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# Synthesis and Solubility of 5,5-Dimethyl-2-(phenyl(phenylamino)methyl)-1,3,2-dioxaphosphinane 2-oxide in Selected Solvents between 278.15 K and 347.15 K

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**ABSTRACT:** A flame retardant with enhanced phosphorus–nitrogen content, 5,5-dimethyl-2-(phenyl(phenylamino)methyl)-1,3,2-dioxaphosphinane 2-oxide (DPPO), was synthesized by the reaction of 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (DDPO) with *N*-benzylideneaniline. The structure of DPPO was characterized by nuclear magnetic resonance (<sup>1</sup>H NMR and <sup>31</sup>P NMR) and Fourier transform infrared (FT-IR) spectroscopy. The thermal stability of DPPO was characterized by thermogravimetric analysis (TGA). The solubilities of DPPO were measured in different solvents including ethyl acetate, methanol, chloroform, acetonitrile, acetone, 1,2-dichloroethane, 1,4-dioxane, dichloromethane, tetrachloromethane, benzene, tetrahydrofuran, and isopropanol at temperature ranging from 278.15 to 347.15 K by the gravimetrical method. The mole fraction solubilities of DPPO in the above-mentioned organic solvents were correlated as the Apelblat equation, and the calculated values with equations shows good consistency



with the experimental values. The root-mean-square deviation was less than 0.1%, and the average relative error was less than 0.04 in all of the experiments.

# INTRODUCTION

For environment concerns, halogen-free flame retardation has aroused great attention in recent years, because halogen-



**Figure 1.** Structure of 5,5-dimethyl-2-(phenyl(phenylamino)methyl)-1,3,2-dioxaphosphinane-2-oxide (DPPO).

containing flame retardant materials produce a lot of smoke and toxic gases during burning.<sup>1</sup> An organic phosphorus—nitrogen flame retardant is considered as a promising halogen-free flame retardant additive due to its advantages of low smoke, low toxicity, low corrosion, and no molten dropping during a fire. The efficiency of phosphorus-based flame retardant depends upon not only the amount of the phosphorus element existing in the compound but also the ability to form the charred residues. More phosphorus volatiles playing the roles of active species in the gas phase are generated during the decomposition of combusting polymeric material.<sup>2</sup> On the other hand, the species enabling the formation of stable residual char is more desirable for the polymer where the main mechanism is based on the gas phase mode of action. The compounds

containing nitrogen and cyclic phosphorus are particularly thermally stable and useful as flame retardants for polymeric materials.<sup>2,3</sup> Owing to the synergism between nitrogen and cyclic phosphorus, it shows an excellent charring effect associated with polymeric materials.

The purpose of this study is to synthesize a nitrogen and cyclic phosphorus-containing compound intumescent flame retardant. The single additive leads to good miscibility with the polymer matrix and good interface stability. An efficient nitrogen and cyclic phosphorus containing compound, 5,5dimethyl-2-(phenyl(phenylamino)methyl)-1,3,2-dioxaphosphinane 2-oxide (DPPO; chemical formula C<sub>18</sub>H<sub>22</sub>NO<sub>3</sub>P; CAS Reg No. 77806-88-3; molecular weight 331.35; chemical structure shown in Figure 1), has been synthesized. As we know that solution crystallization is an important unit operation in separation and purification for a compound in an industrial process,<sup>3,4</sup> the solubilities of organic compounds in different solvents play a role in crystallization isolation procedures. To identify the proper solvent and temperature range for the crystallization process, many contributions of the solvent and solute still need to be investigated experimentally. Among all of the factors, both temperature and solvent are considered as the most two important ones. Complete and accurate solubility

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data can provide important foundation for solvent selection in the synthesis and purification of compounds. Therefore, inexpensive and effective solvents for the compound synthesis and recrystallization have been found and then can be a guide for the compound for industrial production. A higher purity of DPPO is required in the application of the polyurethane flame retardant. To further improve and optimize the process of recrystallization and purification, it is imperative for us to know the solubility of DPPO in a variety of organic solvents at different temperatures. However, a systematic study of the solubility of this nitrogen and cyclic phosphorus containing flame retardant in different solvent systems has not been reported.

