodynamic properties of DPT, such as solution enthalpy, have also been calculated.



INTRODUCTION

3,7-Dinitro-1,3,5,7-tetraazabicyclo [3.3.1] nonane (DPT) is well-known as the key intermediate of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) synthesized from hexamethylenetetramine (HA).[1] HMX is one of the most powerful explosives and can be synthesized by nitrify DPT with nitric acid and nitrogen pentoxide (Figure 1). Such a process was confirmed as the most efficient and economic method with lower cost, high purity, easy control, and environmentally friendly for the production of HMX.[2,3]

DPT is an unstable explosive, which has a lower impact sensitivity than TNT. Pure DPT compound is white diamond crystal of two kinds of form, whose melting points are 495.15 K to 496.15 K and 477.15 K to 478.15 K.[4] Its density is 1.63 g·cm^{-3}.[3] Wright first synthesized DPT by sulfuric acid and methenamine dinitrate with 31 % yield in 1949.[1] After that, different synthetic schemes were reported to improve the procedure and the yield.[5,6] Along with the improvement of DPT synthesis, its purification also attracted considerable concerns.[4] It is reported that high-purity DPT can recrystallized from acetone, ethyl acetate, nitromethane, 4-dioxane, and acetic anhydride.[7]

In general, the explosive properties of high energy compound are significantly influenced by its purity.[8,9] In addition, its crystallization properties such as crystal shape, particle size distribution, crystal morphology, and polycrystalline, also contributes to its combustion rate and ballistic propulsion.[10,11] Therefore, in order to get high purity product in reasonable crystal size and shape, the solubility of DPT in different solvents is critical to the recrystallization solvent and procedure optimization.[12]

Considering DPT is a sensitive explosive compound, the traditional gravimetric analysis for the determination of the solubility is inconvenient due to the amount used.[13] In this research, we used high-performance liquid chromatography (HPLC) to determine the concentration of DPT in solution. Therefore, a relatively far less amount of solid DPT was needed to obtain the oversaturated solution in less volume solvents. The solubility of DPT was decided in acetonitrile, methanol, acetone, DMSO, ethylene dichloride, ethyl acetate, ethyl acetate and methanol mixture, and acetonitrile and water mixture in the temperature range from 288.15 K to 308.15 K. The thermodynamic properties of DPT were also determined based on its solubility.

EXPERIMENTAL SECTION

Chemicals and Analytical Method. The DPT (3,7-dinitro-1,3,5,7-tetraazabicyclo [3.3.1] nonane, $C_5H_{10}N_6O_2$, CAS: 101-25-7) with a purity of 99.98 % was provided by Xi'an Modern Chemistry Research Institute, China. The acetonitrile, methanol, 1,1-dichloroethane, DMSO, acetone, and ethyl acetate were purchased from local suppliers without further purification (Table 1). Deionized water (18.25 MΩ·

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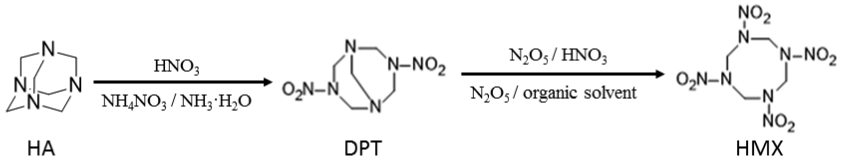

Figure 1. Synthetic route of HMX.

cm^{-1}) was obtained from a Millipore Mili-Q Plus water system. All solutions were filtered through 0.45 μm membranes (China) before usage.

Table 1. Information of Chemicals Used in This Work

chemical name	source	mass fraction purity	analysis method	purification method
DPT	Xi'an Modern Chemistry Research Institute, China	99.98 %	HPLC[a]	none
acetonitrile	J.T. Baker Co., Ltd.	99.99 %	GC[b]	none
methanol	J.T. Baker Co., Ltd.	99.99 %	GC	none
1,1-dichloroethane	J.T. Baker Co., Ltd.	99.99 %	GC	none
DMSO	J.T. Baker Co., Ltd.	99.99 %	GC	none
acetone	J.T. Baker Co., Ltd.	99.99 %	GC	none
ethyl acetate	J.T. Baker Co., Ltd.	99.99 %	GC	none

[a] High-performance liquid chromatography. [b] Gas chromatography.

