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Solubilities of Tris(*o*-phenylenedioxy)cyclotriphosphazene in Selected Solvents

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Supporting Information

ABSTRACT: Tris-(*o*-phenylenedioxy)-cyclotriphosphazene (TPP) was synthesized and characterized by elemental analysis (EA) and nuclear magnetic resonance (NMR). The melting point and the enthalpy of fusion of TPP were measured by da ifferential scanning calorimeter (DSC), and the thermal stability of TPP was measured by thermogravimetric analysis (TGA). Using a static analytical method, the solubility data of TPP in nine solvents were measured and correlated with an empirical equation. Moreover, using the Scatchard—Hildebrand model, activity coefficients have also been calculated and compared with the experimental values. The partial molar excess enthalpies at infinite dilution were also predicted.

INTRODUCTION

Cyclophosphazene has a cycle structure comprised of nitrogen and phosphorus atoms. Many studies of flame retardants have focused attention on these atoms. The flame retardants reported in many papers have these heteroatoms.[1,2] Hence, the phosphazene structure has good flame retardant properties, and cyclophosphazene compounds could be used as flame retardants.[3,4] Tris-(*o*-phenylenedioxy)-cyclotriphosphazene (hereafter abbreviated as TPP; its formula is shown in Scheme 1) (CAS RN 311-03-5) is a cyclophosphazene derivative and could be used as a nonhalogen flame retardant for acrylonitrile butadiene styrene (ABS)[5] and poly(butylene terephthalate) (PBT).[6] Moreover, TPP can be used as building blocks for preparation of assembled materials.[7] As a result of its unique features, organic zeolites and molecular self-assembled materials seem to constitute a competing alternative for strategic industrial and environmental applications such as gas storage, selective gas recognition, and separation, where absorption properties of materials are emerging at the forefront of present-day research.[8−10] For example, TPP nanochannels show a strong affinity for including simple-shaped gas molecular and aliphatic or aromatic molecules.[11−13] The one-dimensional arrangement of functional molecules using the TPP nanochannel is particularly interesting from the point of view of developing new molecular devices.[14]

TPP can be prepared according to the literature.[15] In the industrial process and design, knowledge of solubilities of these compounds in different solvents is very important for their preparation and purification. To the best of our knowledge, the solubilities of TPP in selected solvents have not been reported in the literature.

In this study, TPP was synthesized and characterized. The solubilities of TPP in ethanol, ethyl acetate, acetone, dichlormethane, tetrahydrofuran (THF), acetonitrile, toluene, chloroform, and 1,2-dichlorethane were also measured.

EXPERIMENTAL SECTION

Materials. Hexachlorocyclotriphosphazene (HCCP) was purchased from Zhangjiagang Xinyi Chemical Co., Ltd. and purified by recrystallization from *n*-heptanes to give a material melting point at (112.5 to 113.5) °C before use. All of the chemicals were analytical grade reagents, which were purchased from Beijing Chemical Factory. They were used without further purification. Their mass fraction purities were all higher than 0.99.

Apparatus and Procedure. The melting points and enthalpy of fusion were determined with a DSC Q100 (TA Instruments USA) differential scanning calorimeter in flowing nitrogen at a heating rate of 10 $K \cdot min^{-1}$. The elemental analysis was performed on an Elementar Vario EL element analyzer. ^1H NMR and ^{31}P NMR spectra were obtained with a BrukerARX-400 and JEOL ECA-600, respectively. Thermogravimetric analysis (TGA) was carried out with an SDT Q600 (TA Instruments USA) thermogravimetric analyzer at a heating rate of 10 $K \cdot min^{-1}$ under nitrogen from (298.15 to 1073.15) K.

The setup for the solubility measurement was the same as that described in the literature.[16] 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 (type 50 L, made from Shanghai Laboratory Instrument Works Co., Ltd.), which is capable of maintaining the temperature within ± 0.05 K. An analytical balance (type TG-328B, Shanghai Balance Instrument Works Co.) with an uncertainty of ± 0.1 mg was used during the mass measurements.

