Solubilities of Phenylphosphinic Acid, Hydroxymethylphenylphosphinic Acid, *p*-Methoxyphenylphosphinic Acid, *p*-Methoxyphenylhydroxymethylphosphinic Acid, Triphenylphosphine, Tri(*p*-methoxyphenyl)phosphine, and Tri(*p*-methoxyphenyl)phosphine Oxide in Selected Solvents

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The solubilities of phenylphosphinic acid from (297.79 to 312.84) K, hydroxymethylphenylphosphinic acid from (307.45 to 357.11) K, *p*-methoxyphenylphosphinic acid from (303.35 to 337.35) K, and *p*-methoxyphenylhydroxymethylphosphinic acid from (303.95 to 346.45) K in water were measured. The concentration of the solution was determined by titration with sodium hydroxide using phenolphthalein as the indicator. The solubilities of triphenylphosphine from (299.65 to 327.15) K in methanol and from (297.45 to 327.65) K in ethanol, tri(*p*-methoxyphenyl)phosphine from (293.35 to 322.65) K in methanol and from (298.25 to 328.15) K in ethanol, and tri(*p*-methoxyphenyl)phosphine oxide from (299.15 to 337.65) K in cyclohexane were determined using a dynamic method. The estimated uncertainty of all the solubility values based on error analysis and repeated observations was within 2.3 %.

Introduction

Phenylphosphine and phenylphosphinic acid and their derivatives are widely used as a fire retardant for organic materials.[1−3] Hydroxymethylphenylphosphinic acid (HMPPA) is a bifunctional copolymeribie phosphorus monomer, and it can be synthesized from phenylphosphinic acid (PPA) and paraformaldehyde as disclosed by a U.S. patent.[3] HMPPA and PPA are compounds of the general formula (a) and (b) as shown in Figure 1. PPA can be synthesized from dichlorophenylphosphine and water as disclosed by a U.S. patent.[7] HMPPA can be polycondensed with ethylene glycol and terephthalic acid to form a flame-retardant poly(ethylene terephthalate).[3] *p*-Methoxyphenylphosphinic acid (MOPPA) and *p*-methoxyphenylhydroxymethyl phosphinic acid (MOHMPPA) can also be synthesized with similar procedures based on these U.S. patents. In practice, HMPPA, PPA, MOPPA, and MOHMPPA are all purified through crystallization from water.

The application of catalyst-binding phosphorus ligands is attracting more and more attention for the nature of enhancement of interfacial catalysis in a biphasic system.[4−6] In these phosphorus ligands, triphenylphosphine (TPP) and tri(*p*-hydroxyphenyl)phosphine oxide (THPPO) are two most useful compounds. Tri(*p*-methoxyphenyl)phosphine (TMOPP) and tri(*p*-methoxyphenyl)phosphine oxide (TMOPPO) are the intermediates for preparation of THPPO. These organic phosphorus compounds, as the formula shown in Figure 1, are all purified though crystallization from solvents. TPP and TMOPP can be purified either in methanol or ethanol, and TMOPPO can be purified in cyclohexane. Knowledge of the solubilities of these compounds in solvents is important for their preparation and purification. These data were not available in the literature.

In this study, seven organic phosphorus compounds, as the formula shown in Figure 1, were synthesized and characterized. The solubilities of these compounds in different solvents as required in the purification process were measured.

Experimental Section

Materials. In this work, all the aqueous solutions were prepared with distilled water. All the chemicals in the synthesis and measurement were of analytical grade as purchased and were used without further purification. The new synthesized compounds were all dried in a thermal-constant vacuum container, and the solvent mass fraction was found to be less than 0.1 %. The aqueous NaOH solution of $c_1 = 0.1381\ \text{mol}\cdot\text{L}^{-1}$ for titration of PPA and HMPPA and that of $c_2 = 0.0486\ \text{mol}\cdot\text{L}^{-1}$ for titration of MOPPA and MOHMPPA were prepared.

Instrumental Analysis and Measurements. Melting point was measured with an X4 Micromelting point meter, and the temperature was uncorrected. The C and H elemental analyses were performed on a Yanaco CHN FOERMT-3 element analyzer. IR spectra (Fourier transform infrared; FTIR) were recorded on a Perkin-Elmer 2000 FTIR spectrometer using KBr pellets. ^{1}H NMR sperctra were recorded with a Varian Unity 200 MHz spectrometer with $(CD_3)_2SO$, D_2O, or $CDCl_3$ as the solvent. Mass spectra (MS) were obtained on a HP-5989 mass spectrometer.