In this work, the solubilities of DPPO in different organic solvents, including ethyl acetate, methanol, chloroform, acetonitrile, acetone, 1,2-dichloroethane, 1,4-dioxane, dichloromethane, tetrachloromethane, benzene, tetrahydrofuran, and isopropanol, were measured at a designated temperature range from 278.15 to 347.15 K at atmospheric pressure by the gravimetrical method. The mole fraction solubilities (x) in the mentioned solvents were correlated as the Apelblat equation, and the calculated values with this equation showed good consistency with experimental values. This aim of this study is to provide basic information for the separation, purification, and application of DPPO.

# EXPERIMENTAL SECTION

**Chemicals Used.** All of the solvents, ethyl acetate, methanol, chloroform, acetonitrile, acetone, 1,2-dichloroethane,

Table 1. Chemical Compounds Used in the Study

chemicals	source	purity (mass fraction)	analysis method
acetone	Tianjinbeilian <sup>b</sup>	≥0.995	$GC^d$
acetonitrile	Tianjinbeilian	≥0.998	GC <sup>d</sup>
chloroform	Tianjinbeilian	≥0.997	$GC^d$
1,2-dichloroethane	Tianjinbeilian	≥0.990	$GC^d$
ethyl acetate	Tianjinbeilian	≥0.995	$GC^d$
methanol	Tianjinbeilian	≥0.995	GC <sup>d</sup>
1,4-dioxane	Tianjinbeilian	≥0.995	GC <sup>d</sup>
dichloromethane	Tianjinbeilian	≥0.995	$GC^d$
tetrachloromethane	Tianjinbeilian	≥0.995	$GC^d$
benzene	Tianjinbeilian	≥0.995	$GC^d$
isopropanol	Tianjinbeilian	≥0.997	GC <sup>d</sup>
tetrahydrofuran	Tianjinbeilian	≥0.995	GC <sup>d</sup>
succinic acid	Tianjinbeilian	≥0.995	GC <sup>d</sup>
distilled water	prepared in the lab		
DPPO <sup>a</sup>	synthesized in the lab	≥0.998	HPLC <sup>c</sup>

<sup>*a*</sup>DPPO = 5,5-dimethyl-2-(phenyl(phenylamino)methyl)-1,3,2-dioxaphosphinane 2-oxide, CAS Reg No. 77806-88-3, light-yellow solid state. <sup>*b*</sup>Tianjinbeilian Chemical Reagent Co,. Ltd. <sup>*c*</sup>High-performance liquid chromatography. <sup>*d*</sup>Gas chromatography.

1,4-dioxane, dichloromethane, tetrachloromethane, benzene, tetrahydrofuran, and isopropanol, were obtained from Tianjinbeilian Chemical Reagent Co., Ltd. All of the chemicals were used without further purification. They were all analytical-grade research reagents, and their purities were higher than 0.99. The mass fraction purities for the organic solvents used are listed in Table 1.

**Apparatus.** The apparatus for the solubility measurement is identical to that described in detailed in the literature. Figure 2



**Figure 2.** schematic diagram of solubility apparatus: 1, thermometer; 2, sample export; 3, rubber plug; 4, equilibrium cell; 5, magneton; 6, magnetic stirrer apparatus; 7, water cycling bath; 8, rubber pipe.

Scheme 1. Synthesis Route of DDPO



Scheme 2. Synthesis Route of DPPO



shows the schematic diagram of the experimental setup. A jacketed equilibrium cell was used for the solubility measurement with a working volume of 120 mL and a magnetic stirrer. A circulating water bath was applied with a thermostat (type 50 L, made from Changzhouzhibirui Laboratory Instrument Work Co., Ltd.), which is capable of maintaining the temperature within  $\pm 0.05$  K. The melting point was determined by a X4 micro melting point apparatus (Beijing Fukai Instrument Co., Ltd.). An analytical balance (BAS124S) with an uncertainty of  $\pm 0.1$  mg was used during the mass measurements. Thermogravimetric analysis (TGA) was carried with a Netzasch STA 409 PC thermogravimetric analyzer at a heating rate of 10 K/min under nitrogen from 307.13 to 955.45 K. IR spectra [Fourier transform infrared (FT-IR)] was recorded on a thermo 6700 FT-IR using KBr pellets. <sup>1</sup>H NMR and <sup>31</sup>P NMR spectra were obtained with a Bruker AVANCE III 500. All samples were run in triplicate, and the average value with the standard deviation is reported.