Synthesis of TPP. TPP was prepared according to the literature (Scheme 1).[15] A stirred mixture of $(NPCl_2)_3$ (20 g, 0.058 mol), catechol (19 g, 0.173 mol), and anhydrous sodium carbonate (36.6 g, 0.346 mol) was allowed to react in boiling tetrahydrofuran (300 mL) for 3 h under N_2 atmosphere. The reaction mixture was then cooled to room temperature. The solid components were filtered off and then washed with aqueous 5 % hydrochloric acid followed by distilled water. The insoluble residue was dried under vacuum for 6 h at 25 °C and then recrystallized from xylene to yield crystals of TPP (15.6 g, 60 %).

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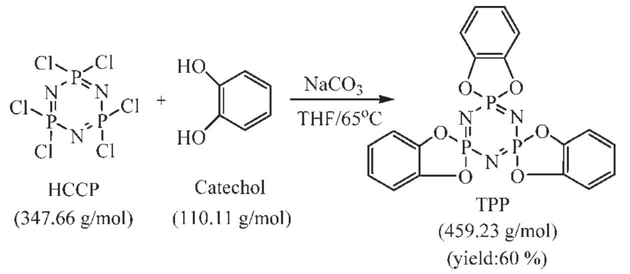
Scheme 1



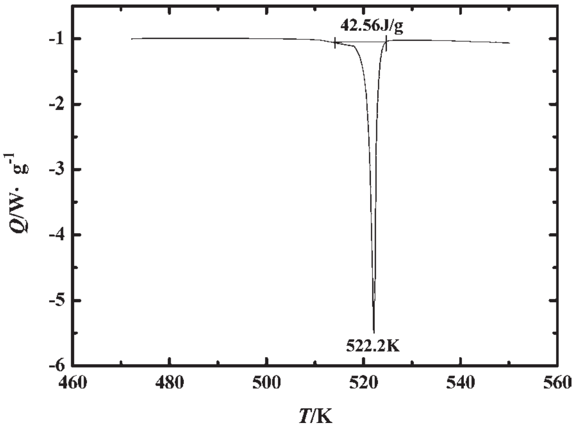


Figure 1. Experimental heat Q flow from the DSC measurement of TPP.

Table 1. Measured Melting Point and Enthalpy of Fusion of TPP

melting point	uncertainty	enthalpy of fusion	uncertainty
K	K	$J \cdot g^{-1} \cdot mol^{-1}$	%
522.2	0.26	42.56	0.93

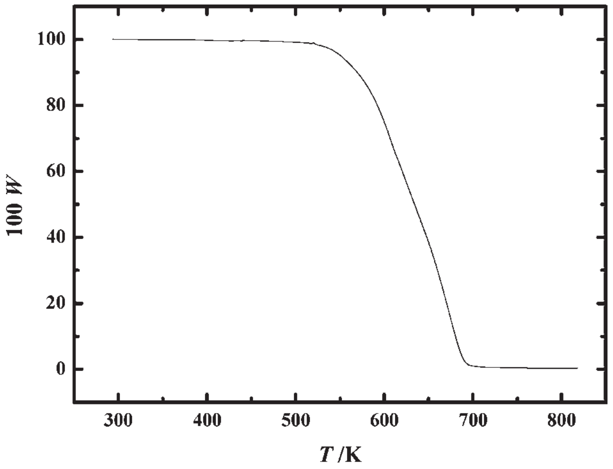


Figure 2. TGA thermograms of TPP under N_2.

Table 2. Thermogravimetric Analyses of TPP and Comparison with Literature Values

TPP	T_{onset}/K	$T_{5\%}$/K	$T_{20\%}$/K	$T_{50\%}$/K
exp.	521.15	551.15	593.15	634.15
lit.[6]	523.15	550.15	588.15	628.15

