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Solubilities of Phenylphosphinic Acid, Methylphenylphosphinic Acid, Hexachlorocyclotriphosphazene, and Hexaphenoxycyclotriphosphazene in Selected Solvents

Na-Na Tian, Li-Sheng Wang,* Mi-Yi Li, Yi Li, and Ru-Yi Jiang

School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, People's Republic of China

S *Supporting Information*

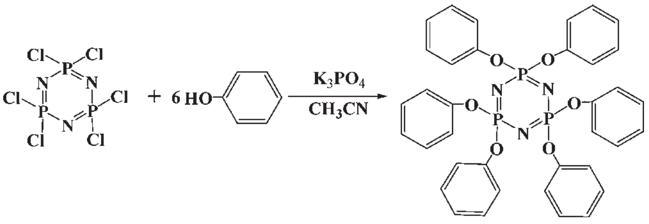
ABSTRACT: Phenylphosphinic acid (PPA), methylphenylphosphinic acid (MPPA), hexachlorocyclotriphosphazene (HCCP), and hexaphenoxycyclotriphosphazene (HPCCP) were prepared and characterized by elemental analysis, nuclear magnetic resonance, differential scanning calorimetry, and thermogravimetric analysis. Using a static analytical method, the solubilities of PPA, MPPA, HCCP, and HPCCP were measured in ten solvents and correlated with an empirical equation. The calculated results showed good agreement with the experimental data. Furthermore, 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

Elemental phosphorus and its various compounds have been used to flame retard a wide variety of polymer-based materials for several decades. Environmental considerations have paved the way in recent years for the increased use of phosphorus-based flame retardants as alternatives to the halogen-containing compounds.

Phenylphosphinic acid (hereafter abbreviated as PPA; its formula is shown in Figure 1) (CAS RN 1779-48-2) has been widely used in a variety of fields.[1−3] Organic titanate containing phenyl phosphinic acid catalyzed polyester exhibits low aldehyde formation during melt processing steps as well as excellent color, and the solid state polymerization rates of polyester are increased.[4] Moreover, it is also used as a modifying agent for use in polyamides, an improver of polysiloxane resins, an antioxidant, and a free radical promoter in emulsion polymerization.[5] Methylphenylphosphinic acid (hereafter abbreviated as MPPA; its formula is shown in Figure 1) (CAS RN 4271-13-0) has been usually used as polymer's additive. Compositions based on branched polyamides including MPPA exhibit good fire resistance, mechanical properties, and heat resistance.[6] Polyimides and polyquinoxalines were modified by MPPA and molded to give self-lubricating antifriction materials with good hardness, flexibility, and reduced wear at elevated temperature.[7] Besides, it is also used for coatings[8] and as bifunctional catalysis for organic reactions of arylamine.[9]

Cyclic phosphazene is a kind of inorganic−organic compound with a backbone of alternating phosphorus and nitrogen atom single and double bonds. Hexachlorocyclotriphosphazene (hereafter abbreviated as HCCP; its formula is shown in Figure 1) (CAS RN 940-71-6) was the first phosphazene compound obtained and the main raw materials for the production of cyclic phosphazene and polyphosphazene. The chloride atoms on the phosphorus atoms of hexachlorocyclotriphosphazene are extremely reactive and can be substituted with many nucleophilic reagents for synthesis of various functional organic cyclic phosphazenes. The cyclic phosphazene compound is very suitable for flame-retardant materials because of its high oxygen index, low smoke emissions, low corrosiveness, and low toxicity of the combustion gases.[10] In addition, it can improve physical and mechanical properties of epoxy resin[11,12] and can also be used as drugs for the treatment of inflammatory diseases, e.g., autoimmune diseases.[13]



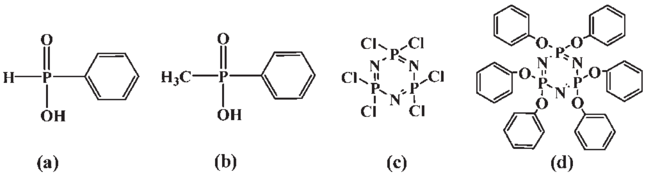


Figure 1. Structures of compounds related in this work: (a) phenylphosphinic acid (PPA), (b) methylphenylphosphinic acid (MPPA), (c) hexachlorocyclotriphosphazene (HCCP), (d) hexaphenoxycyclotriphosphazene (HPCCP).

Hexaphenoxycyclotriphosphazene (hereafter abbreviated as HPCCP; its formula is shown in Figure 1) (CAS RN 1184-10-7), which belongs to the derivatives of HCCP, can be prepared from phenol in a reaction with HCCP and has been widely used as flame-retardant additives of various resin compositions for improving their properties such as thermoplastic resin composition,[14] polyamide,[15] and epoxy resin.[16]

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Table 1. Characterization Data of Melting Point and Elemental Analysis for PPA, MPPA, HCCP, and HPCCP and Comparison with the Literature Values

	melting point/K		
compd	exp.[a]	lit.	elemental analysis (%, cal)
PPA	356.00	353.15 to 356.15;[24] 357.15;[25] 353.15[26]	C, 51.31 % (50.72 %); H, 5.01 % (4.97 %)
MPPA	409.35	409.15 to 409.65[27]	C, 53.12 % (53.85 %); H, 5.25 % (5.81 %)
HCCP	385.86	385.15 to 386.15;[28] 384.15 to 386.15[29]	N, 11.98 % (12.09 %)
HPCCP	387.11	384.15 to 385.15[22]	C, 62.08 % (62.34 %); H, 4.36 % (4.36 %); N, 6.03 % (6.06 %)

[a] The uncertaity of the melting point measurement is 0.26 K.