**Synthesis of 5,5-Dimethyl-1,3,2-dioxaphosphinane 2-oxide (DDPO).** The DDPO was prepared by the reaction as follows: In a 100 mL three-necked around-bottomed flask equipped with a magnetic stirrer, reflux condenser, thermometer, and oil bath. First, 3.12 g (0.03 mol) of neopentyl glycol and 9 mL of 1,2-dichloroethane were added and stirred for 30 min at room temperature. Second, 4.13 g (0.03 mol) of phosphoryltrichloride was dropwise added to the reaction mixture at 278.15 K. The reaction mixture was reacted for 3 h



Figure 3. <sup>1</sup>H NMR spectrum of DPPO.



at 318.15 K until HCl evolution has subsided. At last, 1.38 g (0.03 mol) of ethanol was dropwise added to three-necked round-bottomed flask at 278.15 K. The reaction mixture was reacted for 4 h at reflux temperature. Then, the reaction mixture was cooled to room temperature. After that was obtained by removing solvent under reduced pressure, then the compound as white solid was extracted from the residue with petroleum ether and diethyl ether (2:1), yield: 64%, mp 329.15-330.15 K. The detailed synthesis route of DDPO was shown in Scheme 1.

Synthesis and Characterization of 5,5-Dimethyl-2-(phenyl(phenylamino)methyl)-1,3,2-dioxaphosphinane 2-Oxide (DPPO). The DDOP was synthesized by the P– (O)–H group reaction with the imidogen group of Schiff base

Table 2. Experimental and Literature Mole Fraction Solubility x of Succinic Acid in Water at Varied Temperatures T and Pressure  $P = 0.1 \text{ MPa}^{a}$ 

	T/K	1000 <i>x</i>		T/K	1000 <i>x</i>
experiment	283.65	6.63	literature	278.15	5.39
	289.00	8.37		283.15	6.80
	293.75	10.40		288.15	8.59
	298.25	12.65		293.15	10.92
	303.15	15.57		298.15	13.37
	308.06	18.75		303.15	15.91
	312.85	22.85		308.15	19.28
	317.77	27.73		313.15	23.84
	322.55	33.82		318.15	29.61
	327.45	40.63		323.15	3.55
	333.15	48.10		328.15	42.37
	337.50	59.00		333.15	48.62
	342.25	68.87		338.15	60.23
<sup>a</sup> Standard unce	rtainties	u are $u(T) =$	= 0.01 K, 1	$\iota(P) = 0.05$	MPa, and

"Standard uncertainties u are u(T) = 0.01 K, u(P) = 0.05 MPa, and  $u_r(x) = 0.02$ .

forming a P–C bond via nucleophilic addition. The yield was 80% with a melting point of 473.15–475.15 K. DPPO was prepared by the reaction in a 100 mL three-necked round-bottomed flask equipped with a magnetic stirrer, reflux condenser, thermometer, and oil batch, and proceeded as follows. First, 3.1 g (0.02 mol) of DDPO and 15 mL of 1,4-dioxane were placed in the three-neck flask. Second, 3.62 g (0.02 mol) of Schiff base (2-(*N*-phenyliminomethyl)phenol) and 30 mL of 1,4-dioxane were dropwise added to the reaction mixture and allowed to react at 70 °C for 2 h. Subsequently, the mixture was cooled to room temperature. The crude product

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was then filtrated from the mixture and washed with acetone. The residue was recrystallized by ethanol, and finally the light yellow powder was obtained. The melting point of DPPO is 447.15–449.15 K, yield: 71%. The detailed synthesis route of DPPO was shown in Scheme 2. On the basis of the above analysis, the purity of DPPO used in this work was higher than 0.99. IR (KBr), 3415 cm<sup>-1</sup> (N–H), 3087, 3062 cm<sup>-1</sup> (Ar–H), 2965–2878 cm<sup>-1</sup> (C–H), 1509–1602 cm<sup>-1</sup> (C=C in ph), 1254 cm<sup>-1</sup> (P=O), 1183 cm<sup>-1</sup> (C–N), 1056 cm<sup>-1</sup> (P–O–C), 754, 735, 697 cm<sup>-1</sup> (ph). The <sup>1</sup>H NMR spectra of DPPO are shown in Figure 3. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) ppm:  $\delta$  = 0.87, 1.13 ppm (6H, 2CH<sub>3</sub>),  $\delta$  = 3.83–4.42 ppm (4H, 2CH<sub>2</sub>),  $\delta$  = 5.38–5.45 ppm (10H, CH),  $\delta$  = 6.35–6.38 ppm (1H, NH),  $\delta$  = 6.51–7.58 ppm (10H, 2Ph) <sup>31</sup>PNMR (DMSO-*d*<sub>6</sub>) ppm:  $\delta$  = 15.45 ppm.

