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Determination and Correlation of Solubility of Tris(3-hydroxypropyl)phosphine Oxide in Selected Solvents

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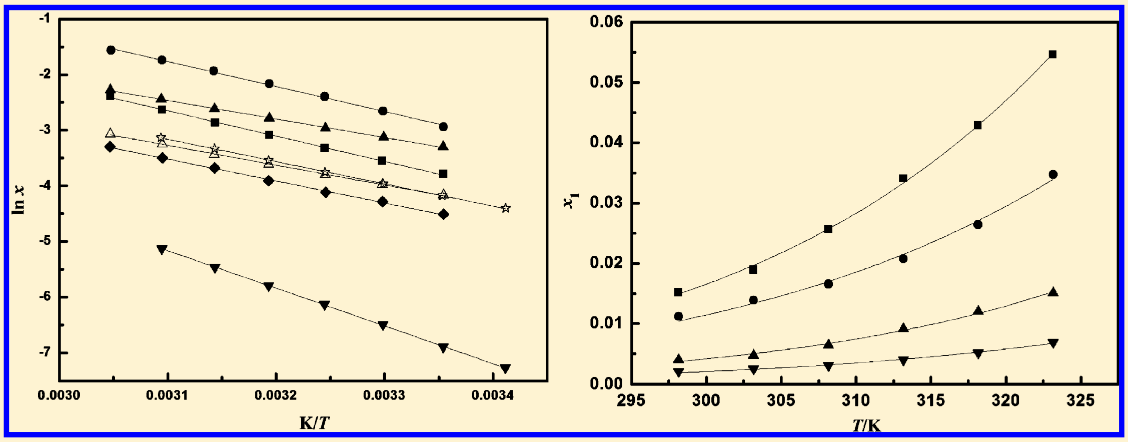
Ⓢ *Supporting Information*



ABSTRACT: The solubility of tris(3-hydroxypropyl)phosphine oxide (THPPO) in selected solvents was measured by a static analytic method over the temperature range from (293 to 328) K in methanol, ethanol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, isobutyl alcohol, acetone, and a binary solvent mixture of ethanol + acetone. Several widely used thermodynamic models, such as the empirical equation and the Buchowski–Ksiazaczak (λh), Scatchard–Hildebrand, Wilson, nonrandom two-liquid (NRTL), and universal quasichemical (UNIQUAC) equations were applied to represent the measurement results. The binary interaction parameters of the above models were found to have a linear dependency on temperature, and the coefficients were regressed. The results show that all of these models can satisfactorily reproduce the experimental data and the NRTL equation can provide the best correlation with an overall relative standard deviation of 0.46 %.

INTRODUCTION

Engineering plastics are an important class of polymeric materials which are widely used in both industry and daily life, such as construction, automobiles, electrical/electronic, and biomaterials. Generally, those compositions are organic and, thus, easily ignitable in a fire situation. Their great uses have been limited by the flammability. Thus, their manufacturers are majorly concerned with rendering their products flame retardant. Many kinds of commercial flame retardants (FRs) are widely used to produce high-performance flame retardancy polyester.[1] The designed component centers on organophosphorus compounds, containing P═O bonds, which have been shown to be excellent flame retardants in the polymer industry.[2] Furthermore, phosphorus compounds have been proved to be more environmentally benign compared to their halogenated analogues.[3]

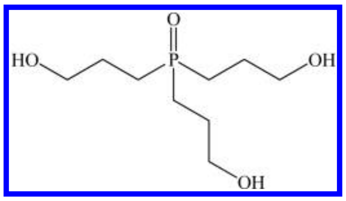


Figure 1. Structures of the tris(3-hydroxypropyl)phosphine oxide (THPPO).