Table 2. Characterization Data of ^{1}H NMR and ^{31}P NMR for PPA, MPPA, HCCP, and HPCCP and Comparison with Literature Values

	^{1}H NMR (δ, ppm)		^{31}P NMR (δ, ppm)	
compd	exp.	lit.	exp.	lit.
PPA	6.14 (d, 1H), 7.47 to 7.79 (m, 5H), 12.64 (d, 1H)	6.16 (d, 1H), 7.44 to 7.80 (m, 5H), 11.28 (d, 1H)[23]	22.09	21.52[23]
MPPA	1.51 to 1.62 (m, 3H), 7.26 to 7.75 (m, 5H), 10.53 (d, 1H)		44.45	
HCCP			19.44	20.30,[28] 20.44[29]
HPCCP	6.92 to 7.18 (m, 5H)	6.85 to 7.18 (m, 5H)	9.37	8.45[22]

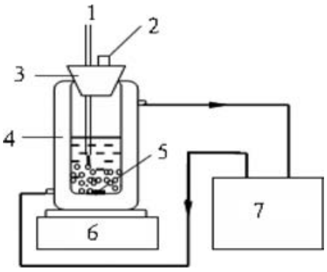

Figure 2. Schematic diagram of the experimental apparatus: 1, thermocouple; 2, sample gauge; 3, rubber plug; 4, jacket; 5, equilibrium cell; 6, magnetic stirrer; 7, water circulator bath.

Table 3. Results of Differential Scanning Calorimeter (DSC) Measurement of PPA, MPPA, HCCP, and HPCCP

substance	enthalpy of fusion/kJ·mol^{-1}	relative uncertainty/%
PPA	12.80	0.42
MPPA	25.45	0.25
HCCP	19.61	0.67
HPCCP	51.07	0.52

The thermal processing of polymers is under high temperature, and the flame-retardant additives for polymer should have good thermal stability and high purity. PPA can be prepared according to a U.S. patent.[17] MPPA was obtained by the hydrolysis of methyl methylphenylphosphinate and recrystallized from ethanol.[18]

To prepare HPCCP, a solution of sodium phenoxide in an anhydrous solvent is added to a solution of HCCP. A variety of organic solvents have been used for substitution reaction of this tape.[19] Knowledge of solubilities of these compounds in different solvents is very important for their preparation and purification. However, to the best of our knowledge, few data are found in the literature.[20] The solubilities of PPA, MPPA, HCCP, and HPCCP in selected organic solvents have not been reported in the literature. In this study, the solubilities of the four organic phosphorus compounds in ten solvents were systematically measured.

EXPERIMENTAL SECTION

Materials. PPA was provided by Shandong Wan Zhao Co., Ltd. MPPA was provided by Yunnan Jin Shan Co., Ltd. HCCP was purchased from Zhangjiagang Xinyi Chemical Co., Ltd. and recrystallized from heptanes before use. All the solvents were analytical grade reagents, which were purchased from Beijing Chemical Factory. Their mass fraction purities were all higher than 0.99. They were used without further purification. The water is double distilled before use.

Apparatus and Procedure. The melting points and enthalpy of fusion were determined with a DSC Q600 differential scanning calorimeter (DSC) in flowing nitrogen at a heating rate of 10 K·min^{-1}. The elemental analysis was performed on an Elementar Vario EL element analyzer. ^{1}H NMR and ^{31}P NMR spectra were obtainned with a BrukerARX-400 and JEOL ECA-600, respectively. Thermogravimetric analysis (TGA) was carried out with an SDT Q600 thermogravimetric analyzer at a heating rate of 10 K·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.[21] Figure 2 shows the schematic diagram of the experimental apparatus. 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 TG328B, Shanghai Balance Instrument Works Co.) with an uncertainty of ± 0.1 mg was used during the mass measurements.

Synthesis of HPCCP. HPCCP was prepared according to the literature.[22] Hexachlorocyclotriphosphazene (8.6 g, 0.025 mol), phenol (14.0 g, 0.15 mol), anhydrous potassium phosphate (60.0 g, 0.28 mol), and 500 mL of acetonitrile were placed in a 1000 mL flask connected with a drying tube. The mixture was refluxed for 3 h and then cooled to room temperature. The solid was filtered and washed twice with 50 mL of acetonitrile. The filtrate and the washings were combined, and the solvent was distilled under reduced pressure. The

Table 4. Mole Fraction Solubilities (x) and Activity Coefficients (γ) of PPA in the Selected Solvents

solvent	T/K	x	γ	$(x - x^{\mathrm{calcd}})/x$
methanol	293.55	0.1726	2.311	−0.0024
	298.15	0.2154	2.051	−0.0246
	303.75	0.2795	1.652	0.0257
	308.35	0.3437	1.471	0.0104
	313.45	0.4292	1.276	0.0112
	318.25	0.5256	1.152	−0.0160
	323.65	0.6554	0.991	−0.0053
ethanol	283.25	0.0889	3.707	0.0085
	288.65	0.1124	3.296	−0.0082
	293.15	0.1357	2.968	−0.0114
	298.35	0.1675	2.561	0.0153
	303.45	0.2046	2.349	−0.0126
	308.25	0.2454	2.069	0.0104
	313.45	0.2969	1.879	0.0008
	318.55	0.3559	1.691	−0.0006
	323.35	0.4198	1.540	−0.0017
ethyl acetate	293.45	0.0144	27.68	−0.0075
	298.15	0.0185	23.39	−0.0547
	303.25	0.0275	17.16	0.0305
	313.45	0.0494	11.27	0.0228
	318.25	0.0661	9.062	0.0477
	328.35	0.1073	6.477	−0.0014
	333.25	0.1356	5.491	−0.0151
	338.55	0.1739	4.602	−0.0264
dichloromethane	288.15	0.0292	12.38	0.0148
	293.35	0.0386	10.29	−0.0196
	296.25	0.0458	9.126	−0.0183
	298.15	0.0528	8.182	0.0144
	303.45	0.0709	6.676	0.0093
	308.25	0.0910	5.625	−0.0022
acetone	293.35	0.0305	13.02	−0.0006
	298.15	0.0448	9.648	0.0182
	303.55	0.0671	7.060	0.0246
	308.25	0.0879	5.823	−0.0408
	313.45	0.1243	4.475	−0.0539
	318.25	0.1862	3.217	0.0304
	323.35	0.2559	2.526	0.0186
chloroform	293.15	0.1336	2.965	0.0116
	298.45	0.1573	2.763	−0.0179
	303.25	0.1861	2.534	−0.0189
	308.25	0.2284	2.242	0.0154
	313.15	0.2691	2.057	0.0175
	318.35	0.3150	1.904	0.0090
	323.25	0.3568	1.809	−0.0185
2-ethoxyethanol	288.15	0.1238	2.921	0.0267
	293.85	0.1359	2.951	−0.0048
	298.25	0.1480	2.927	−0.0129
	303.45	0.1647	2.873	−0.0126
	313.15	0.2053	2.697	0.0174
	318.25	0.2265	2.645	0.0204
	323.65	0.2395	2.711	−0.0211
	328.25	0.2593	2.676	−0.0223
	333.45	0.2834	2.634	−0.0218
	338.35	0.3084	2.588	−0.0181
	343.25	0.3435	2.480	0.0112
	348.25	0.3719	2.442	0.0128
	353.25	0.3970	2.435	0.0028
	358.55	0.4340	2.376	0.0137
	363.15	0.4590	2.372	0.0041
toluene	293.15	0.0187	21.18	−0.0582
	298.35	0.0282	15.38	0.0199
	303.45	0.0389	12.16	0.0233
	313.25	0.0652	8.510	−0.0426
	318.15	0.0934	6.402	0.0406
	323.35	0.1247	5.182	0.0446
	328.15	0.1615	4.290	0.0479
	333.55	0.1985	3.767	−0.0234
	338.45	0.2545	3.141	−0.0193
	343.15	0.3158	2.694	−0.0320
	348.35	0.4130	2.202	−0.0084
benzene	299.15	0.0540	8.147	0.0198
	303.65	0.0709	6.695	−0.0537
	308.55	0.1108	4.645	0.0293
	313.25	0.1454	3.812	−0.0370
	318.45	0.2254	2.665	0.0382
	323.15	0.3085	2.089	0.0342
	328.35	0.4152	1.674	−0.0094
	333.15	0.5544	1.341	−0.0259
water	297.79	0.0095	45.42	0.0312
	300.25	0.0111	40.42	−0.0033
	302.40	0.0129	35.93	−0.0161
	305.22	0.0159	30.59	−0.0238
	309.93	0.0218	24.17	−0.0643
	312.84	0.0305	18.08	0.0604
	318.15	0.0433	13.81	0.0368
	323.35	0.0572	11.29	−0.0406
	328.15	0.0850	8.152	0.0361
	333.45	0.1102	6.774	−0.0461
	338.25	0.1606	4.965	0.0305
	343.15	0.2076	4.097	−0.0096