**Thermogravimetric Analysis.** To determine thermal properties of DPPO, the thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) of DPPO have been conducted under nitrogen from 298.15 to 853.15 K. The thermogravimetric curve of DPPO is shown in Figure 4. The initial thermal decomposition temperature of DPPO was around 464.15 K. The maximum thermal degradation rate of DPPO was 2.6%/min at 526.15 K. The weight loss was 90% at the temperature ranging from 465.15 to 528.15 K, and the char residue yield at 536.75 K was 3.60%.

**Solubility Measurement.** The static equilibrium method was used to determine the solubility of DPPO in different organic solvent in including ethyl acetate, methanol, chloro-form, acetonitrile, acetone, 1,2-dichloroethane, 1,4-dioxane, dichloromethane, tetrachloromethane, benzene, tetrahydrofuran, and isopropanol in the present work. The static equilibrium method was validated by experimental solubilities of succinic acid in water compared with the solubilities in the literature.<sup>5</sup> The data of experiment and literature were presented in Table 2. It indicated that our experimental method is correct. The apparatus included a 120 mL jacketed glass vessel with a magnetic stirrer as described in the literature. To prevent the evaporation of solvent, the equilibrium cell was sealed by a rubber stopper. The equilibrium cell was keep at a constant temperature by circulating water bath with a thermostat (type DC0520, made from Changzhou Laboratory Instrument Works Co., Ltd.) with the uncertainty of  $\pm 0.05$  K. For each measurement, excessive DPPO and moderate solvent were added to the equilibrium cell which was sealed by a rubber stopper. The equilibrium cell was stirred for 2-3 h to ensure equilibrium at the constant temperature. Then the stirring was stopped to allow any solid to settle down from the solution, and the solution was kept still for 4-5 h. A preheated injector withdrew 2 mL of the clear upper portion of the solution which was transferred quickly to a previously weighed measuring vial  $(m_0)$ . The vial was tightly and promptly closed and weighed  $(m_1)$  to obtain to mass of the sample  $(m_1 - m_0)$ . After that, the solvent in the vial was sufficiently evaporated by a vacuum drying oven at about 333 K. The mass of the vial  $(m_2)$  was then obtained again. From the thermogravimetric analysis, the decomposition temperature of DPPO was found to be around 464.15 K. Consequently, we can make certain that the DPPO solute cannot be volatilized at a temperature used in the vacuum evaporation of the solvent. Different dissolution times were tested to determine a suitable equilibrium time. Once the solubility was determined at one temperature, the residue including excess solid was heated to another temperature, and the determination procedure was carried out repeatedly. It was discovered that 2 h was enough for DPPO to reach equilibrium time in all solvents. The experimental mole fraction solubility in different organic pure solvents is calculated by eq 1:<sup>3</sup>

$$x^{\text{exptl}} = \frac{\frac{\frac{m_2 - m_0}{M_1}}{\frac{m_2 - m_0}{M_1} + \frac{m_1 - m_2}{M_2}}$$
(1)

where  $M_1$  is the molar mass of DPPO and  $M_2$  is the molar mass of the solvent. During our experiments, three parallel

measurements were carried out at the same composition of solvent for each temperature, and an average value was calculated. Nuclear magnetic resonance [<sup>1</sup>H NMR (DMSO- $d_6$ )] was employed to analyze the solid samples before and after experiment. As shown in the Figure 5, the resulting patterns showed that there were no solvent peaks in the solid residues. By comparison of these spectra, there was no difference between pure compound and its residue after solvent evaporation in the various solvents. It could be concluded that solid solvates were not formed in the solvents tested.

# RESULTS AND DISCUSSION

The mole fraction solubilities (x) of DPPO were measured in ethyl acetate, methanol, chloroform, acetonitrile, acetone, 1,2-



**Figure 6.** Mole fraction solubility data for DPPO in organic solvents: ■, chloroform; ●, 1,2-dichloroethane; ▼, tetrachloromethane; ▲, dichloromethane. Solid lines, values calculated from the modified Apelblat equation.