Among these phosphorus flame retardants, tris(3-hydroxypropyl)phosphine oxide (THPPO, chemical structure as shown in Figure 1, CAS No. 51805-42-6) has been commercially applied in polymerization.[4] It has been found that THPPO is more compatible in polyphenylene oxide compositions with high thermal stability and excellent fire retardancy.[5] The merits that may be attributed to the THPPO flame retardant include no corrosion, high ultraviolet stability, nontoxicity, and minimal adverse change in the overall properties of the polymer. It becomes a widely used reactive flame retardant for polyurethanes,[4,6] epoxy resins,[7] and poly(phenylene ether)-styrene.[8]

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Table 1. Description of the Solute and Solvents Used in This Paper

chemical name	source	initial mass fraction purity	water content (%)	purification method	analysis method
THPPO	synthesized	0.986	0	recrystallization	HPLC[a]
methanol	Beijing Chemical Factory	0.995	0.1	none	GC[b]
ethanol	Beijing Chemical Factory	0.995	0.3	none	GC[b]
n-propyl alcohol	Beijing Chemical Factory	0.995	0.2	none	GC[b]
isopropyl alcohol	Beijing Chemical Factory	0.995	0.2	none	GC[b]
n-butyl alcohol	Beijing Chemical Factory	0.994	0.1	none	GC[b]
isobutyl alcohol	Beijing Chemical Factory	0.995	0.1	none	GC[b]
acetone	Beijing Chemical Factory	0.995	0.3	none	GC[b]

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

The solubilities of THPPO in the single and mixed solvents not only are helpful for the fundamental data for the products' characteristics such as crystal size distribution, crystal habits, purity, and yields,[9] but also supply the fundamental data for the modeling of solubility and understanding of interactions between THPPO and various solvents. In the industrial purification process, THPPO is usually crystallized with isopropyl alcohol.[10] In this study, we reported a new and efficient method to purify the THPPO. To obtain more systematic and useful thermodynamic information on the crystallization of THPPO from some organic solvents, the solubility of THPPO in the seven selected organic solvents was measured in this study cover the temperature range from (293 to 328) K. Moreover, the solubility of THPPO in mixed solvents ethanol + acetone were investigated with different solvent compositions. The Buchowski−Ksiazaczak (λh),[11] Scatchard−Hildebrand,[12] Wilson,[13] nonrandom two-liquid (NRTL),[14] and UNIQUAC[15] model were applied to represent the solubility data. Comparison and discussion of the solubility and the capability of the models were carried out.

■ EXPERIMENTAL SECTION

Materials. Tris(3-hydroxypropyl)phosphine (THPP, CAS No. 4706-17-6, a 30 % aqueous solution) was kindly provided by TianJin LianKuan Fine Chemicals Co., China. Hydrogen peroxide solution (30 %) was purchased from the Weisi Chemical Reagents Co., Beijing, China. Table 1 shows the description of solute and solvents used in this paper, including THPPO, methanol, ethanol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, isobutyl alcohol, and acetone.

Apparatus and Procedure. Several instruments were used to characterize the properties of THPPO. A differential scanning calorimeter (DSC) Q100 (TA Instruments) was used to determinate the melting point and enthalpy of fusion with a constant heating rate of 10 °C·min^{-1} in the range from (298.15 to 415.15) K, under a high pure nitrogen dynamic atmosphere at 25 mL·min^{-1}. The uncertainty and calibration of DSC instrument is similar to the literature.[16] An Elementar Vario EL element analyzer was used to perform the elemental analysis. A Bruker ARX-400 was used to obtain ^{1}H nuclear magnetic resonance (NMR) spectra with DMSO-d_6 as a solvent. ^{31}P NMR spectra were obtained by using a JEOL ECA-600 with D_2O as a solvent. Thermogravimetric analysis (TGA) was performed using a TA Instrument SDT Q600 thermal analyzer at a heating rate of 10 °C·min^{-1} in the range from (300 to 850) K, under high pure N_2 flow at 100 mL·min^{-1}.

The procedure of the measurement was described specifically in ref 17. A jacketed equilibrium cell was used for the solubility measurement with a working volume of 120 mL and a magnetic stirrer, and a circulating water bath was used with a thermostat, which is capable of maintaining the temperature within ± 0.05 K. The temperature of the inner chamber of the vessel was measured by a calibrated mercury-in-glass thermometer (uncertainty of ± 0.05 K). The mass of the sample was weighed using an analytical balance with a precision of ± 0.1 mg (type FA2104B, Shanghai Yueping Scientific Instrument Co.).