residue was dissolved in ethyl acetate and washed with 10 % NaOH solution three times and then with water and dried over anhydrous sodium sulfate. After filtration and evaporation, the product was purified by recrystallization from ethyl acetate and dried to get HPCCP (14.23 g). The yield was 82 %.

Characterization of Compounds. Characterization data of NMR, EA, and melting point for PPA, MPPA, HCCP, and HPCCP with the corresponding literature values[23−29] are listed in Tables 1 and 2. The results obtained are in good agreement with those listed in the literature. On the basis of the above analysis, the mass fraction purity of PPA, MPPA, HCCP, and HPCCP used in this work was higher than 95 %.

Solubility Measurement. The solubilities were measured by a gravimetric method.[30] For each measurement, an excess mass of PPA, MPPA, HCCP, and HPCCP 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

Table 5. Mole Fraction Solubilities (x) and Activity Coefficients (γ) of MPPA in the Selected Solvents

solvent	T/K	x	γ	$(x - x^{\text{calcd}})/x$
ethanol	293.25	0.2055	0.317	−0.0134
	298.15	0.2658	0.287	0.0222
	303.35	0.3325	0.270	0.0191
	308.25	0.3901	0.266	−0.0282
	313.55	0.4861	0.250	−0.0248
	318.45	0.6142	0.227	0.0154
	323.15	0.7336	0.216	0.0127
	328.25	0.8716	0.208	−0.0047
ethyl acetate	288.35	0.0484	1.142	−0.0114
	293.15	0.0621	1.044	0.0145
	298.25	0.0750	1.020	−0.0270
	303.45	0.0941	0.955	−0.0263
	313.35	0.1516	0.796	0.0398
	318.15	0.1818	0.760	0.0318
	328.15	0.2654	0.683	0.0324
	333.35	0.3042	0.681	−0.0182
	338.15	0.3593	0.651	−0.0198
	343.25	0.4277	0.619	−0.0188
dichloromethane	288.55	0.0465	1.196	0.0111
	293.65	0.0697	0.946	−0.0289
	296.15	0.0904	0.791	0.0192
	298.35	0.1045	0.734	−0.0200
	303.25	0.1640	0.545	0.0306
	308.35	0.2347	0.444	−0.0135
methanol	298.35	0.3172	0.242	−0.0010
	303.15	0.3432	0.260	−0.0024
	308.15	0.3718	0.279	−0.0032
	313.25	0.4060	0.296	0.0049
	318.35	0.4392	0.317	0.0063
	323.15	0.4708	0.337	0.0053
	328.25	0.4987	0.364	−0.0099
chloroform	293.15	0.1117	0.581	0.0054
	298.25	0.1317	0.581	−0.0078
	303.15	0.1558	0.572	−0.0050
	308.35	0.1883	0.554	0.0147
	313.15	0.2142	0.560	−0.0082
	318.45	0.2552	0.546	0.0050
	323.15	0.2882	0.550	−0.0129
	328.15	0.3398	0.533	0.0080
toluene	293.25	0.1201	0.542	−0.0048
	298.35	0.1470	0.522	0.0178
	303.25	0.1675	0.534	−0.0180
	308.35	0.2043	0.510	0.0128
	313.15	0.2292	0.524	−0.0255
	323.25	0.3271	0.486	0.0231
	328.35	0.3768	0.484	0.0168
	333.25	0.4182	0.494	−0.0167
	338.15	0.4792	0.488	−0.0145
	343.45	0.5643	0.471	0.0086
2-ethoxyethanol	298.15	0.2522	0.302	−0.0035
	303.15	0.2889	0.308	0.0170
	313.25	0.3479	0.346	−0.0185
	318.15	0.3972	0.348	0.0117
	323.35	0.4406	0.362	0.0102
	328.25	0.4716	0.385	−0.0182
	333.15	0.5193	0.397	−0.0150
	338.45	0.5866	0.402	0.0090
	343.35	0.6392	0.415	0.0071
	348.35	0.6965	0.429	0.0058
	353.15	0.7509	0.444	−0.0002
benzene	293.25	0.0386	1.686	0.0093
	298.15	0.0541	1.409	−0.0209
	303.15	0.0809	1.102	0.0186
	308.35	0.1126	0.926	−0.0153
	313.25	0.1625	0.741	0.0181
	318.15	0.2183	0.633	−0.0093
	323.25	0.3012	0.528	−0.0130
	328.15	0.4194	0.432	0.0150
	333.35	0.5628	0.368	−0.0029
acetone	293.15	0.0473	1.370	−0.0096
	298.15	0.0609	1.251	−0.0161
	303.25	0.0816	1.095	0.02053
	308.15	0.0995	1.042	−0.0190
	313.35	0.1268	0.952	−0.0206
	318.15	0.1649	0.838	0.0239
	323.25	0.2041	0.779	0.0124
water	298.15	0.0154	4.948	−0.0093
	303.35	0.0204	4.401	0.0286
	310.45	0.0270	4.109	−0.0055
	314.25	0.0320	3.876	−0.0005
	320.45	0.0414	3.563	−0.0005
	324.15	0.0477	3.416	−0.0073
	329.25	0.0579	3.221	−0.0137
	333.65	0.0679	3.076	−0.0229
	338.75	0.0865	2.744	0.0295
	343.45	0.0968	2.747	−0.0267
	348.25	0.1197	2.489	0.0172