Figure 7. Mole fraction solubility data for DPPO in organic solvents:
▲, acetonitrile; ▼, acetone; ■, methanol; ●, isopropanol. Solid lines, values calculated from the modified Apelblat equation.

dichloroethane, 1,4-dioxane, dichloromethane, tetrachloromethane, benzene, tetrahydrofuran, and isopropanol at temperatures ranging from 278.15 to 347.15 K by the gravimetrical



Figure 8. Mole fraction solubility data for DPPO in organic solvents: ▲, tetrahydrofuran; ■, 1,4-dioxane; ▼, ethyl acetate; ●, benzene. Solid lines, values calculated from the modified Apelblat equation.

method which had been clarified in previous work.<sup>6,7</sup> The mole fraction solubility values of DPPO are presented graphically in Figures 6 to 8. All of the data are presented in Table 3.

It can be seen from Figures 6, 7, and 8 that, within the experimental temperature range, the solubility of DPPO in 12 organic solvents increased with rising temperature. At same temperature, the solubilities of DPPO in chloroform, 1,2dichloroethane, and dichloromethane were higher than those in the other selected organic solvents. The solubility of DPPO in chloroform is the largest than that in the other solvents at the same temperature. If the temperature decreases from 327.75 to 283.15 K, the maximum solubility of DPPO decreases from  $6.461 \times 10^{-3}$  to  $3.817 \times 10^{-3}$ . Among the 12 solvents, the solubility of DPPO in chloroform is the most suitable solvent to improve the purification process of DPPO. But the solubility of DPPO in tetrachloromethane was lower than those in the other selected organic solvents. It was deduced that the polarity in solution might play a dominant role. As shown in Figure 7, the solubilies of DPPO in isopropanol and methanol were lower than those in the acetone, 1,4-dioxane, tetrahydrofuran, acetonitrile, dichloromethane, 1,2-dichloroethane, and chloroform. Figure 8 shows the solubilities of DPPO in tetrahydrofuran, 1,4-dioxane, ethyl acetate, and benzene. The solubility of DPPO in tetrahydrofuran is similar to its in 1,4-dioxane. The solubility of DPPO in ethyl acetate is similar to its in benzene. It further can be seen that solubilities of DPPO in tetrahydrofuran and 1,4-dioxane were higher than those in ethyl acetate and benzene. The order of solubility of DPPO is as follows: chloroform > 1,2-dichloroethane > dichloromethane > acetonitrile > (1,4-dioxane, tetrahydrofuran) > acetone > methanol > (ethyl acetate, benzene) > isopropanol > tetrachloromethane.

The temperature dependence of the solubility of DPPO in selected solvents is represented by the modified Apelblat equation  $^{5,8-12}$  according to eq 2:

$$\ln x = A + \frac{B}{T/K} + C \ln(T/K)$$
(2)

with

Ε

# Table 3. Experimental Mole Fraction Solubility ( $x^{exp}$ ) of DPPO in Different Solvents at Varied Temperatures *T* and Pressure *P* = 0.1 MPa<sup>*a*</sup>