The purity and content analysis of DPT was performed on a Shimadzu HPLC system (Japan), which consists of two LC-20AT pumps, a SPD-20 UV detector and a SIL-10A auto sampler. A C18 column (250 mm × 4.6 mm, 5 μm, Agela) and a UV detector at 254 nm length was adopted. Aliquots of 10 μL of the reconstituted samples were injected for HPLC analysis.

■ EXPERIMENTAL PROCEDURE

First, put an extra amount of DPT solid into a glass vial with 5 mL of acetonitrile, methanol, 1,1-dichloroethane, DMSO, acetone, mixtures of ethyl acetate and methanol, and mixtures of acetonitrile and water respectively to get the supersaturated solutions. Then, incubate the vial in temperature thermostatic reaction bath with magnetic stirring water bath at 288.15 K, 293.15 K, 298.15 K, 303.15 K, and 308.15 K, respectively. The temperature was determined using a pure solvent bottle with a thermometer inside. The temperature fluctuation of the thermostatic reaction bath was controlled below ± 0.5 K, and the temperature uncertainty is ± 0.1 K. Withdraw aliquots of 1 mL supernatant of each vial by a syringe with a 0.22 μm membrane after the dissolution equilibrium of DPT with another 12 h standing at the corresponding temperature.[14,15] Transfer the solution to a dried weighted double dish, and weigh the dish quickly to determine the mass of the solution (m_0) with the uncertainty of ± 0.1 mg. After the solution is completely dried under nitrogen, dissolve the residue in acetonitrile, and exactly dilute to 10 mL. Take 10 μL of the reconstituted samples for HPLC analysis. All of the experiments were carried out 5 times simultaneously and analyzed by HPLC.

■ RESULT AND DISCUSSION

High-Performance Liquid Chromatography (HPLC) Detection. The purity of DPT was determined by HPLC. The chromatographic conditions were optimized, and a symmetrical sharp peak was obtained; the mass fraction purity is 0.9998 when methanol/water (10:90, v/v) was used as mobile phase, and the flow rate was 1.0 mL·min^{-1} (Figure 2).

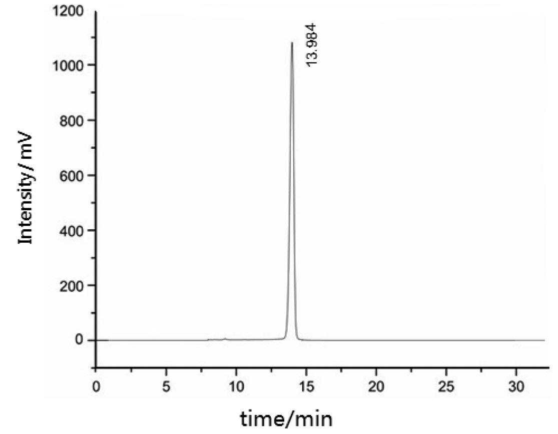

Figure 2. HPLC chromatogram of DPT.

The DPT standard solution was prepared from 0.003 mg·mL^{-1} to 3.0 mg·mL^{-1} in acetonitrile. The calibration curve of chromatogram peak area to concentration of DPT by HPLC was established (Figure 3). The limit of detection is 0.003 mg·mL^{-1}.

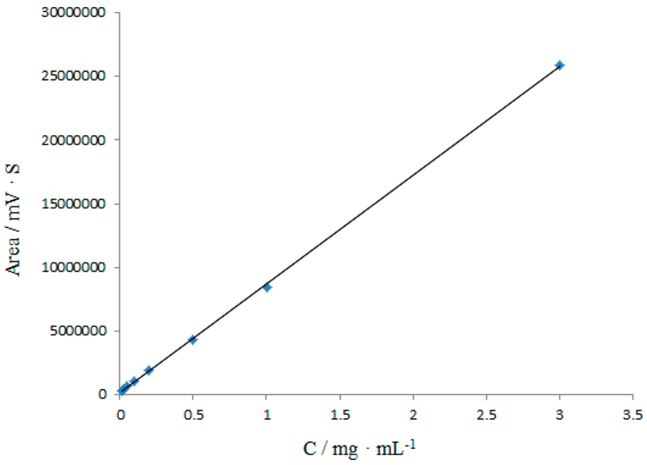

Figure 3. Linear relationship between the chromatogram peak area (Y) and the concentration (X) of DPT in acetonitrile.