the water bath approached a constant value, then the actual value of the 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[31]

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

Different dissolution times were tested to determine a suitable equilibrium time. It was found that 2 h was enough for PPA, MPPA, HCCP, and HPCCP 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

Table 6. Mole Fraction Solubilities (x) and Activity Coefficients (γ) of HCCP in the Selected Solvents

solvent	T/K	x	γ	$(x - x^{\text{calcd}})/x$
ethanol	298.45	0.0106	16.24	0.0312
	303.25	0.0164	10.96	−0.0503
	308.45	0.0295	7.262	−0.0074
	313.35	0.0487	4.988	$-4 \cdot 10^{-6}$
	319.85	0.0938	3.085	0.0217
	324.35	0.1464	2.237	0.0420
	328.15	0.1943	1.717	−0.0230
	333.55	0.3163	1.192	−0.0174
ethyl acetate	298.55	0.0701	2.387	$5.8 \cdot 10^{-5}$
	303.35	0.0829	2.283	−0.0017
	308.35	0.0988	2.183	0.0027
	313.45	0.1160	2.089	−0.0057
	319.95	0.1442	1.978	0.0044
	324.15	0.1635	1.912	0.0006
	328.05	0.1848	1.854	0.0063
	333.65	0.2149	1.776	−0.0066
diethyl ether	293.25	0.0944	1.541	0.0023
	296.15	0.1035	1.513	−0.0028
	299.05	0.1140	1.486	−0.0016
	301.15	0.1225	1.467	0.0027
	303.25	0.1303	1.449	−0.0021
	305.15	0.1388	1.432	0.0014
THF	293.25	0.1772	0.820	0.0015
	299.15	0.1991	0.853	−0.0012
	303.15	0.2150	0.875	−0.0025
	308.35	0.2381	0.905	0.0010
	312.85	0.2592	0.930	0.0034
	318.95	0.2867	0.964	−0.0040
	323.15	0.3100	0.987	0.0021
	328.35	0.3374	1.016	−0.0002
acetone	293.15	0.0296	4.875	−0.0040
	300.45	0.0426	4.177	0.0110
	303.25	0.0478	3.945	−0.0042
	308.25	0.0600	3.570	−0.0023
	313.25	0.0743	3.242	−0.0065
	318.35	0.0937	2.947	0.0090
	322.95	0.11170	2.712	−0.0038
dichloromethane	293.15	0.1142	1.265	−0.0018
	298.05	0.1331	1.243	0.0019
	300.55	0.1435	1.232	0.0026
	303.35	0.1554	1.221	0.0001
	305.65	0.1653	1.211	−0.0045
	308.35	0.1795	1.200	0.0018
acetonitrile	293.15	0.0018	83.49	0.0067
	299.85	0.0025	68.65	0.0035
	303.25	0.0030	62.36	−0.0009
	308.45	0.0040	54.07	0.0062
	313.05	0.0049	47.84	−0.0209
	318.55	0.0066	41.53	−0.0022
	323.25	0.0082	36.93	−0.0113
	328.25	0.0105	32.72	0.0009
	332.35	0.0128	29.72	0.0211
	338.25	0.0162	25.97	−0.0028
2-ethoxyethanol	299.95	0.0322	5.572	0.0321
	303.35	0.0365	4.984	−0.0426
	308.35	0.0532	4.250	0.0474
	313.15	0.0635	3.664	−0.0393
	318.65	0.0862	3.108	−0.0287
	323.35	0.1158	2.712	0.0229
	328.05	0.1473	2.376	0.0272
	332.45	0.1715	2.107	−0.0369
	338.25	0.2303	1.806	−0.0167
	343.15	0.2988	1.593	0.0178
	348.35	0.3734	1.399	0.0086
	353.15	0.4568	1.245	0.0017
toluene	298.15	0.0585	2.822	−0.0037
	301.55	0.0645	2.798	−0.0032
	303.25	0.0677	2.787	−0.0030
	308.45	0.0782	2.752	−0.0024
	312.85	0.0880	2.724	−0.0018
	318.25	0.1013	2.692	−0.0012
	322.85	0.1138	2.665	−0.0006
	328.25	0.1298	2.634	$-4.8 \cdot 10^{-5}$
n-heptane	293.15	0.0046	31.27	−0.0053
	298.25	0.0069	24.73	0.0226
	303.35	0.0094	19.71	−0.0276
	308.45	0.0139	15.83	0.0168
	313.45	0.0182	12.86	−0.0385
	318.35	0.0266	10.55	0.0267
	323.05	0.0356	8.779	0.0242
	328.15	0.0462	7.234	−0.0214

value is given. The maximum standard deviation of each triplicate data is 0.24 %, and the minimum is 0.16 %. The estimated relative uncertainty of the solubility values based on error analysis and repeated observations was within 0.02.

RESULTS AND DISCUSSION

The results of DSC measurements are summarized in Table 3. An analysis report for the uncertaity of DSC measurement is provided in the Supporting Information. The TGA results show that there is a single-step decomposition, and no or very little residues remain for MPPA, HCCP, and HPCCP.

The mole fraction solubilities x of PPA, MPPA, HCCP, and HPCCP in selected solvents measured in this work are summarized in Tables 4 to 7 and plotted as $\ln x$ vs $1/T$ in Figures 3 to 7. From these figures, it can be seen that a trend of increasing solubility with temperature is observed.