For each measurement, an excess mass of THPPO was added to a known mass of the solvent. Then the equilibrium cell was heated to a constant temperature with continuous stirring. After at least 2 h, the stirring was stopped, and the solution was kept still until it was clear. A preheated on−off injector with a cotton filter withdrew 2 mL of the clear upper portion of the solution to another previously weighed measuring vial. The vial was quickly and tightly closed and weighed to determine the mass of the sample. Then the vial was uncovered with a piece of filter paper to prevent dust contamination. After the solvent in the vial had completely evaporated, the vial was dried and reweighed to determine the mass of the constant residue solid.

Each experimental data point was repeated three times, and the mean value of them was chosen as solubility. The mole fraction solubility of the THPPO in solvents was calculated as follows:

$$x = \frac{m_1/M_1}{m_1/M_1 + m_1/M_2} \tag{1}$$

where m_1 and m_2 represent the mass of the solute and solvent, and M_1 and M_2 are the molecular weights of the solute and solvent, correspondingly.

Synthesis and Characterization of THPPO. The THPP solution is oxidized by stirring with the dropwise solution of a 30 % hydrogen peroxide. When the temperature decreases, adding 1 mL of carbon disulfide into the solution of phosphine oxide until no red coloration can be detected visually in the carbon disulfide layer. Following oxidation with hydrogen peroxide, the solvents are removed by heating to 80 °C under vacuum. The crude product was stored at room temperature for a few days, and the hard solid crystal product was formed. Recrystallization of 200 g of this product mixture from acetone + ethanol (300 mL 2:1 v/v) gave 96 g of THPPO, which is a white solid.

^{1}H NMR (DMSO-d_6): δ (ppm): 1.52—1.69 (m, 12H, PCH_2CH_2), 3.47 (t, 6H, CH_2OH), 4.69 (s, 3H, OH). The result matches well with the ^{1}H NMR spectra reported by Moiseev et al.[18] ^{31}P NMR (D_2O-d_6): δ = 60.91 ppm, which agrees with the literature data.[10,18] Elemental analysis (%, calcd): C, 48.29 % (48.21 %); H, 9.36 % (9.44 %). It shows a high purity of the THPPO sample. The DSC and TGA results are given in Figures 2 and 3. The melting point of THPPO was characterized at 387.76 K (ref 10, 382.15 K), and the

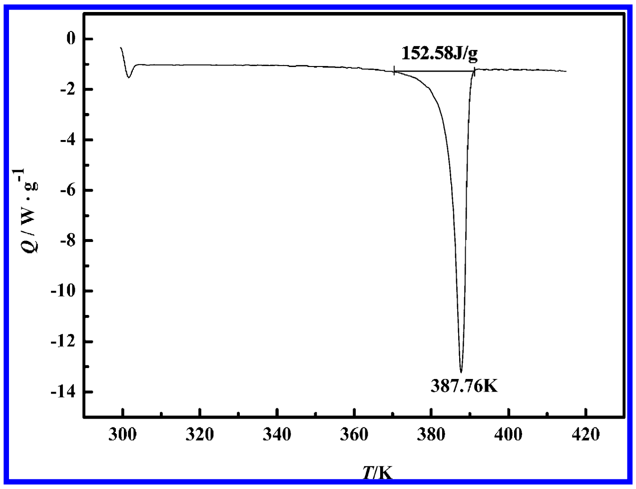

Figure 2. Experimental heat Q flow from DSC measurement of THPPO.

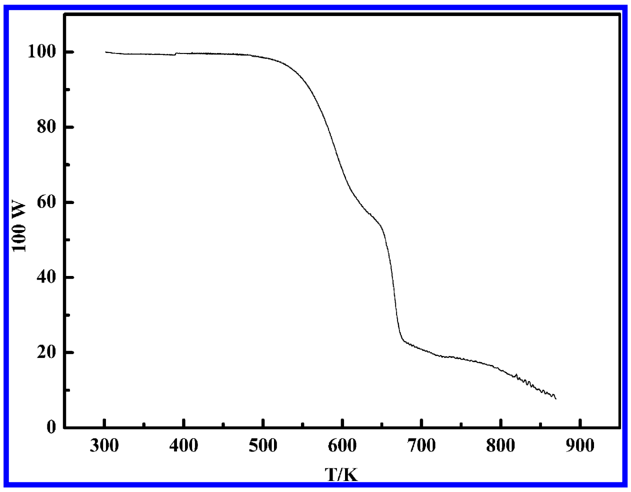

Figure 3. TGA thermograms of THPPO under N_2.

uncertainty of the melting point measurement is 0.26 K. The enthalpy of fusion of THPPO was 34.21 $\mathrm{kJ\cdot mol^{-1}}$, and the relative uncertainty of the enthalpy of fusion is 0.25 %. From Figure 3, the THPPO has good thermal stability before the initial decomposition temperature (480.2 K).