The linear fitting equation is $Y = 8.3 \cdot 10^6 X + 2.5 \cdot 10^5$ over the concentration range of 0.003 mg·mL^{-1} to 3.0 mg·mL^{-1}.

Solubility. The solubility of DPT is expressed by mole fraction of the solute in the solution. While the DPT concentration in solubility experiments were estimated by the HPLC method according to the calibration curve, the mass of the solute in the sample solution was calculated by product of

Table 2. Solubility of DPT as a Function of Temperature in Different Solvents under 0.1 MPa

solvent	T/K	x	x^{calc}	100δ
acetonitrile	288.15	$1.54176 \cdot 10^{-7}$	$1.55108 \cdot 10^{-7}$	−0.604519891
	293.15	$1.78147 \cdot 10^{-7}$	$1.75950 \cdot 10^{-7}$	1.233424867
	298.15	$1.99383 \cdot 10^{-7}$	$1.98741 \cdot 10^{-7}$	0.3217413
	303.15	$2.25782 \cdot 10^{-7}$	$2.24005 \cdot 10^{-7}$	0.78705409
	308.15	$2.49821 \cdot 10^{-7}$	$2.50868 \cdot 10^{-7}$	−0.418824629
methanol	288.15	$5.48247 \cdot 10^{-9}$	$5.48825 \cdot 10^{-9}$	−0.105455565
	293.15	$5.79752 \cdot 10^{-9}$	$5.89257 \cdot 10^{-9}$	−1.639492793
	298.15	$6.36131 \cdot 10^{-9}$	$6.31146 \cdot 10^{-9}$	0.783648856
	303.15	$6.66727 \cdot 10^{-9}$	$6.75198 \cdot 10^{-9}$	−1.270460111
	308.15	$7.23540 \cdot 10^{-9}$	$7.19718 \cdot 10^{-9}$	0.528200092
acetone	288.15	$7.06336 \cdot 10^{-8}$	$7.11535 \cdot 10^{-8}$	−0.735995228
	293.15	$7.98181 \cdot 10^{-8}$	$7.97073 \cdot 10^{-8}$	0.138898981
	298.15	$8.90498 \cdot 10^{-8}$	$8.89464 \cdot 10^{-8}$	0.116072584
	303.15	$1.01512 \cdot 10^{-7}$	$9.90658 \cdot 10^{-8}$	2.409672406
	308.15	$1.07572 \cdot 10^{-7}$	$1.09701 \cdot 10^{-7}$	−1.979894997
DMSO	288.15	$9.27470 \cdot 10^{-7}$	$9.28945 \cdot 10^{-7}$	−0.159026313
	293.15	$1.04711 \cdot 10^{-6}$	$1.05013 \cdot 10^{-6}$	−0.288116712
	298.15	$1.17879 \cdot 10^{-6}$	$1.18220 \cdot 10^{-6}$	−0.289613711
	303.15	$1.35958 \cdot 10^{-6}$	$1.32812 \cdot 10^{-6}$	2.314143304
	308.15	$1.46033 \cdot 10^{-6}$	$1.48277 \cdot 10^{-6}$	−1.536332083
1,1-dichloroethane	288.15	$7.04587 \cdot 10^{-9}$	$7.09331 \cdot 10^{-9}$	−18.978783344
	293.15	$8.45871 \cdot 10^{-9}$	$8.47768 \cdot 10^{-9}$	19.924440234
	298.15	$9.87569 \cdot 10^{-9}$	$9.93588 \cdot 10^{-9}$	−0.609550243
	303.15	$1.22858 \cdot 10^{-8}$	$1.16125 \cdot 10^{-8}$	5.480214213