Synthesis of PPA. PPA was prepared according to the literature[7] with a yield of 85 %, with mp of (80 to 83) °C. The measured acidimetric equivalent is 281.53 mg of $\text{NaOH}\cdot\text{g}^{-1}$, (theoretical: 281.67 mg of $\text{NaOH}\cdot\text{g}^{-1}$, purity 99.9 %). Elemental analysis (%, calculated): C, 51.31 (50.70); H, 4.48 (4.93); IR (KBr): 1591.93 (O−H) (acid); 1439.44 (Ar−P); 1198.35 (P═O) cm^{-1}. ^{1}H NMR (200 MHz, D_2O) (ppm): $\delta = 7.38$ to 7.58 (5H, m, Ar−H). MS (EI): $m/z = 142.0$ (M).

HMPPA. HMPPA was prepared according to literature[3] with a yield of 76 %, with mp of (137 to 140) °C, acidimetric equivalent 232.974 mg of $\text{NaOH}\cdot\text{g}^{-1}$ (theoretical 232.541 mg of $\text{NaOH}\cdot\text{g}^{-1}$, purity 99.8 %). Elemental analysis (%, calcu-

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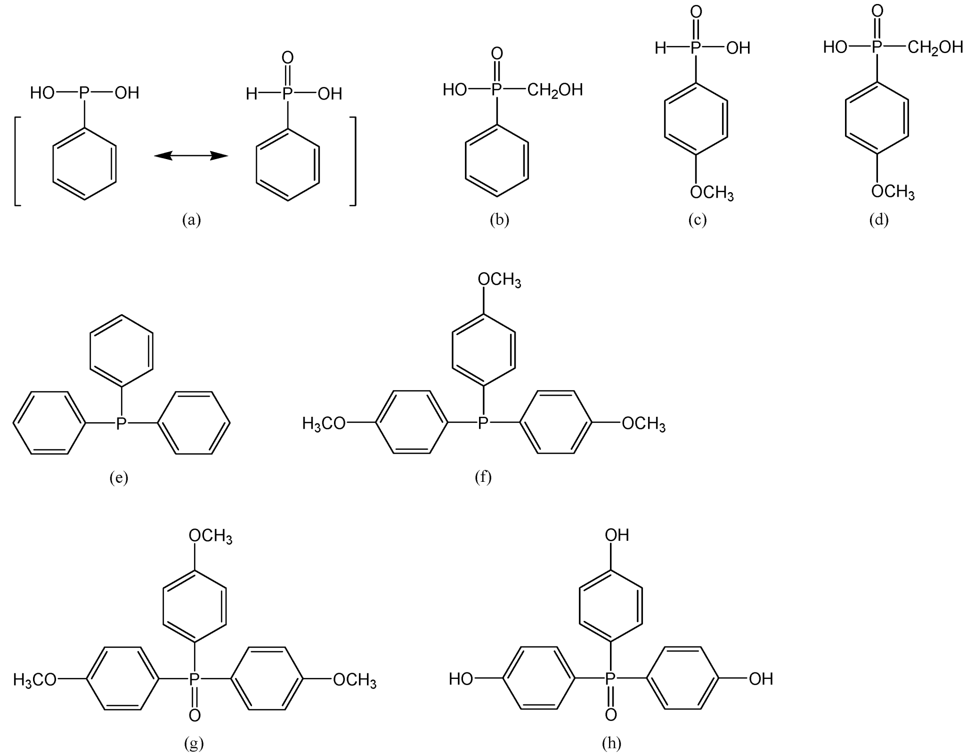

(a) (b) (c) (d) (e) (f) (g) (h)

Figure 1. Formula of the organic phosphorus compounds related in this work: (a) phenylphosphinic acid (PPA) (CASRN 1779-48-2), (b) hydroxymethylphenylphosphinic acid (HMPPA) (CASRN 61451-78-3), (c) *p*-methoxyphenylphosphinic acid (MOPPA) (CASRN 53534-65-9), (d) *p*-methoxyphenylhydroxymethyl phosphinic acid (MOHMPPA), (e) triphenylphosphine (TPP) (CASRN 603-35-0), (f) tri(*p*-methoxyphenyl)phosphine (TMOPP) (CASRN 855-38-9), (g) tri(*p*-methoxyphenyl)phosphine oxide (TMOPPO) (CASRN 803-17-8), and (h) tri(*p*-hydroxyphenyl)phosphine oxide (THPPO).

lated): C, 41.39 (41.86); H, 4.83 (5.23). IR (KBr): 3469.35 (O−H) (alcoholic); 1591.40 (O−H) (acid); 1439.29 (Ar−P); 1156.95 (P═O) cm^{-1}. ^{1}H NMR (200 MHz, D_2O) (ppm): δ = 7.41 to 7.67 (5H, m, Ar−H); 3.82, 3.83 (2H,d,-CH_2). MS (EI): $m/z = 171.1$ (M − 1).