RESULTS AND DISCUSSION

Results and Analysis. The mole fraction solubilities of THPPO in seven organic solvents, methanol, ethanol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, isobutyl alcohol, and acetone against temperatures are listed in Table 2, which are also plotted as ln x versus $1/T$ in Figure 4, and THPPO in ethanol + acetone binary mixed solvents in Table 3. It can be found from Figure 4 that the solubility data increase with the temperature in all selected solvents. The solubility of THPPO in the seven selected solvents decrease in the order at constant temperature: methanol > *n*-propyl alcohol > ethanol > isobutyl alcohol > isopropyl alcohol > *n*-butyl alcohol > acetone. The solubility of THPPO are different in different solvents, which was probably contribution to the theory of "like dissolves like"[19−21] and the certain polarity of THPPO.

The solubility data were fitted with a temperature dependency expression:

Table 2. Mole Fraction Solubilities (x) and Activity Coefficients (γ) of THPPO in the Selected Solvents (0.1 MPa)[a]

solvent	T/K	x	γ	$(x - x^{\mathrm{calcd,\ eq\ 2}})/x$
methanol	298.11	0.05267	0.7804	−0.0327
	303.15	0.07018	0.7368	0.0029
	308.18	0.09102	0.7090	0.0201
	313.10	0.11501	0.6921	0.0241
	318.22	0.14427	0.6817	0.0191
	323.14	0.17565	0.6818	0.0001
	328.11	0.20979	0.6923	−0.0336
ethanol	298.12	0.02262	1.8180	0.0201
	303.22	0.02858	1.8150	−0.0027
	308.17	0.03605	1.7894	−0.0116
	313.10	0.04556	1.7472	−0.0010
	318.08	0.05687	1.7195	−0.0158
	323.11	0.07185	1.6647	−0.0046
	328.16	0.09188	1.5837	0.0246
n-propyl alcohol	298.16	0.03690	1.1165	0.0112
	303.11	0.04383	1.1777	0.0010
	308.13	0.05171	1.2453	−0.0126
	313.12	0.06198	1.2854	−0.0036
	318.16	0.07312	1.3418	−0.0067
	323.21	0.08659	1.3868	−0.0010
	328.18	0.10249	1.4208	0.0116
isopropyl alcohol	298.13	0.01552	2.6510	0.0131
	303.21	0.01870	2.7727	−0.0010
	308.15	0.02243	2.8734	−0.0077
	313.17	0.02704	2.9525	−0.0063
	318.19	0.03210	3.0601	−0.0144
	323.11	0.03865	3.0947	0.0006
	328.18	0.04653	3.1296	0.0156
n-butyl alcohol	298.13	0.01099	3.7437	0.0108
	303.21	0.01377	3.7653	0.0147
	308.11	0.01632	3.9424	−0.0223
	313.17	0.02003	3.9859	−0.0243
	318.15	0.02524	3.8855	0.0098
	323.1	0.03025	3.9525	0.0010
	328.23	0.03695	3.9485	0.0103
isobutyl alcohol	293.11	0.01224	2.6537	0.0086
	298.21	0.01535	2.6903	0.0012
	303.13	0.01895	2.7263	−0.0062
	308.15	0.02337	2.7579	−0.0119
	313.17	0.02908	2.7454	−0.0017
	318.14	0.03571	2.7452	0.0039
	323.23	0.04364	2.7538	0.0061
acetone	293.15	0.00070	46.490	0.0036
	298.14	0.00101	40.755	−0.0157
	303.16	0.00151	34.260	0.0111
	308.21	0.00217	29.778	0.0085
	313.17	0.00303	26.349	−0.0050
	318.12	0.00425	23.047	−0.0025
	323.15	0.00593	20.202	$-5.50\cdot10^{-5}$

[a] The standard uncertainty u is $u(T)$ = 0.01 K; the relative standard uncertainty u is $u_r(x)$ = 0.02.