	308.15	$1.32061 \cdot 10^{-8}$	$1.34592 \cdot 10^{-8}$	−10.26622687
acetonitrile/water (9:1, v/v)	288.15	$6.63718 \cdot 10^{-8}$	$6.52624 \cdot 10^{-8}$	1.675063348
	293.15	$9.33191 \cdot 10^{-8}$	$9.37267 \cdot 10^{-8}$	−0.436082937
	298.15	$1.12919 \cdot 10^{-7}$	$1.12926 \cdot 10^{-7}$	−0.006509495
	303.15	$1.2855 \cdot 10^{-7}$	$1.28126 \cdot 10^{-7}$	0.329681559
	308.15	$1.41183 \cdot 10^{-7}$	$1.42326 \cdot 10^{-7}$	−0.809611225
acetonitrile/water (7:3, v/v)	288.15	$1.72144 \cdot 10^{-8}$	$1.70292 \cdot 10^{-8}$	0.954765745
	293.15	$2.14717 \cdot 10^{-8}$	$2.15498 \cdot 10^{-8}$	−0.131937878
	298.15	$2.55069 \cdot 10^{-8}$	$2.57764 \cdot 10^{-8}$	−0.77679513
	303.15	$2.92089 \cdot 10^{-8}$	$2.92205 \cdot 10^{-8}$	−0.039796138
	308.15	$3.18355 \cdot 10^{-8}$	$3.15705 \cdot 10^{-8}$	0.832259367
ethyl acetate	288.15	$1.02331 \cdot 10^{-7}$	$1.02634 \cdot 10^{-7}$	−0.263202867
	293.15	$1.16018 \cdot 10^{-7}$	$1.17265 \cdot 10^{-7}$	−1.070414909
	298.15	$1.31245 \cdot 10^{-7}$	$1.31926 \cdot 10^{-7}$	−0.519231925
	303.15	$1.54888 \cdot 10^{-7}$	$1.54268 \cdot 10^{-7}$	0.405665452
	308.15	$1.84357 \cdot 10^{-7}$	$1.84233 \cdot 10^{-7}$	0.067695099
ethyl acetate/methanol(9:1, v/v)	288.15	$1.02511 \cdot 10^{-7}$	$1.05265 \cdot 10^{-7}$	−2.681647775
	293.15	$1.14334 \cdot 10^{-7}$	$1.17269 \cdot 10^{-7}$	−2.558796733
	298.15	$1.29761 \cdot 10^{-7}$	$1.29261 \cdot 10^{-7}$	0.385876203
	303.15	$1.5111 \cdot 10^{-7}$	$1.51268 \cdot 10^{-7}$	−0.099337088
	308.15	$1.83476 \cdot 10^{-7}$	$1.82326 \cdot 10^{-7}$	0.627002014
ethyl acetate/methanol(7:3, v/v)	288.15	$9.94584 \cdot 10^{-8}$	$9.92526 \cdot 10^{-8}$	0.206966209
	293.15	$1.10495 \cdot 10^{-7}$	$1.10726 \cdot 10^{-7}$	−0.209063018
	298.15	$1.20859 \cdot 10^{-7}$	$1.20926 \cdot 10^{-7}$	−0.055816445
	303.15	$1.43807 \cdot 10^{-7}$	$1.43126 \cdot 10^{-7}$	0.473744264
	308.15	$1.72432 \cdot 10^{-7}$	$1.73326 \cdot 10^{-7}$	−0.51850375
ethyl acetate/methanol(5:5, v/v)	288.15	$2.85673 \cdot 10^{-8}$	$2.84408 \cdot 10^{-8}$	0.442843353
	293.15	$4.62264 \cdot 10^{-8}$	$4.65752 \cdot 10^{-8}$	−0.754109069
	298.15	$6.71797 \cdot 10^{-8}$	$6.90759 \cdot 10^{-8}$	−2.821182748
	303.15	$9.4769 \cdot 10^{-8}$	$9.51575 \cdot 10^{-8}$	−0.40996652
	308.15	$1.17712 \cdot 10^{-7}$	$1.17408 \cdot 10^{-7}$	0.258795033