Characterization of TPP. ^{1}H NMR ($CDCl_3$-d_6), δ (ppm): 7.11 to 7.09 (m, 1H), 7.02 to 7.04 (m, 1H); ^{31}P NMR ($CDCl_3$-d_6): δ = 33.73 ppm. Elemental analysis (%, cal): C, 47.23 % (47.08 %); H, 2.66 % (2.63 %); N, 9.01 % (9.15 %). These results show a high purity of the TPP sample as certified by the specification. The result of DSC measurement of TPP was shown in Figure 1. The melting point of TTP was 522.2 K, [lit.,[17] (516.15 to 517.15) K]. The enthalpy of fusion of TPP was 42.56 $J \cdot g^{-1}$. The results of the measured melting point and the enthalpy of fusion of TPP and uncertainties are listed in Table 1. The result of TGA measurement of TPP is shown in Figure 2. It is showed that there is a single-step decomposition, and no or very little residues remain for TPP. The thermogravimetric analyses in this work are compared with the literature values[6] and are listed in Table 2. The results obtained are in good agreement with those listed in the literature.

Solubility Measurement. The solubilities were measured by a gravimetric method.[18] For each measurement, an excess mass of TPP was added to a known mass of solvent. Then the equilibrium cell was heated to a constant temperature with continuous stirring. After at least 2 h (the temperature of the water bath approached a constant value, then the actual value of temperature was recorded), 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 (m_0). The vial was quickly and tightly closed and weighed (m_1) to determine the mass of the sample ($m_1 - m_0$). 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 (m_2) to determine the mass of the constant residue solid ($m_2 - m_0$). Thus, the solid concentration of the sample solution in mole fraction, x, could be determined from eq 1[19]

$$x = \frac{(m_2 - m_0)/M_1}{(m_2 - m_0)/M_1 + (m_1 - m_2)/M_2} \tag{1}$$

where M_1 and M_2 is the molecular weight for solute and solvent, respectively.

Different dissolution times were tested to determine a suitable equilibrium time. It was found that 2 h was enough for TPP in solvent to reach equilibrium. During our experiments, three parallel measurements were performed at the same composition of solvent for each temperature, and an average value is given. The maximum standard deviation of each triplicate data is 0.25 %, and the minimum is 0.14 %. The estimated relative uncertainty of the solubility values based on error analysis and repeated observations was within 2 %.

RESULTS AND DISCUSSION

The mole fraction solubility x of TPP in selected solvents measured in this work is summarized in Table 3 and plotted as ln x vs $1/T$ and T in kelvin in Figure 3. From this figure, it can be seen that a trend of increasing solubility with temperature is observed.

Table 3. Mole Fraction Solubilities (x), Solubilities (m, g/100 g Solvent), and Activity Coefficients (γ) of TPP in the Selected Solvents