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

where A and B are model parameters. The values of A and B for each solvent together with the relative standard deviations (RSD) are presented in Table 4. The RSD was calculated as follows:

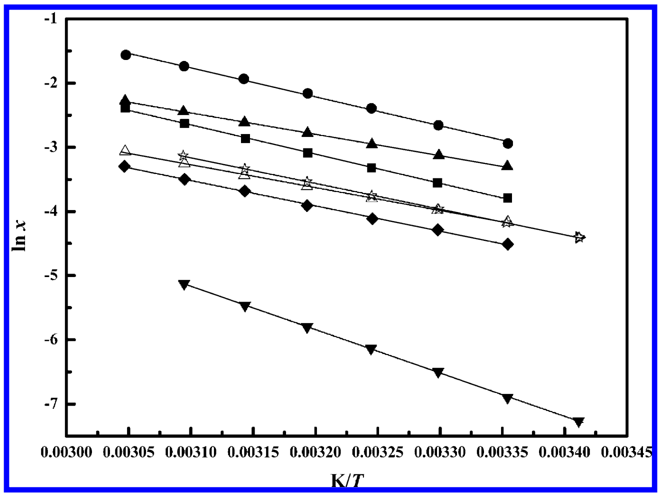

Figure 4. Mole fraction solubilities of THPPO in selected solvents. Experimental data: ●, methanol; ■, ethanol; ▲, *n*-propyl alcohol; ☆, isobutyl alcohol; ◆, *n*-butyl alcohol; △, isopropyl alcohol; ▼, acetone; —, solubility curve calculated from eq 2.

Table 3. Mole Fraction Solubilities (x) of THPPO in Ethanol (x_2) + Acetone (x_3) (0.1 MPa)[a]

$x_2/(x_2 + x_3)$	T/K	x	$(x - x^{\text{calcd,eq5}})/x$
0.7998	298.15	0.01518	0.0223
	303.15	0.01888	−0.0374
	308.15	0.02565	0.0006
	313.15	0.03407	0.0230
	318.15	0.04289	−0.0004
	323.15	0.05465	−0.0054
0.5979	298.15	0.0112	0.0292
	303.15	0.01388	0.0124
	308.15	0.01655	−0.0387
	313.15	0.02073	−0.0351
	318.15	0.02642	−0.0097
	323.15	0.03476	0.0488
0.3986	298.15	0.00400	0.0638
	303.15	0.00475	−0.0587
	308.15	0.00640	−0.0468
	313.15	0.00914	0.0306
	318.15	0.01202	0.0314
	323.15	0.01508	−0.0089
0.2075	298.15	0.00212	0.0535
	303.15	0.00254	−0.0101
	308.15	0.00312	−0.0457
	313.15	0.00402	−0.0274
	318.15	0.00517	−0.0075
	323.15	0.00692	0.0533

[a] The standard uncertainty u is $u(T) = 0.01$ K; the relative standard uncertainty u is $u_r(x) = 0.02$.

$$\text{RSD} = \left[\frac{1}{N} \sum_{i=1}^{N} \left(\frac{x_i^{\text{exp}} - x_i^{\text{calc}}}{x_i^{\text{exp}}} \right)^2 \right]^{1/2} \tag{3}$$

where N is the number of experimental data points and x_i^{exp} and x_i^{calc} stand for the experimental data and calculated values, respectively. It can be seen from Table 4, eq 2 can be used to regress the experimental date of THPPO in seven pure solvents.

Table 4. Parameters of eq 2 and Relative Standard Deviation (RSD) of THPPO in the Selected Solvents

solvent	A	B	RSD/%
methanol	12.215	−4509.2	2.25
ethanol	11.454	−4550.3	1.47
n-propyl alcohol	7.8530	−3328.6	0.83
isopropyl alcohol	7.7849	−3566.7	1.02
n-butyl alcohol	8.7061	−3943.6	1.52
isobutyl alcohol	9.2576	−4006.6	0.66
acetone	15.787	−6758.6	0.83