solvent	$T^{a}/K$	$x \cdot 1000^{b}$	$\varepsilon / \%^{c}$	solvent	T/K	$x \cdot 1000^{b}$	$\varepsilon / \%^{c}$
ethyl acetate	293.65	2.32	2.12	acetonitrile	278.00	5.57	2.01
	298.25	2.78	-5.08		285.65	6.80	-1.37
	303.15	3.85	3.24		288.75	7.46	-1.74
	308.05	4.60	-0.58		293.75	8.87	0.12
	312.95	5.61	-0.23		298.25	10.07	-1.26
	317.95	6.71	0.10		303.25	11.87	-0.49
	322.95	7.81	-0.16		308.15	14.23	2.21
	327.95	9.13	2.04		312.75	16.13	0.22
	332.75	9.70	-2.99		317.65	19.15	1.81
	337.65	11.12	1.09		322.45	21.82	-0.38
chloroform	278.75	35.22	2.12		327.75	25.76	-0.63
	283.65	38.17	-5.08		335.35	32.83	-0.61
	288.85	40.34	3.24	1,2-dichloroethane	278.65	10.21	1.08
	293.95	41.96	-0.39		283.65	11.88	-1.59
	298.35	44.42	0.34		288.65	14.26	-0.48
	303.25	47.15	0.63		293.25	16.94	1.55
	307.75	49.16	-0.52		298.15	19.11	-2.02
	313.15	52.67	-0.15		303.15	22.92	0.82
	317.95	54.84	-2.04		308.25	26.50	0.28
	322.75	59.10	-0.54		313.15	31.01	2.00
1.4 diarrama	327.95	64.61	1.70		318.15	34.98	0.28
1,4-dioxane	285.05	6.09	0.52		323.15	39.47	-0.92
	200.05	7.30	-2.18		320.13	43.09	-5.07
	295.05	7.37 8 97	-3.18	mathanal	279.15	1.51	-1.06
	298.13	10.26	0.98	methanoi	278.13	2.00	-1.00
	308.15	12.06	1.51		285.05	2.00	-2.00
	313.15	13.86	-0.41		203.15	3.12	2.66
	318.15	16.15	-1.27		298.15	3.67	0.04
	323.15	18.98	-1.46		303.15	4 50	-0.17
	328.15	22.95	0.94		307.95	5.41	-0.71
acetone	278.15	2.44	3.30		313.15	6.62	-0.81
	283.75	3.14	-5.61		318.15	7.96	-1.18
	288.15	4.32	1.30		323.15	9.84	1.58
	293.75	5.78	0.37	dichloromethane	278.65	7.71	-1.21
	298.65	7.28	-1.26		283.25	9.94	2.82
	302.75	8.98	0.14		288.65	12.05	-2.29
	307.85	11.20	-0.76		293.25	15.19	0.77
	311.75	13.75	3.05		298.85	18.90	-1.16
	317.15	17.13	3.27		302.95	23.15	2.16
	321.25	18.59	-4.18		308.35	27.37	-2.81
tetrachloromethane	278.15	0.15	1.41		310.95	31.66	1.55
	283.15	0.19	-5.00	benzene	278.65	1.10	2.75
	288.35	0.26	-0.38		283.65	1.31	-2.41
	293.65	0.34	1.97		288.15	1.62	-0.82
	298.15	0.44	5.29		293.25	2.01	-1.03
	302.17	0.51	-0.12		298.25	2.45	-1.72
	307.95	0.66	-1.16		303.15	3.01	-0.58
	312.55	0.85	2.03		307.95	3.81	3.86
	317.55	1.03	-0.91		313.15	4.64	3.90
	321.55	1.21	-2.28		318.05	5.19	-3.08
	326.65	1.43	-7.98		322.65	6.34	0.30
	332.15	2.03	3.77		327.15	7.11	-4.35
	337.15	2.46	2.56		332.65	9.30	3.46
isopropanol	278.15	0.40	1.28		337.55	10.73	1.30
	283.15	0.50	-0.58		343.15	12.29	-3.74
	288.35	0.66	0.69		347.5	14.91	1.61
	293.65	0.80	-5.53	tetrahydrofuran	278.65	5.83	2.39
	298.15	1.06	0.86		283.65	6.48	-2.57
	302.17	1.28	0.85		288.15	7.64	0.42

# Table 3. continued

solvent	$T^{a}/K$	$x \cdot 1000^{b}$	$\varepsilon / \%^{c}$	solvent	T/K	$x \cdot 1000^{b}$	$\varepsilon / \%^{c}$
	307.95	1.77	5.41		293.25	8.58	-2.80
	312.55	2.03	-2.04		298.25	10.22	0.59
	317.55	2.54	-2.07		303.15	11.73	1.03
	321.55	3.18	2.39		307.95	13.28	0.77
	326.65	3.89	-0.09		313.15	15.25	1.31
	332.15	4.85	-2.25		318.05	16.92	-0.46
	337.55	6.26	0.18		322.65	18.72	-1.46
	343.15	7.91	-0.26		327.15	21.49	1.78
	347.5	9.58	0.75		332.65	23.66	-1.14
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<sup>*a*</sup>Standard uncertainties *u* are u(T) = 0.01 K, u(P) = 0.05 MPa. <sup>*b*</sup>Standard uncertainties *u* is  $u_r(x) = 0.02$ . <sup>*c*</sup>Relative deviations;  $\varepsilon_i = (x_i^{cal} - x_i^{expl})/(x_i^{expl*}100\%)$ .