solvent	T/K	$10^3 x$	m	γ	$(x - x^{\text{calc}})/x$
ethanol	293.95	0.0952	0.0997	318.5	0.0011
	298.05	0.1173	0.1196	288.6	−0.0020
	303.25	0.1527	0.1495	253.8	0.0016
	308.35	0.1938	0.1894	227.3	−0.0066
	313.35	0.2341	0.2493	201.5	0.0015
	318.15	0.3080	0.3091	180.9	0.0050
	322.95	0.3801	0.3789	163.6	0.0041
	328.15	0.4511	0.4687	147.7	$8.8 \cdot 10^{-5}$
	332.45	0.5620	0.5585	136.2	−0.0049
ethyl acetate	298.15	0.4186	0.2190	81.08	0.0102
	303.35	0.5627	0.2816	72.10	0.0042
	308.25	0.6746	0.3547	65.14	−0.0071
	313.45	0.8562	0.4487	58.25	−0.0109
	318.25	1.0662	0.5583	52.39	−0.0082
	323.15	1.3283	0.6942	47.03	−0.0026
	328.15	1.6551	0.8667	42.17	0.0051
	332.45	1.8833	1.0341	38.59	0.0091
acetone	294.35	0.2501	0.1977	122.6	−0.0067
	298.35	0.3231	0.2531	105.6	0.0071
	303.45	0.4293	0.3401	90.76	−0.0094
	308.65	0.5882	0.4668	75.48	0.0095
	313.35	0.7593	0.6014	65.53	0.0061
	318.15	0.9771	0.7756	57.03	0.0016
	323.25	1.2602	0.9975	49.69	−0.0084
dichloromethane	288.15	1.0822	0.5845	24.00	0.0011
	291.55	1.2671	0.6875	22.42	−0.0012
	294.45	1.4516	0.7851	21.14	−0.0010
	298.35	1.7521	0.9478	19.50	0.0024
	303.45	2.1901	1.1866	17.76	−0.0025
	308.65	2.7632	1.4963	16.06	0.0012
THF	291.95	0.9214	0.5865	31.16	0.0004
	298.25	1.1151	0.7333	29.62	0.0020
	303.65	1.3677	0.8738	28.58	−0.0025
	307.95	1.5854	1.0079	27.69	−0.0021
	313.25	1.8788	1.1932	26.57	0.0020
	318.35	2.1771	1.3916	25.71	0.0002
	323.15	2.4953	1.5963	24.94	−0.0010
	328.25	2.9224	1.8525	24.10	0.0010
acetonitrile	293.25	0.1165	0.1790	180.3	−0.0135
	298.15	0.2171	0.2462	156.4	−0.0035
	303.25	0.2886	0.3245	134.3	0.0158
	308.15	0.3689	0.4141	118.5	0.0170
	313.55	0.4712	0.5260	106.1	−0.0049
	318.25	0.5863	0.6604	95.30	−0.0084
	323.15	0.7432	0.8285	84.08	0.0044
	328.35	0.9222	1.0302	76.03	−0.0107
	333.15	1.1499	1.2880	67.58	0.0035
toluene	293.15	0.6667	0.3342	44.28	−0.0115
	298.25	0.8679	0.4340	39.30	0.0047
	303.15	1.0785	0.5389	35.85	0.0005
	308.35	1.3687	0.6838	32.11	0.0120
	313.55	1.6988	0.8487	29.39	0.0053
	318.25	2.0468	1.0238	27.30	−0.0041
	323.15	2.4879	1.2441	25.10	−0.0046
	328.35	3.0502	1.5248	22.97	−0.0027
	333.15	3.6659	1.8359	21.17	0.0009
	338.25	4.4176	2.2127	19.58	−0.0009
chloroform	293.25	1.7184	0.6627	17.33	0.0035
	298.15	2.1405	0.8249	15.86	−0.0064
	303.05	2.7034	1.0414	14.30	0.0026
	308.05	3.3397	1.2890	13.11	−0.0043
	313.65	4.2681	1.6495	11.74	0.0046
	318.55	5.1896	2.0067	10.83	−0.0012
	323.05	6.2785	2.4308	9.932	0.0089
	328.75	7.7069	2.9848	9.187	−0.0070
1,2-dichloroethane	293.25	0.4095	0.1903	72.65	−0.0077
	298.35	0.5852	0.2693	58.33	0.0143
	303.15	0.7646	0.3530	50.56	−0.0228
	308.15	1.0692	0.4971	41.01	0.0055
	313.25	1.4977	0.6971	33.14	0.0387
	318.55	1.9483	0.9067	28.84	−0.0015
	323.15	2.5197	1.1724	24.79	−0.0017
	328.55	3.2406	1.5084	21.72	−0.0429
	333.15	4.1878	1.9526	18.56	−0.0271
	338.25	5.8219	2.7166	14.85	0.0420

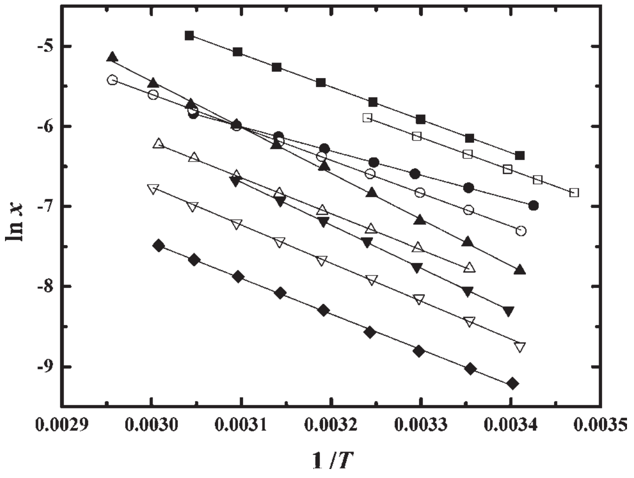


Figure 3. Mole fraction solubilities of TPP in selected solvents: experimental data: ■, chloroform; □, dichloromethane; ●, THF; ○, toluene; ▲, 1,2-dichloroethane; △, ethyl acetate; ▼, acetone; ▽, acetonitrile; ◆, ethanol; —, solubility line calculated from eq 2.