Table 5. Regressed Parameters and the Relative Standard Deviation (RSD) of the λh Equation for THPPO in Ethanol (x_2) + Acetone (x_3) Mixed Solvents

mixed solvents	λ	h	RSD/%
$x_2 = 0.7998$	0.6994	7118.91	2.02
$x_2 = 0.5979$	0.2392	16855.36	3.22
$x_2 = 0.3986$	0.2157	24325.64	4.42
$x_2 = 0.2075$	0.0530	80551.33	3.81

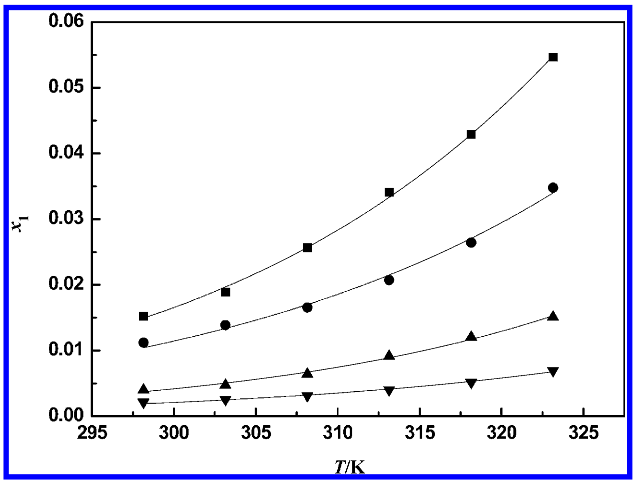

Figure 5. Mole fraction solubilities of THPPO in binary ethanol (x_2) + acetone (x_3) solvent mixtures: Experimental data: ■, $x_2 = 0.7998$; ●, $x_2 = 0.5979$; ▲, $x_2 = 0.3986$; ▼, $x_2 = 0.2075$. —, solubility curve calculated by the λh equation.

Table 6. Solubility Parameter (δ), Molar Volume (V), UNIQUAC Volume Parameter (r), and Surface Parameter (q) of the Selected Solvents and THPPO

	δ_i	$10^6\ V_i$		
solvent	$(\text{J}\cdot\text{cm}^{-3})^{1/2}$	$\text{m}^3\cdot\text{mol}^{-1}$	r	q
methanol	29.52	40.70	1.4311	1.432
ethanol	26.42	58.52	2.5755	2.588
n-propyl alcohol	24.56	74.94	3.2499	3.128
isopropyl alcohol	23.58	76.78	3.2491	3.124
n-butyl alcohol	23.29	91.94	3.9243	3.668
isobutyl alcohol	23.75	93.03	3.9235	3.664
acetone	19.77	73.93	2.5735	2.336
THPPO	27.48	193.7	10.351	9.693

The equilibrium solubility for nonelectrolyte solute is often described by the following rigorous thermodynamics equation:[22]

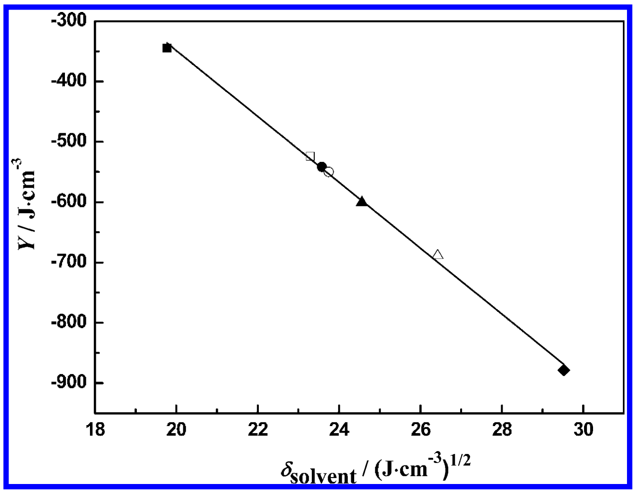

Figure 6. Residual function Y for THPPO versus solvent solubility parameters $\delta_{solvent}$. ■, acetone; □, n-butyl alcohol; ●, isobutyl alcohol; ○, isopropyl alcohol; ▲, n-propyl alcohol; △, ethanol; ◆, methanol; —, regression line.