[a] Standard uncertainties u are $u(T) = 0.1$ K, $u_r(p) = 0.05$, and $u_r(x) = 0.04$.

the concentration (c) and the volume of diluted (V). Thus, the mole fraction of the solute can be easily calculated according to the following equation.

$$x = \frac{m_1/M_1}{m_1/M_1 + (m_0 - m_1)/M_2} \quad (1)$$

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where x is the mole fraction; m_0 is the mass of the solution; m_1 is the mass of the solute (DPT) as the product of the concentration (c) and the volume of diluted (V); M_1 is the molecular weight of solute; M_2 is the molecular weight of solvent.

According to the thermodynamic principle of solid–liquid equilibrium, there is a relationship between the solubility (x) and the temperature (T).[16]

$$\ln \gamma x = -\frac{\Delta H_{tp}}{R}\left(\frac{1}{T_{tp}} - \frac{1}{T}\right) - \frac{\Delta C_p}{R}\left(\ln\frac{T_{tp}}{T} - \frac{T_{tp}}{T} + 1\right) - \frac{\Delta V}{RT}(P - P_w) \tag{2}$$

Here, γ is activity factor of the solute; x is the mole fraction; T is the absolute temperature, K; T_{tp} is the triple point temperature of the solute, K; ΔH_{tp} is the enthalpy of fusion at the triple point temperature, J·mol^{-1}; R is molar gas constant, J·(mol·K)$^{-1}$; ΔC_p is the heat capacity difference; ΔV is the volume difference; P is the vapor pressure at the point temperature, Pa; P_w is the vapor pressure at the time of solid–liquid equilibrium, Pa.

Considering the heat capacity difference and volume difference is too low to count, the equation can be simplified as follows:

$$\ln \gamma x = -\frac{\Delta H_m}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \tag{3}$$

Here T_m is the melting point temperature of the solute, K; ΔH_m is the enthalpy of fusion at this temperature, J/mol;

The activity factor can also be expressed as following,

$$\ln \gamma = a + \frac{b}{T} \tag{4}$$

While input eq 4 to eq 3,

$$\ln x = \left(\frac{\Delta H_m}{RT_m} - a\right) - \left(\frac{\Delta H_m}{R} - b\right)\frac{1}{T} \tag{5}$$

Considering $((\Delta H_m/RT_m) - a)$ and $((\Delta H_m/R) - b)$ are all constants, the mole fraction can finally be expressed as following,

$$\ln x = A + \frac{B}{T(\mathrm{K})} \tag{6}$$

Here A and B are parameters of the exponential expression.

So, the solubility can also be calculated with eq 6, while the linearity between ln x and T was established.

The relative deviation (δ) is defined in eq 7.

$$\delta = \frac{x - x^{\mathrm{calc}}}{x} \tag{7}$$

Here, x^{calc} is the calculated solubility from eq 6.

The solubilities of DPT in acetonitrile, methanol, 1,1-dichloroethane, DMSO, acetone, and mixed solvents in the range of 288.15 K to 308.15 K are listed in Table 2. The linear relationship between mole fraction and inverse absolute temperature was obtained (Figure 4).

The solubilities of DPT in all solvents increased at an exponential rate with raising the temperature in all of the experiments. Then the linear relationship between ln x and inverse absolute temperature was also illustrated in Figure 5.

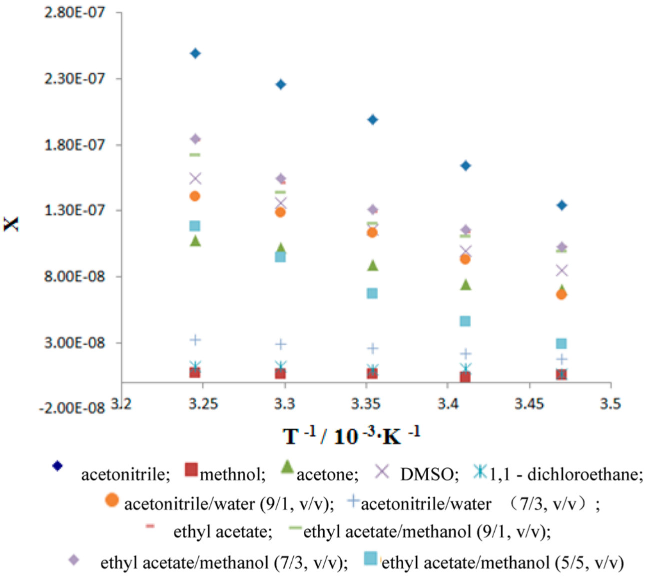

Figure 4. Temperature dependence of mole fraction of DPT in several solvents: blue ◆, acetonitrile; red ■, methanol; green ▲, acetone; purple ×, DMSO; blue $*$, 1,1-dichloroethane; orange ●, acetonitrile/water (9:1, v/v); blue +, acetonitrile/water (7:3, v/v); orange –, ethyl acetate; green –, ethyl acetate/methanol (9:1, v/v); purple ◆, ethyl acetate/methanol (7:3, v/v); blue ■, ethyl acetate/methanol (5:5, v/v).