The solubilities were correlated as a function of temperature by

$$\ln x = A + B/T \tag{2}$$

The parameters A and B for each solvent are listed in Table 4. The root-mean-square relative errors (RSD), defined by eq 3, are also presented in Table 4. The smoothed data calculated from eq 2 are compared with the data listed in Table 3.

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

Table 4. Parameters of eq 2 and Root-Mean Square Deviations of the Measured Solubility Calculated from eq 3 TPP in Selected Solvents

solvent	A	B	RSD
ethanol	6.1211	−4521.4	0.0036
ethylacetate	7.3038	−4499.9	0.0077
acetone	9.8223	−5330.6	0.0074
dichloromethane	7.3681	−4093.0	0.0017
THF	3.3797	−3027.4	0.0016
acetonitrile	7.3743	−4712.7	0.0104
toluene	6.7655	−4122.4	0.0061
chloroform	7.6201	−4102.8	0.0054
1,2-dichloroethane	11.780	−5739.7	0.0258

Table 5. Solubility Parameter and Liquid Molar Volume of Selected Solvents[22] and TPP

substance	δ_i $(\mathrm{J \cdot cm^{-3}})^{1/2}$	$10^6\ V_i$ $\mathrm{m^3 \cdot mol^{-1}}$
ethanol	26.42	58.52
ethyl acetate	18.35	98.59
acetone	19.77	73.93
dichloromethane	20.38	64.43
THF	19.13	81.94
acetonitrile	24.09	52.68
toluene	18.35	106.6
chloroform	19.03	80.66
1,2-dichloroethane	20.25	79.44
TPP	21.80	236.9

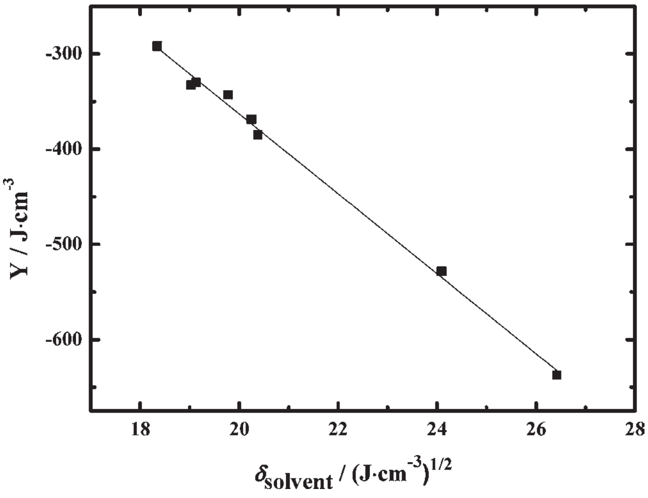


Figure 4. Residual function Y for TPP versus solvent solubility parameters $\delta_{\mathrm{solvent}}$: regression line: $Y = -41.979\ \delta_{\mathrm{solvent}} + 476.65$ ($R^2 = 0.9961$).