The solubilities were correlated as a function of temperature by

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

The parameters A and B for each solvent are provided in the Supporting Information. The relative standard deviations (RSD) are also presented in the Supporting Information. The smoothed data calculated from eq 2 are compared with the experimental data, and the results are listed in Tables 4 to 7. The results show that eq 2 can be used to correlate the solubility data. Within the temperature range of the measurements, the solubilities of PPA, MPPA, HCCP,

Table 7. Mole Fraction Solubilities (x) and Activity Coefficients (γ) of HPCCP in the Selected Solvents

solvent	T/K	x	γ	$(x - x^{\text{calcd}})/x$
ethanol	298.25	0.0096	0.926	0.0075
	300.95	0.0099	1.076	−0.0006
	303.25	0.0102	1.215	−0.0030
	308.15	0.0110	1.564	−0.0072
	313.45	0.0119	2.012	$-7\cdot10^{-5}$
	318.75	0.0129	2.578	0.0029
	323.05	0.0136	3.150	−0.0002
	328.35	0.0147	3.981	0.0018
ethyl acetate	298.15	0.0592	0.148	0.0079
	300.95	0.0655	0.162	0.0085
	303.25	0.0699	0.178	−0.0082
	308.25	0.0829	0.208	−0.0098
	313.25	0.0983	0.241	−0.0067
	319.05	0.1194	0.284	0.0005
	323.15	0.1364	0.317	0.0055
	328.25	0.1588	0.366	0.0030
diethyl ether	293.15	0.0101	0.612	0.0010
	296.25	0.0122	0.633	0.0046
	299.05	0.0140	0.662	−0.0125
	300.35	0.0154	0.665	0.0078
	303.15	0.0178	0.694	−0.0076
	306.05	0.0211	0.708	0.0057
THF	293.25	0.1510	0.041	−0.0052
	298.15	0.1746	0.050	0.0115
	304.35	0.2001	0.067	−0.0086
	308.25	0.2225	0.078	0.0022
	314.25	0.2526	0.100	−0.0125
	318.45	0.2852	0.114	0.0125
	323.15	0.3151	0.137	0.0079
	328.25	0.3461	0.168	−0.0084
acetone	293.15	0.0295	0.209	0.0032
	296.45	0.0349	0.224	0.0076
	300.25	0.0423	0.240	0.0168
	304.35	0.0496	0.269	−0.0160
	308.25	0.0588	0.293	−0.0239
	314.25	0.0782	0.323	−0.0040
	318.35	0.0930	0.349	−0.0057
	323.15	0.1166	0.371	0.0209
dichloromethane	293.35	0.0990	0.063	0.0064
	295.95	0.1108	0.068	−0.0096
	300.35	0.1385	0.074	0.0023
	303.15	0.1583	0.078	0.0044
	306.05	0.1790	0.083	−0.0066
	310.35	0.2194	0.090	0.0030
acetonitrile	298.25	0.0040	2.227	0.0042
	303.55	0.0060	2.100	0.0164
	308.25	0.0082	2.100	−0.0241
	313.35	0.0122	1.960	0.0029
	318.35	0.0170	1.913	−0.0129
	323.45	0.0243	1.809	0.0038
	328.15	0.0332	1.741	0.0069
	333.25	0.0457	1.685	0.0021
2-ethoxyethanol	298.15	0.0065	1.350	−0.0023
	300.95	0.0074	1.433	0.0100
	303.25	0.0081	1.531	0.0019
	310.15	0.0106	1.842	−0.0142
	314.55	0.0126	2.036	−0.0104
	318.75	0.0148	2.240	−0.0093
	323.65	0.0182	2.454	0.0086
	328.05	0.0212	2.713	0.0036
	333.15	0.0259	2.951	0.0267
	343.25	0.0352	3.743	−0.0075
	348.35	0.0420	4.077	0.0052
	353.15	0.0478	4.545	−0.0136
toluene	298.05	0.0572	0.153	0.0028
	300.95	0.0650	0.164	0.0132
	303.35	0.0717	0.174	0.0151
	310.25	0.0904	0.217	−0.0196
	314.45	0.1063	0.240	−0.0145
	318.65	0.1233	0.268	−0.0187
	323.55	0.1499	0.295	0.0033
	327.95	0.1734	0.330	−0.0023
	333.15	0.2089	0.366	0.0108
	338.25	0.2461	0.411	0.0097
n-heptane	298.15	0.0035	2.516	0.0049
	303.45	0.0039	3.206	−0.0069
	308.35	0.0044	3.929	−0.0040
	313.05	0.0049	4.742	−0.0003
	318.25	0.0056	5.779	0.0074
	323.35	0.0062	7.076	$5.9\cdot10^{-5}$
	328.25	0.0069	8.453	0.0041
	333.15	0.0075	10.18	−0.0058

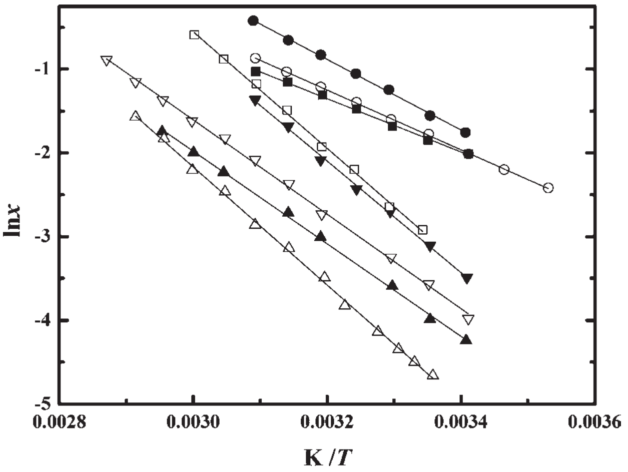

Figure 3. Mole fraction solubilities of phenylphosphinic acid in selected solvents. Experimental data: ●, methanol; ○, ethanol; ■, chloroform; □, benzene; ▼, acetone; ▽, toluene; ▲, ethyl acetate; △, water; —, solubility curve calculated from eq 2.

and HPCCP in all of the investigated solvents increased with increasing temperature.