Table 7. Solubility Parameter δ (J·cm^{-3})$^{1/2}$ of the THPPO

T/K	δ from intercept	δ from slope	R^{2a}
298.15	27.25	27.29	0.9980
303.15	27.29	27.32	0.9976
308.15	27.34	27.39	0.9970
313.15	27.43	27.49	0.9962
318.15	27.57	27.65	0.9950
323.15	27.79	27.90	0.9932

[a] R^2 = correlation coefficient.

$$\ln\frac{1}{x_1\gamma_1} = \frac{\Delta_{fus}H}{RT_m}\left(\frac{T_m}{T} - 1\right) \quad (4)$$

With the experimental x_1, T, $\Delta_{fus}H$, and T_m values, the activity coefficients of THPPO in solid–liquid equilibrium are obtained and presented in Table 2.

The measured solubilities of THPPO in ethanol + acetone binary mixed solvents were presented in Table 3. The Buchowski–Ksiazaczak λh equation is a well-known two-parameter model, as first proposed by Buchowski et al.[11] For most solid–liquid equilibrium systems, it can be used to describe the SLE relations very well.[23–26] In our study, the λh equation was used to correlate the experimental data of THPPO in ethanol + acetone:

$$\ln\left[1 + \frac{\lambda(1 - x_1)}{x_1}\right] = \lambda h\left(\frac{1}{T} - \frac{1}{T_m}\right) \quad (5)$$

where T_m is the melting point of the THPPO. λ and h are model parameters which could be obtained from the experimental data by nonlinear regression.

The optimized parameters λ and h for THPPO in ethanol + acetone binary solvent mixtures are summarized in Table 5 together with the RSD values. The experimental data can be regressed by the λh equation with an average RSD of 3.34 % and in each case no less than 5 % (Table 5). From Figure 5, it can be seen that the λh equation can be well reproduced the solubility data. The solubility of THPPO in ethanol + acetone binary mixed solvents decreases with the raise of acetone composition at constant temperature.

Table 8. Regression Results of Wilson, NRTL, and UNIQUAC Equation: Parameter Values of eq 8 and Relative Standard Deviation (RSD) of THPPO in Selected Solvents

	Wilson					NRTL					UNIQUAC				
solvent	a_{12}	b_{12}	a_{21}	b_{21}	RSD %	a_{12}	b_{12}	a_{21}	b_{21}	RSD %	a_{12}	b_{12}	a_{21}	b_{21}	RSD %
methanol	5249.46	−9.905	3194.26	−18.79	0.18	6785.1	−1.34	860.49	−16.73	0.18	375.62	−3.842	7059.5	−14.56	0.20
ethanol	−3096.43	14.81	2724.18	−5.29	0.29	3779.5	6.06	−3464.6	2.345	0.30	385.42	−2.349	−1023.8	7.059	0.29
n-propyl alcohol	−13161	56.43	−1496.55	−5.33	0.30	−13706	40.09	10489	−25.54	0.31	1683	−8.581	−4803.2	21.32	0.40
isopropyl alcohol	−1746.53	15.44	−6935.41	22.35	0.26	−7990.6	35.27	51710	904.3	0.27	−448.98	−0.689	−808.5	8.049	0.25
n-butyl alcohol	−190.98	6424.2	−2991.35	6.71	1.27	2723.7	8.287	−6223.9	15.91	1.05	381.54	−2.067	−1437.6	7.859	1.08
isobutyl alcohol	19397	2193.7	−1867.8	0.2174	0.45	−2874.7	17.67	21353	86.12	0.30	1971.7	−10.93	−6905.6	32.90	0.31
acetone	−13200	325.87	20339	−53.60	0.94	22923	−46.4	144338	−315.5	0.80	2283.8	−11.22	−328.64	31.91	0.84
overall					0.53					0.46					0.48

From Tables 2 and 3, for $x_2 = 0.7998$, the binary mixed solvents have higher solubilities than isopropyl alcohol when the temperature is more than 308 K, but have nearly the same when the temperature decreases to 303 K. This result indicates the new method mentioned above of purified THPPO is more efficient than previously.