Table 6. Parameters of eq 7 and AAD of Measured Activity Coefficients with the Calculated Results from eqs 6 and 8 for Solutes in Selected Solvents

solvent	a	b	AAD %
ethanol	0.04724	$-4.8 \cdot 10^{-5}$	0.30
ethylacetate	0.07817	$-1.2 \cdot 10^{-4}$	0.66
acetone	0.11543	$-2.1 \cdot 10^{-4}$	0.72
dichloromethane	0.06510	$-1.1 \cdot 10^{-4}$	0.14
THF	0.01859	$5.2 \cdot 10^{-5}$	0.13
acetonitrile	0.07317	$-9.3 \cdot 10^{-5}$	0.91
toluene	0.06069	$-9.2 \cdot 10^{-5}$	0.49
chloroform	0.06199	$-1.2 \cdot 10^{-4}$	0.46
1,2-dichloroethane	0.12964	$-2.8 \cdot 10^{-4}$	2.01

where calc stands for the calculated values and N is the number of experimental points. The results show that eq 2 can be used to correlate the solubility data. Within the temperature range of the measurements, the solubilities of TPP in all of the investigated solvents increased with an increase in temperature. The solubility of TPP in chloroform shows the highest value and in ethanol shows the lowest values. The order of mole fraction solubility of TPP in the select solvent at (288.15 to 323.15) K is chloroform > dichlormethane > THF > toluene > 1,2-dichloroethane > ethyl acetate > acetone > acetonitrile > ethanol.

To obtain the activity coefficients of TPP in the solvents from the experimental data, the following equilibrium equation for solute was derived with an approximation[20] for the term of the difference of the heat capacities between the solid and the liquid phases of the solute being negligible.

$$\ln \frac{1}{x_1 \gamma_1} = \frac{\Delta_{\mathrm{fus}} H}{R T_{\mathrm{m}}} \left(\frac{T_{\mathrm{m}}}{T} - 1 \right) \tag{4}$$

where $\Delta_{\mathrm{fus}}H$ refers to the enthalpy of fusion; T_{m} is the melting temperature; R is the gas constant; and x_1 and γ_1 refer to the mole fraction and activity coefficient of solute in the saturated solution, respectively. With the experimental x_1, T, $\Delta_{\mathrm{fus}}H$, and T_{m} values known, the activity coefficients of TPP in different solvents were obtained from eq 4. The results are listed in Table 3. The experimental data shows that the higher the temperature, the greater the solubility and the smaller the activity coefficient in all selected solvents. For example, the solubility of TPP in chloroform shows the largest value and in ethanol shows the lowest value, while its activity coefficient in chloroform is the lowest and in ethanol is the largest at same temperature. A relatively small solubility and a large activity coefficient result from the deviation from ideal behavior.

Correlation. The Scatchard−Hildebrand activity coefficient model for regular solution,[21] eq 5, will be used to correlate the activity coefficients listed in Table 6. On the basis of this model and a further simplification, the activity coefficient model used for the correlation in this paper can be expressed as

$$RT \ln \gamma_1 = V_1 {x_2}^2 (\delta_1 - \delta_2)^2 \tag{5}$$

where γ_1 is the activity coefficient of solute, V_1 is the molar volume of the subcooled liquid of pure solid solute, δ_1 and δ_2 are the solubility parameters of the solute and solvent, R is the gas constant, T is temperature in kelvin, and x_2 refers the mole fraction of the solvent. The value of molar volume of the subcooled liquid for solid solute TPP was estimated using advanced chemistry development (ACD/Laboratories) Software V11.02, and the results are listed in Table 5. The solubility parameter δ_2 of the solvents are obtained from literature.[22] A residual function Y can

Table 7. Coefficients of eq 8, Infinite Dilution Activity Coefficients at 298.15 K, and Values of $H_1^{E,\infty}$ Derived from eq 9 for Solutes in Selected Solvents

		b'		$H_1^{E,\infty}$
solvent	a'	K	$\gamma_{1(298.15K)}^{\infty}$	$kJ \cdot mol^{-1}$
ethanol	−1.5803	2159.0	287.4	17.9
ethylacetate	−2.7067	2121.6	82.20	17.6
acetone	−5.2275	2952.6	107.3	24.5
dichloromethane	−2.7340	1705.7	19.82	14.2
THF	1.2355	645.07	29.94	5.36
acetonitrile	−2.7986	2340.1	156.0	19.4
toluene	−2.0968	1723.2	39.76	14.3
chloroform	−2.8806	1684.3	15.94	14.0
1,2-dichloroethane	−7.0772	3329.9	59.82	27.7

be rearranged from eq 5:

$$Y = \frac{RT \ln \gamma_1}{V_1 {x_2}^2} - {\delta_2}^2 = -2\delta_2\delta_1 + {\delta_1}^2 \qquad (6)$$

The equation shows that there is a linear relation between Y and the solvent solubility parameter δ_2 for a given solvent and temperature T ($T = 298.15$ K). The value of the solute solubility parameter δ_1 can be obtained from the slope of this line. This is displayed in Figure 4. The result is also listed in Table 5.