MOPPA. MOPPA was prepared according to literature[7] with dichlorophenylphosphine replaced with dichloromethoxyphenylphosphine. A yield of 82 %, and mp (114 to 115) °C, acidimetric equivalent 231.660 mg of NaOH·g^{-1} (theoretical: 232.541 mg of NaOH·g^{-1}, purity 99.6 %) were obtained. Elemental analysis (%, calculated): C, 49.13 (48.84); H, 4.95 (5.23). IR (KBr): 2376.36 (P−H); 1595.82 (O−H) (acid); 1440.11 (Ar−P); 1176.04 (P═O); 848.07, 815.55, 799.82 (Ar−OCH_3) cm^{-1}. ^{1}H NMR (200 MHz, D_2O) (ppm): δ = 6.94 to 7.56 (4H, m, Ar−H); 3.71 (3H, s, −OCH_3). MS (EI): $m/z = 172.1$ (M).

MOHMPPA. MOHMPPA was prepared according to literature[3] with PPA replaced with MOPPA. A yield of 70 %, mp (153 to 159) °C, acidimetric equivalent 199.083 mg of NaOH·g^{-1} (theoretical: 198.005 mg of NaOH·g^{-1}, purity 99.5 %). Elemental analysis (%, calculated): C, 48.26 (47.52); H, 5.07 (5.45); IR (KBr): 3362.1 (O−H) (alcoholic); 1598.1 (O−H) (acid); 1441.8 (Ar−P); 1187.2 (P═O); 854.1, 817.8, 752.9 (Ar−OCH_3) cm^{-1}. ^{1}H NMR (200 MHz, D_2O) (ppm): δ = 6.94 to 7.61 (4H, m, Ar−H); 3.76, 3.78 (2H, d, −CH_2), 3.71 (3H, s, −OCH_3). MS (EI): $m/z = 202.0$ (M).

TPP. TPP was prepared according to literature[8] with a yield of 14 %, mp (79 to 80) °C. MS (EI): $m/z = 261.7$ (M). ^{1}H NMR (200 MHz, $CDCl_3$) (ppm): δ = 7.321 to 7.354 (12H, m, Ar−H); IR (KBr): 1088.3 (Ar−P), 1431.1, 1474.0, 1581.5 (C═C) cm^{-1}.

TMOPP. TMOPP was prepared according to literature[8] with a yield of 25 %, mp (130 to 131) °C. MS (EI): $m/z = 352.2$ (M). ^{1}H NMR (200 MHz, $CDCl_3$) (ppm): δ = 6.921 to 7.763 (4H, m, Ar−H), 3.806 (3H, s, O−CH_3). IR (KBr): 1244.18 (C−O), 1438.78 (Ar−P), 1496.66, 1564.64, 1590.59 (C═C) cm^{-1}.

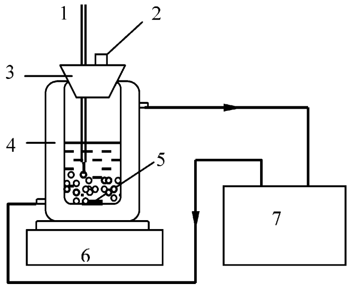

Figure 2. Schematic diagram of solubility apparatus: 1, thermocouple; 2, sample gauge; 3, rubber plug; 4, jacket; 5, equilibrium cell; 6, magnetic stirrer; 7, water cycling bath.

TMOPPO. TMOPPO was prepared according to literature,[9] and the obtained sample was recrystallized in cyclohexane with a yield of 86 %, mp (143 to 144) °C. MS (EI): $m/z = 367.7$ (M). ^{1}H NMR (200 MHz, $CDCl_3$) (ppm): δ = 6.881 to 7.534 (4H, m, Ar−H), 3.770 (3H, s, O−CH_3). IR (KBr): 1254.18 (C−O), 1443.25 (Ar−P), 1503.05, 1569.34, 1597.36 (C═C), 1179.73 (P═O) cm^{-1}. The obtained TMOPPO was then used to prepare THPPO according to literature,[10] with a yield of 50 %, mp (273 to 275) °C. ^{1}H NMR (200 MHz, $(CD_3)_2SO$ (ppm): δ = 10.159 (1H, s, O−H), 6.843 to 7.365 (4H, m, Ar−H). IR (KBr): 1121.8, 1276.3 (C−O), 1174.6 (P═O), 1431.2 (Ar−P), 1504.1, 1583.3, 1601.2 (C═C), 3346.3 (O−H) cm^{-1}.