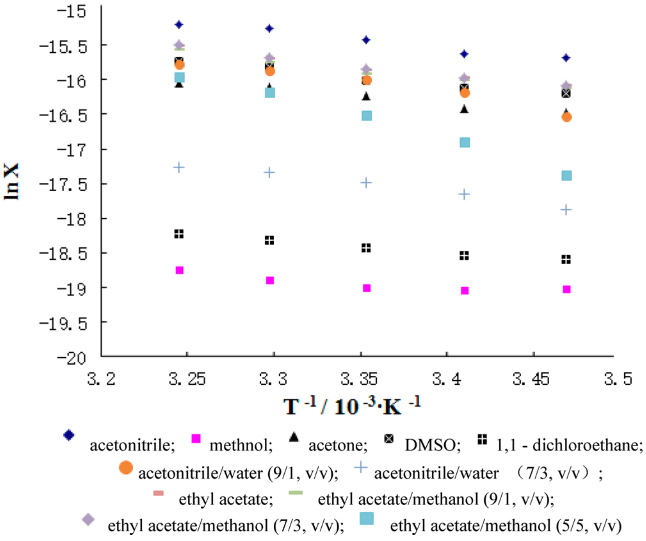

Figure 5. Temperature dependence of ln x of DPT in several solvents: blue ◆, acetonitrile; pink ■, methanol; black ▲, acetone; ■ with ×, DMSO; ■ with +, 1,1-dichloroethane; orange ●, acetonitrile/water (9:1, v/v); gray +, acetonitrile/water (7:3, v/v); orange –, ethyl acetate; green –, ethyl acetate/methanol (9:1, v/v); purple ◆, ethyl acetate/methanol (7:3, v/v); blue ■, ethyl acetate/methanol (5:5, v/v).

Therefore, the regression parameters of A and B involved in eq 6 can be obtained, and the exact data are listed in Table 3. Moreover, the calculated mole fractions and the relative deviations are recorded in Table 2.

Enthalpy of Solution. To insight into the DPT dissolve process in each solvents, we calculated the enthalpy of solution ($\Delta_{sol}H$) by van't Hoff equation.

Table 3. Parameters of eqs 6 and 8 for DPT in Different Solvents

solvent	A	B	R^2	$\Delta_{sol}H/(\mathrm{KJ \cdot mol^{-1}})$
acetonitrile	−8.2636	−2136.9	1	−17.7662
methanol	−14.8400	−1204.8	1	−10.0167
acetone	−9.7814	−1924.1	1	−81.3259
DMSO	−6.6770	−2078.3	1	−17.2790
1,1-dichloroethane	−8.9205	−2835.0	0.9997	−23.1503
acetonitrile/water (9:1, v/v)	−4.8601	−3340.9	0.9902	−28.5326
acetonitrile/water (7:3, v/v)	−8.3195	−2743.7	0.9977	−22.8723
ethyl acetate	−7.2237	−2560.4	0.9902	−20.8435
ethyl acetate/methanol(9:1, v/v)	−7.7805	−2396.1	0.9947	−19.9432
ethyl acetate/methanol(7:3, v/v)	−7.7310	−2428.1	0.9988	−20.4324
ethyl acetate/methanol(5:5, v/v)	−4.6425	−6322.2	0.9928	−80.9874

$$\ln x = \frac{-\Delta_{\mathrm{sol}}H}{R(T/\mathrm{K})} + \frac{-\Delta_{\mathrm{sol}}S}{R} \qquad (8)$$

Here, $\Delta_{\mathrm{sol}}H$ is the enthalpy of solution; $\Delta_{\mathrm{sol}}S$ is the entropy of solution, R is the gas constant; T is the absolute temperature. All of the data are shown in Table 3, and R^2 is the correlation coefficient for eq 8.

■ CONCLUSIONS

The solubility of DPT in several solvents under the temperature ranging from 288.15 K to 308.15 K was measured by the HPLC method. Besides the commonly used solvents, it was also studied in acetonitrile−water mixture and ethyl acetate-methanol mixture in different ratio. The solubility of DPT increased as exponential rate as temperature increased in all of the tested solvents. Moreover, the enthalpy of solution was calculated by van't Hoff equation.

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Notes

The authors declare no competing financial interest.

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