The prediction accuracy of the simplified Scatchard–Hildebrand regular solution model eq 5 can be further improved if a binary interaction parameter l_{12} is added to eq 5 as given by[20]

$$RT \ln \gamma_1 = V_1 {x_2}^2[(\delta_1 - \delta_2)^2 + 2l_{12}\delta_1\delta_2 \qquad (7)$$

In this work, the parameter l_{12} was correlated as a function of temperature by

$$l_{12} = a + bT \qquad (8)$$

The parameters a and b for each solvent obtained by regression from the experimental data are listed in Table 6. The average absolute relative error (AAD) of the activity coefficients calculated by eq 7 is also list in Table 6 where the AAD is defined as

$$\text{AAD} = \frac{1}{N}\sum_i \left| \frac{\gamma_1^{\text{exp}} - \gamma_1^{\text{cal}}}{\gamma_1^{\text{exp}}} \right| \qquad (9)$$

where exp stands for experimental values, cal stands for calculated values respectively of the activity coefficients, and N is the number of data points.

The activity coefficient at infinite dilution of solutes γ_1^∞ are extrapolated based on eq 7 to satisfy the condition $x_2 \to 1$. The results of γ_1^∞ were correlated with temperature by the following equation:

$$\ln \gamma_1^\infty = a' + b'/T \qquad (10)$$

According to the Gibbs–Helmholtz equation, the value for the partial molar excess enthalpy at infinite dilution $H_1^{E,\infty}$ can be directly obtained from the slope of a straight line derived from eq 10[23]

$$\frac{\partial \ln \gamma_1^\infty}{\partial(1/T)} = \frac{H_1^{E,\infty}}{R} \qquad (11)$$

The coefficients a', b', and the values of $H_1^{E,\infty}$ derived from eq 11 are listed in Table 7.

The infinite dilution activity coefficients at 298.15 K are calculated and listed in Table 7. There are only little differences between the values listed in Table 7 and the results in Table 3 at the same temperature. These results are useful for the estimating of the heat of dissolution of the phosphorus-containing compounds in the selected solvents.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{1}H NMR, ^{31}P NMR spectra of TPP, and uncertainty analysis for the melting point and enthalpy of fusion of TPP. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Shin, Y. J.; Shin, Y. R.; Park, S. J.; Shin, J. S. Flame retardants containing cyclophosphazene ring for acrylonitrile-butadiene-styrene copolymers. *Polymer* **2007**, *31*, 273–277.

(2) Onishi, H.; Tan, J. Cyclic phosphorus compounds as flame retardants, and halogen-free fire-resistant thermoplastic resin compositions containing them. J.P. Patent 11,217,462, 1999.

(3) Horacek, H.; Pieh, S. The importance of intumescent systems for fire protection of plastic materials. *Polym. Int.* **2000**, *49*, 1106–1114.

(4) Wu, Q.; Lu, J. P.; Qu, B. J. Preparation and characterization of microcapsulated red phosphorus and its flame-retardant mechanism in halogen-free flame retardant polyolefins. *Polym. Int.* **2003**, *52*, 1326–1331.

(5) Shin, Y. J.; Ham, Y. R.; Kim, S. H.; Lee, D. H.; et al. Application of cyclophosphazene derivatives as flame retardants for ABS. *J. Ind. Eng. Chem.* **2010**, *16*, 364–367.

(6) Levchik, G. F.; Grigoriev, Y. V.; Balabanovich, A. I.; Levchik, S. V.; Klatt, M. Phosphorus-nitrogen containing fire retardants for poly(butylene terephthalate). *Polym. Int.* **2000**, *49*, 1095–1100.