Procedure. The setup for the solubility measurement was the same as that described in the literature.[11,12] Figure 2 shows the schematic diagram of the experimental apparatus. The equilibrium cell was a sealed 120 mL glass measuring flask. A thermocouple is immersed into the solution of the measuring flask, and the uncertainty of the thermocouple is 0.01 K. The

Table 1. Mole Fraction Solubilities of Seven Organic Phosphorus Compounds in Selected Solvents

solute	solvent	T/K	$10^3 s^{\text{exp}}$	$\lvert(s^{\text{exp}} - s^{\text{cal}})/s^{\text{exp}}\rvert$
PPA	water	297.79	9.46	0.0328
		300.25	11.09	0.0018
		302.40	12.94	0.0139
		305.22	15.93	0.0220
		309.93	21.77	0.0620
		312.84	30.47	0.0627
HMPPA	water	307.45	9.90	0.0404
		317.46	20.60	0.0194
		327.57	42.40	0.0519
		338.15	96.60	0.0362
		342.45	116.60	0.0635
		346.58	166.20	0.0241
		352.8	247.40	0.0295
		357.11	312.00	0.0019
MOPPA	water	303.35	2.26	0.0531
		308.05	2.61	0.0115
		312.97	2.97	0.0505
		317.25	3.47	0.0548
		322.15	4.41	0.0091
		327.75	5.29	0.0076
		333.10	6.30	0.0143
		337.35	7.73	0.0492
MOHMPPA	water	303.95	2.01	0.0547
		307.72	2.25	0.0133
		312.55	2.64	0.0265
		317.4	3.26	0.0061
		322.15	3.77	0.0424
		327.94	4.61	0.0586
		332.59	5.75	0.0017
		337.72	6.65	0.0376
		342.36	8.44	0.0438
		346.45	9.72	0.0494
TPP	ethanol	297.45	8.05	0.0509
		302.25	9.95	0.0050
		307.35	12.70	0.0394
		312.45	16.50	0.0485
		317.55	22.30	0.0045
		323.05	29.00	0.0138
		327.65	38.60	0.0518
TPP	methanol	299.65	3.74	0.0321
		303.55	4.41	0.0068
		307.45	5.19	0.0154
		311.35	6.15	0.0260
		315.25	7.27	0.0358
		318.95	8.75	0.0137
		322.75	10.60	0.0189
		327.15	13.00	0.0308
TMOPP	ethanol	298.25	$3.74 \cdot 10^{-1}$	0.0428
		303.75	$4.91 \cdot 10^{-1}$	0.0591
		308.05	$6.67 \cdot 10^{-1}$	0.0360
		313.35	1.02	0.0490
		317.75	1.28	0.0078
		322.35	1.68	0.0000
		328.15	2.36	0.0000
TMOPP	methanol	293.35	$1.90 \cdot 10^{-1}$	0.0526
		298.25	$2.40 \cdot 10^{-1}$	0.0083
		303.15	$3.07 \cdot 10^{-1}$	0.0521
		308.05	$4.17 \cdot 10^{-1}$	0.0216
		313.15	$5.63 \cdot 10^{-1}$	0.0000
		318.15	$7.10 \cdot 10^{-1}$	0.0338
		322.65	$9.83 \cdot 10^{-1}$	0.0580
TMOPPO	cyclohexane	299.15	$5.39 \cdot 10^{-1}$	0.0223
		304.05	$8.24 \cdot 10^{-1}$	0.0583
		308.85	1.07	0.0467
		313.95	1.51	0.0795
		318.45	2.31	0.0260
		323.65	3.26	0.0061
		328.45	4.36	0.0275
		332.85	5.96	0.0017
		337.65	8.48	0.0425

jacket of the flask was bathed with constant-temperature water, and the temperature control uncertainty is within ± 0.1 K. A magnetic stirrer was utilized for solution preparation. The uncertainty of the analytical balance was 0.1 mg. The mass of sample of PPA taken for titration ranged from 0.22 g to 0.72 g, that of HMPPA ranged from 0.28 g to 0.95 g, that of MOPPA ranged from 0.07 g to 0.22 g, and that of MOHMPPA ranged from 0.07 g to 0.33 g.