PPA is a most soluble substance in all selected solvents, especially at a relatively higher temperature. In polar solvents,

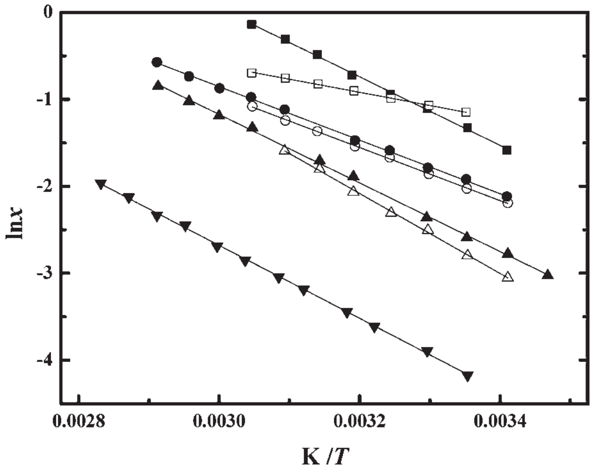

Figure 4. Mole fraction solubilities of methylphenylphosphinic acid in selected solvents. Experimental data: ■, ethanol; □, methanol; ●, toluene; ○, chloroform; ▲, ethyl acetate; Δ, acetone; ▼, water; —, solubility curve calculated from eq 2.

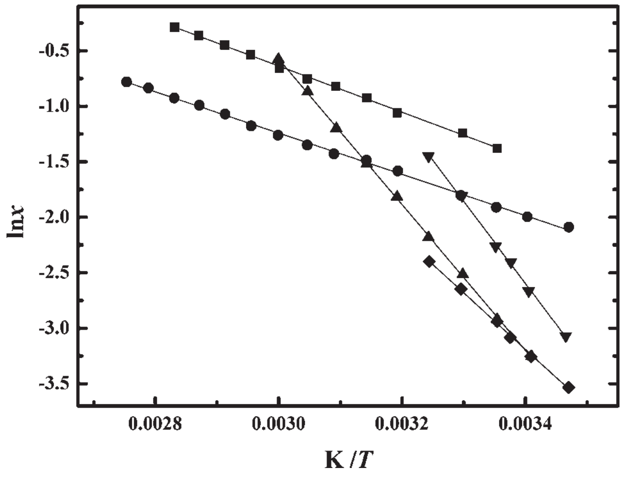

Figure 5. Mole fraction solubilities of phenylphosphinic acid (PPA) and methylphenylphosphinic acid (MPPA) in selected solvents. Experimental data: ●, PPA in 2-ethoxyethanol; ♦, PPA in dichloromethane; ■, MPPA in 2-ethoxyethanol; ▼, MPPA in dichloromethane; ▲, MPPA in benzene; —, solubility curve calculated from eq 2.

PPA shows good solubility because of intermolecular hydrogen bonds between the hydrogen atom in PPA and the hydroxyl group in the solvent molecule such as water,[20] ethanol, methanol, and 2-ethoxyethanol. In addition, it was found that PPA has higher solubility in toluene and benzene which was related to the theory of similarity and compatibility.[32−34] Thus, the investigated solvents could be recommended as the better solvent for the purification of PPA, especially polar solvents. Compared with PPA, due to the similar structure, MPPA shows similar soluble behavior. However, the molecular volume of MPPA is bigger than PPA because of the introduction of a methyl group, so the solubilities of MPPA are smaller than PPA.

The order of mole fraction solubility of HCCP in the select solvent at constant temperature is THF > dichloromethane > diethyl ether > ethyl acetate > toluene > acetone >2-ethoxyethanol > ethanol > *n*-heptane > acetonitrile. The solubility of HCCP in THF shows the highest value and in acetonitrile shows the lowest values. Compared with HCCP, HPCCP shows also good solubility in THF, dichloromethane, ethyl acetate, and toluene. When the chloride atom on the phosphorus atom of HCCP is substituted by a phenoxy group, the solubility of HPCCP in toluene is increased to some extent. This is due to the introduction of the benzene ring and the theory of similarity and compatibility.

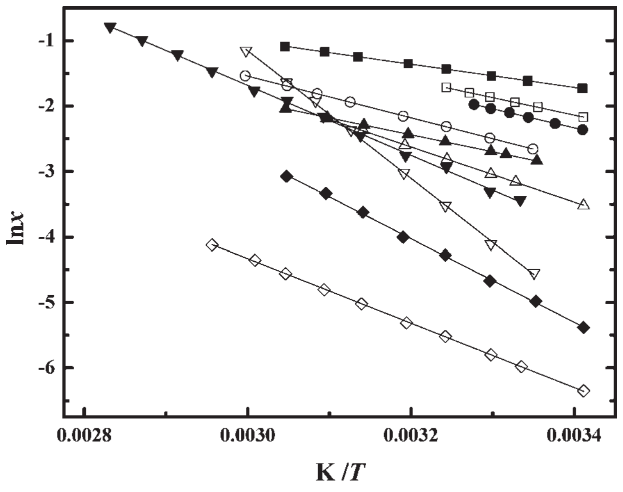

Figure 6. Mole fraction solubilities of hexachlorocyclotriphosphazene in selected solvents. Experimental data: ■, THF; □, dichloromethane; ●, diethyl ether; ○, ethyl acetate; ▲, toluene; Δ, acetone; ▼, 2-ethoxyethanol; ▽, ethanol; ♦, *n*-heptane; ◊, acetonitrile; —, solubility curve calculated from eq 2.

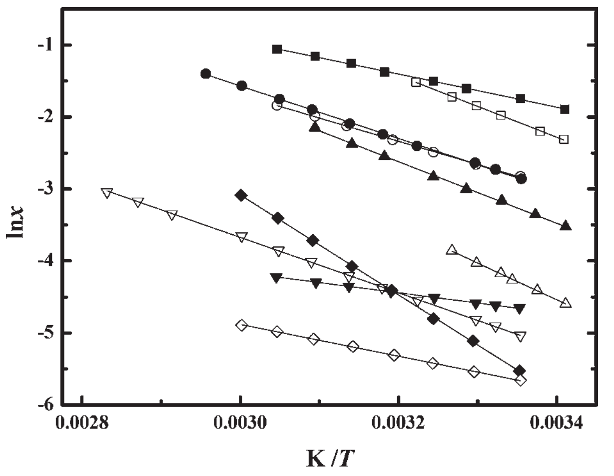

Figure 7. Mole fraction solubilities of hexaphenoxycyclotriphosphazene in selected solvents. Experimental data: ■, THF; □, dichloromethane; ●, toluene; ○, ethyl acetate; ▲, acetone; Δ, diethyl ether; ▼, ethanol; ▽, 2-ethoxyethanol; ♦, acetonitrile; ◊, *n*-heptane; —, solubility curve calculated from eq 2.