Correlation with Scatchard−Hildebrand Model. According to Scatchard−Hildebrand theory,[12] the regular-solution equation can be expressed as follows:

$$RT \ln \gamma_1 = V_1\phi_2^2(\delta_1 - \delta_2)^2 \tag{6}$$

Transforming eq 6 for a residual function Y yields:

$$Y = \frac{RT \ln \gamma_1}{V_1\phi_2^2} - \delta_2^2 = -2\delta_2\delta_1 + \delta_1^2 \tag{7}$$

With the activity coefficients listed in Table 1, the solubility parameter of the solvents obtained from the literature,[27] and the molar volume of the subcooled liquid for THPPO (using ACD/Laboratories Software V11.02; the value is 193.7 $\text{cm}^3\cdot\text{mol}^{-1}$), the value of the solute solubility parameter δ_1 can be determined by the slope of this line (see Table 6). The linear dependence between Y and δ_2 at 303.15 K is displayed in Figure 6. Values of solubility parameter of THPPO from (298.15 to 323.15) K given in Table 7 indicate that δ_1 approaches to a constant in the considered temperature range. The average value of THPPO solubility parameter δ_1 is 27.48 $(\text{J}\cdot\text{cm}^{-3})^{1/2}$.

Correlation with Wilson, NRTL, and UNIQUAC Models. The Wilson,[13] NRTL,[14] and UNIQUAC[15] activity coefficient models are employed in this study to correlate the experimental data through eq 4. These models have been successfully used to correlate the solid−liquid equilibrium properties for many nonideal solutions over wide temperature ranges.[28−30] Physical properties of pure components that are required in the modeling work are obtained from the literature.

The parameters r and q are the UNIQUAC volume parameter and surface parameter of pure component, which can be calculated from the procedure described earlier.[31] A new group, P═O, was introduced, and its structure parameters were calculated from bond distance and the van der Waals radii taken from literature,[32,33] by means of the purely geometric method discussed by Bondi.[34] The van der Waals group volume (r) and surface area (q) parameters for P═O are 1.2817 and 1.233, which is a little different from our previous work,[35] because the P═O band length is presumably elongated which each phosphine oxide unit is hydrogen bonded to three hydroxyl groups from three different adjacent molecules.[33] The calculated r and q values for each compound are given in Table 5.

The binary cross-interaction parameters in the Wilson equation ($\Delta\lambda_{12}$ and $\Delta\lambda_{21}$), the NRTL equation (Δg_{12} and Δg_{21}), and the UNIQUAC equation (Δu_{12} and Δu_{21}) are assumed to have a linear dependency on temperature, that is

$$k_{ij} = a_{ij} + b_{ij}T \tag{8}$$

where k denotes any interaction parameter mentioned above. The parameters a and b are fitted from experimental data using the following objective function:

$$\min f = \sum_{i=1}^{N_p} (\ln \gamma_i^{\text{exp}} - \ln \gamma_i^{\text{cal}})^2 \tag{9}$$

The experimental activity coefficient obtained from Table 2. The eq 9 was minimized by Levenberg−Marquardt method. Table 8 lists the optimized parameter values for each model and the comparison of the correlation results in terms of overall relative standard deviation. It can be seen that all of the models can reproduce the experimental results well with the optimized parameters. The Scatchard−Hildebrand equation also gives comparable correlation results (RSD % = 1.35) with the local composition models. The smaller b values for the UNIQUAC equation imply that its binary interaction parameters are less sensitive to temperature than other two local composition models. The comparison of the correlated results by different models in terms of overall relative standard deviation is Scatchard−Hildebrand 1.35 %, Wilson 0.53 %, NRTL 0.46 %, and UNIQUAC 0.48 %, respectively. The NRTL model gives the best correlation results in terms of overall relative standard deviation.

■ CONCLUSIONS

In this work, we have synthesized and purified THPPO by a new and efficient method. The solubility data of THPPO in seven organic solvents and ethanol + acetone binary mixed solvents were determined by a static analytic method, and the results were compared. The experimental results show that THPPO has the higher solubility in methanol and lower value in acetone. The solubility data of THPPO in all solvents increases with the temperature, and the solubilities in acetone show the strongest dependency on temperature. The measured solubility data were correlated by the λh, Scatchard−Hildebrand, Wilson, NRTL, and UNIQUAC equations. All of the models are capable of giving satisfactory correlations with optimized parameters. The solubility parameter of THPPO was calculated by the Scatchard−Hildebrand model. The NRTL model gives the best overall correlation results with an overall relative standard deviation of 0.46 %.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and ^{31}P NMR spectra of TPPPO information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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