Table 4. Parameters of the Modified Apelblat Equation and Deviations for DPPO in Different Solvents

solvent	Α	В	С	$\sigma/\%$	RSD/%	$R^2$
ethyl acetate	450.4182	-24256.7641	-65.8000	1.7637	0.1120	0.9973
chloroform	-80.4968	2580.4258	12.0616	0.9690	0.0116	0.9949
1,4-dioxane	-198.7460	6354.2575	30.3096	1.1363	0.0139	0.9990
acetone	171.8738	-11594.7676	-24.2066	2.3233	0.0289	0.9976
acetonitrile	-139.9639	3659.8377	21.6056	1.0715	0.0129	0.9992
1,2-dichloroethane	20.0643	-3434.1305	-2.1911	1.4355	0.0173	0.9963
methanol	-26.1125	-2216.9068	4.9040	1.1793	0.0141	0.9986
dichloromethane	-13.6825	-2741.0458	3.3154	1.8469	0.0199	0.9975
tetrachloromethane	-42.7908	-2140.7668	7.4061	2.6806	0.0345	0.9981
benzene	-27.0389	-2138.3525	4.9515	2.3264	0.0267	0.9987
isopropanol	-95.7275	330.3769	15.4034	1.6826	0.0236	0.9993
tetrahydrofuran	0.0767	-2302.8961	0.5362	1.3939	0.0160	0.9985



**Figure 9.** Temperature dependence of the solubility of DPPO in 12 solvents:  $\blacktriangleleft$ , tetrachloromethane;  $\blacktriangledown$ , isopropanol;  $\blacksquare$ , ethyl acetate;  $\bigstar$ , benzene;  $\blacklozenge$ , methanol;  $\boxdot$ , acetone;  $\bigtriangleup$ , 1,4-dioxane;  $\bigstar$ , tetrahydrofuran;  $\Box$ , acetonitrile;  $\bigcirc$ , dichloromethane;  $\blacktriangleright$ , 1,2-dichloroethane;  $\diamondsuit$ , chloroform.

$$A = \frac{\Delta_{\text{fus}} H_1}{RT_{t1}} - \frac{\Delta_{\text{fus}} C_{p1}}{R} (\ln T_{t1} + 1) - a$$
(3)

$$B = -\frac{\Delta_{\rm fus} H_1}{R} + \frac{\Delta_{\rm fus} C_{p1}}{R} T_{t1} - b \tag{4}$$

$$C = \frac{\Delta_{\text{fus}} C_{p1}}{R} \tag{5}$$

Table 5.	Values	of the	Literature	Parameters	for	Different
Solvents						

solvent	polarity	dipole moments (µ)	dielectric constant $(\varepsilon)$	Hilderbrand solubility parameter $(\delta_{\rm H})$ (293.15 K)
ethanol	6.6	1.7	32.60	14.5
acetonitrile	6.2	3.2	37.50	11.9
acetone	5.4	2.9	20.70	10.0
1,2-dichloroethane	3.3	1.8	10.45	9.8
chloroform	4.4	1.1	4.80	9.3
ethyl acetate	4.3	1.7	6.02	9.1
1,4-dioxane	4.8	1.5	2.21	9.9
dichloromethane	3.4	3.8	9.10	9.7
tetrachloromethane	1.6	0	2.24	8.6
benzene	3.0	0	2.28	9.2
isopropanol	4.3	5.6	18.30	11.5
tetrahydrofuran	4.2	5.67	7.58	9.2

where x is the mole fraction solubility of DPPO and T (K) is the absolute temperature.  $\Delta_{\rm fus}H_1$  (J·mol<sup>-1</sup>) denotes the enthalpy change upon the melting of the solute at the its triple point temperature  $T_{\rm t1}$  (K), and  $\Delta_{\rm fus}C_{p1}$  (J·K<sup>-1</sup>·mol<sup>-1</sup>) is the difference between the heat capacities of the solute in the liquid and solid phases. Both a and b are constants. R (J·mol<sup>-1</sup>· K<sup>-1</sup>) is the molar gas constant.