To obtain the activity coefficients of PPA, MPPA, HCCP, and HPCCP in the solvents from the experimental data, the following equilibrium equation for solute was derived as a fair approximation[35]

$$\ln \frac{1}{x_1 \gamma_1} = \frac{\Delta_{\mathrm{fus}} H}{R T_{\mathrm{m}}} \left(\frac{T_{\mathrm{m}}}{T} - 1 \right) \qquad (3)$$

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 solution, respectively. With the experimental x_1, T, $\Delta_{\mathrm{fus}}H$, and T_{m} values known, the activity coefficients of PPA, MPPA, HCCP, and HPCCP in different

Table 8. Solubility Parameter and Liquid Molar Volume of Selected Solvents[36] and PPA, MPPA, HCCP, and HPCCP

substance	$\delta_i/(\mathrm{J \cdot cm^{-3}})^{1/2}$	$10^6 V_i/\mathrm{m^3 \cdot mol^{-1}}$
methanol	29.52	40.70
ethanol	26.42	58.52
2-ethoxyethanol	21.54	97.46
toluene	18.35	106.6
acetone	19.77	73.93
ethyl acetate	18.35	98.59
dichloromethane	20.38	64.43
chloroform	19.03	80.66
benzene	18.71	89.48
THF	19.13	81.94
acetonitrile	24.09	52.68
n-heptane	15.21	147.0
diethyl ether	15.53	104.7
PPA	25.40	119.0
MPPA	24.10	129.8
HCCP	23.20	135.3
HPCCP	22.70	525.5

solvents were obtained from eq 3. The results are listed in Tables 4 to 7. The experimental data show that the higher the temperature, the greater the solubility, and the smaller the activity coefficient in all selected solvents. For example, the solubility of PPA in methanol shows the largest value and in water shows the lowest value, while its activity coefficient in methanol is the lowest and in water is the largest at the same temperature. Compared with the activity coefficients of PPA and HCCP, the variation range of the activity coefficients for MPPA and HPCCP is relatively small. Generally, a relatively small solubility and a large activity coefficient result from the deviation from ideal behavior, which illustrated that the interaction between the solutes and the solvents is weak and that the polar or specific chemical force between the molecules of the solid is strong.

Correlation. The Scatchard–Hildebrand activity coefficient model for regular solution,[35,36] eq 4, will be used to correlate the activity coefficients listed in Tables 4 to 7. 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

$$RT \ln \gamma_1 = V_1 x_2^2 (\delta_1 - \delta_2)^2 \qquad (4)$$

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 to the mole fraction of the solvent. The density of the PPA + ethanol binary solution at 298.15 K related in this work was measured according to ref 37. At a specific composition and with the density of ethanol known,[38] the value of molar volume of the subcooled liquid for solid solute PPA can be obtained, and the results are listed in Table 8. However, these values of MPPA, HCCP, and HPCCP cannot be determined with the same method because of relatively lower solubility. They were estimated using advanced chemistry development (ACD/Laboratories) Software V11.02, and the results are listed in Table 8. On the basis of eq 4 and with the solubility parameter δ_2 of the solvents obtained from the literature,[38] the solubilty parameter of the solute δ_1 can be determined. The results are also listed in Table 8.

Table 9. Parameters of Equation 7 and AAD of Measured Activity Coefficients with the Calculated Results from Equations 6 and 5 for Solutes in Selected Solvents

solvent	*a*	*b*	*c*	AAD %
		PPA		
methanol	0.0964	$-3.09 \cdot 10^{-4}$	0	1.94
ethanol	0.3783	$-2.31 \cdot 10^{-3}$	$3.72 \cdot 10^{-6}$	1.18
ethyl acetate	1.0534	$-6.19 \cdot 10^{-3}$	$9.12 \cdot 10^{-6}$	1.41
dichloromethane	0.1524	$-4.33 \cdot 10^{-4}$	0	1.03
acetone	0.8715	$-4.97 \cdot 10^{-3}$	$7.08 \cdot 10^{-6}$	3.41
chloroform	1.5047	$-9.82 \cdot 10^{-3}$	$1.59 \cdot 10^{-5}$	3.08
2-ethoxyethanol	0.6807	$-4.56 \cdot 10^{-3}$	$7.81 \cdot 10^{-6}$	3.97
toluene	1.4788	$-8.98 \cdot 10^{-3}$	$1.36 \cdot 10^{-5}$	2.27
benzene	1.6142	$-9.78 \cdot 10^{-3}$	$1.47 \cdot 10^{-5}$	2.99
water	0.2929	$-2.70 \cdot 10^{-3}$	$3.80 \cdot 10^{-6}$	3.24
		MPPA		
ethyl acetate	−1.1233	$7.52 \cdot 10^{-3}$	$-1.30 \cdot 10^{-5}$	3.12
dichloromethane	−2.9893	$2.15 \cdot 10^{-2}$	$-3.87 \cdot 10^{-5}$	1.79
methanol	−0.5503	$3.72 \cdot 10^{-3}$	$-6.97 \cdot 10^{-6}$	1.15
chloroform	−1.0599	$7.03 \cdot 10^{-3}$	$-1.21 \cdot 10^{-5}$	3.01
toluene	−3.9452	$2.57 \cdot 10^{-2}$	$-4.25 \cdot 10^{-5}$	4.77
acetone	−0.5514	$3.96 \cdot 10^{-3}$	$-7.24 \cdot 10^{-6}$	1.58
water	−0.1354	$-5.60 \cdot 10^{-4}$	$8.10 \cdot 10^{-7}$	1.14
		HCCP		
ethanol	0.3317	$-9.97 \cdot 10^{-4}$	0	2.26
ethyl acetate	0.1984	$-1.32 \cdot 10^{-3}$	$2.12 \cdot 10^{-6}$	2.30
diethyl ether	−0.0545	$-4.75 \cdot 10^{-5}$	0	0.05
THF	−0.0810	$1.91 \cdot 10^{-4}$	0	0.58
acetone	0.0756	$-1.90 \cdot 10^{-4}$	0	0.62
dichloromethane	0.0027	$-1.85 \cdot 10^{-5}$	0	0.03
acetonitrile	0.1292	$-2.00 \cdot 10^{-4}$	0	0.68
2-ethoxyethanol	0.1259	$-3.18 \cdot 10^{-4}$	0	1.44
toluene	−0.0528	$1.68 \cdot 10^{-4}$	0	0.54
n-heptane	0.2200	$-7.58 \cdot 10^{-4}$	0	1.10
		HPCCP		
ethanol	−0.0757	$2.14 \cdot 10^{-4}$	0	1.13
ethyl acetate	−0.1260	$4.84 \cdot 10^{-4}$	$-5.98 \cdot 10^{-7}$	0.57
diethyl ether	−0.0950	$6.43 \cdot 10^{-5}$	0	0.45
THF	−0.2191	$1.20 \cdot 10^{-3}$	$-2.01 \cdot 10^{-6}$	2.05
acetone	−0.1472	$7.94 \cdot 10^{-4}$	$-1.21 \cdot 10^{-6}$	1.26
dichloromethane	−0.8222	$5.52 \cdot 10^{-3}$	$-9.52 \cdot 10^{-6}$	0.96
acetonitrile	0.0081	$-2.15 \cdot 10^{-5}$	0	0.87
2-ethoxyethanol	−0.0431	$1.45 \cdot 10^{-4}$	0	2.99
toluene	−0.2004	$1.00 \cdot 10^{-3}$	$-1.50 \cdot 10^{-6}$	3.99
n-heptane	−0.1734	$3.30 \cdot 10^{-4}$	0	1.59