(7) Sozzani, P.; Comotti, A.; Bracco, S.; Simonutti, R. A family of supramolecular frameworks of polyconjugated molecules hosted in aromatic nanochannels. *Angew. Chem., Int. Ed.* **2004**, *43*, 2792–2797.

(8) Chae, H. K.; Siberio-Perez, D. Y.; Kim, J. Y.; Eddaoudi, G. M.; Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M. A route to high surface area, porosity and inclusion of large molecules in crystals. *Nature* **2004**, *427*, 523–527.

(9) Ward, M. D. Molecular Fuel Tanks. *Science* **2003**, *300*, 1104–1105.

(10) Kuznicki, S. M.; Bell, V. A.; Nair, S.; Hillhouse, H. W.; Jacubinas, R. M.; Braunbarth, C. M.; Toby, B. H.; Tsapatsis, M. A titanosilicate molecular sieve with adjustable pores for size-selective adsorption of molecules. *Nature* **2001**, *412*, 720–724.

(11) Gahungu, G.; Zhang, B.; Zhang, J. P. Influence of the substituted side group on the molecular structure and electronic properties of TPP and related implications on organic zeolites use. *J. Phys. Chem. B* **2007**, *111*, 5031–5033.

(12) Couderc, G.; Hertzsch, T.; Behrnd, N. R.; Kraemer, K.; Hulliger, J. Reversible sorption of nitrogen and xenon gas by the guest-free zeolite tris(o-phenylenedioxy)cyclotriphosphazene (TPP). *Microporous Mesoporous Mater.* **2006**, *88*, 170–175.

(13) Sozzani, P.; Comotti, A.; Bracco, S.; Simonutti, R. Cooperation of multiple CH-π interactions to stabilize polymers in aromatic nanochannels as indicated by 2D solid state NMR. *Chem. Commun.* **2004**, *7*, 768–769.

(14) Hertzsch, T.; Budde, F.; Weber, E.; Hulliger, J. Supramolecular-wire confinement of I2 molecules in channels of the organic zeolite

tris(o-phenylenedioxy)-cyclotriphosphazene. *Angew. Chem., Int. Ed.* **2002**, *41*, 2281–2284.

(15) Allcock, H. R.; Walsh, E. J. Phosphonitrilic compounds. X.[1] synthesis of spirophosphazenes with five-, six-, and seven-membered exocyclic rings at phosphorus. *Inorg. Chem.* **1971**, *10*, 1643–1647.

(16) Guo, X. Z.; Wang, L. S.; Tian, N. N. Solubilities of (2,5-dihydroxyphenyl) diphenyl phosphine oxide in selected solvents. *J. Chem. Eng. Data* **2010**, *55*, 1745–1749.

(17) Allcock, H. R. Trispiro[1,3,5,2,4,6-triazatriphosphorine-2,2′:4,2″:6,2‴-tris[1,3,2] benzodioxaphospholes. U.S. Patent 3,294,872, 1966.

(18) Wang, Z. W.; Sun, Q. X.; Wu, J. S.; Wang, L. S. Solubilities of 2-carboxyethyl phenylphosphinic acid and 4-carboxyphenylphenylphinic acid in water. *J. Chem. Eng. Data* **2003**, *48*, 1073–1075.

(19) Guo, X. Z.; Wang, L. S. Solubilities of phosphorus-containing compounds in selected solvents. *J. Chem. Eng. Data* **2010**, *55*, 4709–4720.

(20) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed.; Prentice Hall: New York, 1999.

(21) Chol, P. B.; Mclaughlin, E. Solubility of aromatic hydrocarbon solids in pyridine and thiophene. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 46–51.

(22) Yaws, C. L. *Chemical properties handbook*; McGraw-Hill: New York, 1999.

(23) Zhou, Q.; Wang, L. S. Activity coefficients at infinite dilution of alkanes, alkenes, and alkyl benzenes in 1-butyl-3-methylimidazolium tetrafluoroborate using gas-liquid chromatography. *J. Chem. Eng. Data* **2006**, *51*, 1698–1701.