By means of the nonlinear fitting of the experimental solubility data, we can obtain the parameters A, B, and C, which are shown in Table 4. The root mean-square deviations (RSD) and the average relative deviations ( $\sigma$ ) were used to distinguish the discrepancy between the measured value and the calculated data, respectively. The relative standard deviations (RSD), defined by eq 6, are also present in Table 4.

$$RSD = \left[\frac{1}{N} \left(\sum_{i=1}^{N} \frac{x_i^{\exp} - x_i^{cal}}{x_i^{\exp}}\right)^2\right]^{1/2}$$
(6)

1 /0

where  $x_i^{exp}$  and  $x_i^{cal}$  stand for the experimental solubility and the solubility calculated from Apelblat equation, respectively; N represents the number of experimental data points. The relative deviation  $\varepsilon_i$  is defined as

$$\varepsilon_i = \frac{x_i^{\exp} - x_i^{cal}}{x_i^{\exp}} \times 100\%$$
<sup>(7)</sup>

The average relative error  $\sigma$  is defined as#tab;

$$\sigma = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{x_i^{\exp} - x_i^{cal}}{x_i^{\exp}} \right| \times 100\%$$
(8)

The results demonstrate that eq 2 can be applied to correlate the solubility data with high accuracy from Figure 9, with the temperature range of the measurement. It can be seen that the solubilities of DPPO in a certain solvent increase with increasing in temperature. The values of *A*, *B*, and *C* used in the modified Apelblat equation, as well as the RSD and  $R^2$ value, were provided in Table 4. These data indicated that the results of Apelblat equation match the experimental data for DPPO in the 12 solvents over the temperature range from 278.15 to 347.15 K. The  $R^2$  values were from 0.9949 to 0.9993. The RSD were all less than 0.1%, and the average relative error was less than 0.04 in all of the experiments.

In general, it is too complicated to elucidate the solubility behavior of DPPO in these solvents to assign to a single reason. The solubility behavior of DPPO may result from many factors, the properties of the solvents including the solubility parameters  $(\delta)$ , the rule of "like dissolves like", molecule structure, dielectric constant ( $\varepsilon$ ), the hydrogen bond, and van der Waals forces and so on.<sup>13</sup> For all of the selected solvents, the properties including polarity, dipole moments  $(\mu)$ , dielectric constant ( $\varepsilon$ ), and Hilderbrand solubility parameter  $(\delta_{\rm H})^{14-16}$  are presented in Table 5. For the specific case of chloroform, it was deduced that hydrogen bonds and polarity in solution might play a dominant role.<sup>17,18</sup> Because of the electronic-withdrawing ability of chlorine atoms, the chloroform contains an active hydrogen. There are two oxygen atoms in DPPO which can form different hydrogen bonds in the chloroform, making DPPO very soluble in the chloroform in agreement with the similar miscibility theory. All of the DPPO molecules, 1,4-dioxane molecules, and tetrahydrofuran have a hexatomic ring containing two oxygen atoms. Based on the principle of "like dissolves like", the solubility of DPPO in 1,4dioxane and tetrahydrofuran are relatively high. The polarities of methanol and acetone are relative strong, so the DPPO solubility in the three solvent is low. Therefore, the solubility of DPPO do not display regularly variation in terms of the polarity and molecule structure of solvents. Further research and experiments need to be done to explore this phenomenon.

# CONCLUSIONS

DPPO was prepared and characterized by IR and NMR. The thermal stability of DPPO was characterized by thermogravimetric analysis (TGA). The solubilities of DPPO in 12 solvents were measured by a gravimetrical method. For all of the selected solvents studied, the solubility of DPPO was increased with an increasing temperature. At ambient temperature, the order of solubility of DPPO is as follows: chloroform > 1,2dichloroethane > dichloromethane > acetonitrile > (1,4dioxane, tetrahydrofuran) > acetone > methanol > (ethyl acetate, benzene) > isopropanol > tetrachloromethane. The better solvents for DPPO are chloroform, dichloromethane, 1,2-dichloroethane, tetrahydrofuran, and acetonitrile, but for the recrystallization, acetonitrile, 1,2-dichloroethane, tetrahydrofuran, and acetone are suitable solvents. The calculated values of DPPO by the Apelblat model were in good agreement with the experimental data. The root-mean-square deviation (RSD) was less than 0.1%, and the average relative error was less than 0.04 in all of the experiments.

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#### Notes

The authors declare no competing financial interest.

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