The prediction accuracy of the simplified Scatchard–Hildebrand regular solution model eq 4 can be further improved if a binary interaction parameter l_{12} is added to eq 4 as given by

$$RT \ln \gamma_1 = V_1 x_2^2 [(\delta_1 - \delta_2)^2 + 2 l_{12} \delta_1 \delta_2] \qquad (5)$$

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

$$l_{12} = a + b(T/\mathrm{K}) + c(T/\mathrm{K})^2 \qquad (6)$$

The parameters *a*, *b*, and *c* for each solvent obtained by regression from the experimental data are list in Table 9. The absolute average deviation (AAD) of the activity coefficients calculated by eq 5 is also listed in Table 9 where the AAD is defined as

$$\mathrm{AAD} = \frac{1}{N} \sum_i \left| \frac{\gamma_1^{\mathrm{exp}} - \gamma_2^{\mathrm{cal}}}{\gamma_1^{\mathrm{exp}}} \right| \qquad (7)$$

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

Table 10. Coefficients of Equation 8 and Values of $H_1^{E,\infty}$ Derived from Equation 9 for Solutes in Selected Solvents

solvent	a'	b'/K	$H_1^{E,\infty}$/kJ·mol^{-1}
PPA			
methanol	−6.6332	2313.5	19.2
ethanol	−2.4624	1140.5	9.48
ethyl acetate	−8.1301	3386.9	28.2
dichloromethane	−6.4158	2619.6	21.8
acetone	−8.7139	3329.2	23.7
chloroform	−4.6966	1850.7	15.4
2-ethoxyethanol	13.162	−3741.8	−31.1
toluene	−7.9197	3230.1	26.9
benzene	−9.5844	3554.7	29.5
water	−9.3469	3931.7	32.7
MPPA			
ethyl acetate	−13.834	4269.6	35.5
dichloromethane	−24.598	7184.5	59.7
methanol	−14.309	3393.1	28.2
chloroform	−9.8506	2795.4	23.2
toluene	−29.839	9102.2	75.7
acetone	−7.4307	2294.2	19.1
water	−1.7562	1010.0	8.40
HCCP			
ethanol	−19.891	6786.4	56.4
ethyl acetate	−0.3154	384.42	3.20
diethyl ether	−0.5571	317.80	2.64
THF	2.7589	−899.56	−7.48
acetone	−2.8370	1320.6	11.0
dichloromethane	−0.2847	171.14	1.42
acetonitrile	−3.6387	2363.0	19.6
2-ethoxyethanol	−5.1725	2092.3	17.4
toluene	2.3273	−348.01	−2.89
n-heptane	−8.7046	3565.4	29.6
HPCCP			
ethanol	16.222	−4863.3	−40.4
ethyl acetate	5.7756	−2361.0	−19.6
diethyl ether	2.8646	−986.87	−8.20
THF	−0.1086	−1266.5	−10.5
acetone	3.4762	−1505.8	−12.5
dichloromethane	−17.344	4164.8	34.6
acetonitrile	−1.4862	684.11	5.69
2-ethoxyethanol	8.9613	−2580.6	−21.5
toluene	4.1993	−1868.2	−15.5
n-heptane	14.399	−4020.0	−33.4

The activity coefficients at infinite dilution of solutes γ_1^∞ are extrapolated based on eq 5 to satisfy the condition $x_2 \rightarrow 1$. The results of γ_1^∞ were correlated with temperature by the following equation

$$\ln \gamma_1^\infty = a' + b'/(T/K) \qquad (8)$$

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 8.[39]

$$\frac{\partial \ln \gamma_1^\infty}{\partial(1/T)} = \frac{H_1^{E,\infty}}{R} \qquad (9)$$

The coefficients a' and b' and the values of $H_1^{E,\infty}$ derived from eq 8 are listed in Table 10. These results are useful for the estimation of the heat of dissolution of the phosphorus-containing compounds in the selected solvents.

■ CONCLUSIONS

The solubilities of PPA, MPPA, HCCP, and HPCCP in the selected organic solvents and water were systematically measured. These data are important contributions to the fulfillment of the demand for purification process design in the organic phosphorus industry. They can be correlated as a linear function of inverse temperature. The solubility data calculated by the equation are in good agreement with the experimental values. Moreover, the activity coefficients of solutes have also been obtained, and the results are correlated with the Scatchard−Hildebrand activity coefficient model. The absolute average deviation of the modeling is less than 5 %. The partial molar excess enthalpies at infinite dilution were also predicted.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** The information of ^{1}H NMR and ^{31}P NMR spectra and the DSC and TGA graphs of PPA, MPPA, HCCP, and HPCCP, an analysis report for the uncertainty of DSC measurement, and the parameters of eq 2. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: +86-10-68911040. E-mail: lishengwang@btamail.net.cn.

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