The solubilities of PPA, HMPPA, MOPPA, and MOHMPPA were measured with a titration method.[11] At each selected temperature, an excess amount of the sample was added to 100 g of distilled water and constant stirring was applied. At an interval of 60 min, the stirrer was stopped and then the solution was settled for 40 min; the excess solid could be observed to settle in the lower portion of the equilibrium cell. The clear solution was withdrawn from the cell to another measuring flask and weighed with an analytical balance. The concentration of the solution was determined by sodium hydroxide titration with phenolphthalein as the indicator. Repeated measurements were performed for different dissolution times to determine how long it would take to reach equilibrium. It was found that 60 min was sufficient for PPA and MOPPA and that 90 min was sufficient for HMPPA and MOHMPPA in distilled water within the measuring temperature ranges. For each temperature, the titration operation was conducted three times, and an averaged value was taken.

The solubilities of TPP, TMOPP, and TMOPPO were determined using a dynamic method.[13] The mixtures of solute and solvent were prepared by mass. The mixture was well stirred using a magnetic stirrer and heated very slowly with a heating rate that did not exceed 2 K·h^{-1} near the dissolution temperature. The temperature at which the last crystal disappeared (disappearance of solution cloudiness) was taken as the temperature of the solution−crystal equilibrium.

Table 2. Regressed Parameters *a* and *b*, the Absolute Average Deviation (AAD) of the Measured Solubility from Calculated Results of Equation 1 and the Experimental Uncertainties for the Different Binary Mixtures

solute	solvent	a	b	AAD/%	uncertainty/%
PPA	water	−7045.4	18.965	3.20	1.8
HMPPA	water	−7714.9	20.441	3.30	1.7
MOPPA	water	−3716.5	6.104	3.10	2.2
MOHMPPA	water	−3923.1	6.640	3.40	2.2
TMOPP	ethanol	−6177.4	12.776	2.79	1.7
TMOPP	methanol	−5288.9	9.407	3.27	1.7
TPP	ethanol	−5061.4	12.141	3.05	2.3
TPP	methanol	−4441.6	9.201	2.25	2.3
TMOPPO	cyclohexane	−7173.4	16.431	3.49	2.2

The solubilities of seven organic phosphorus compounds in some solvents determined in this work are summarized in Table 1. The estimated uncertainty of the solubility values, based on error analysis and repeated observations, was within 2.3 %. The uncertainty for the different binary mixtures is listed in Table 2.

Correlation

As shown in Figures 3 to 5, the logarithm of the mole fraction solubilities (s) determined in this work plotted against the inverse temperature shows good linearity. A trend of increasing solubil-

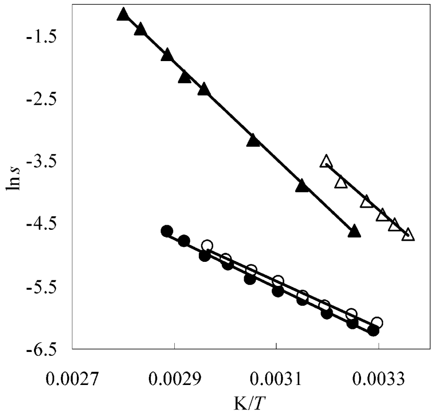

Figure 3. Temperature dependence of mole fraction Solubilities of PPA, HMPPA, MOPPA, and MOHMPPA in Water: —, calculated data; △, measured data of PPA in water; ▲, measured data of HMPPA in water; ○, measured data of MOPPA in water; ●, measured data of MOHMPPA in water.

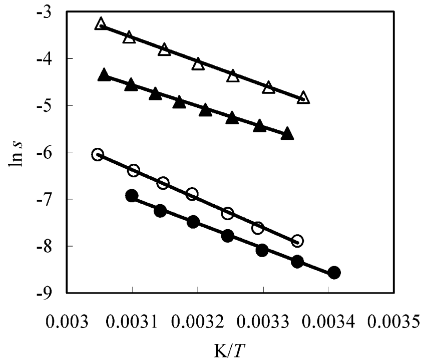

Figure 4. Temperature dependence of mole fraction solubilities of TPP and TMOPP in methanol and ethanol: —, calculated data; △, measured data of TPP in ethanol; ▲, measured data of TPP in methanol; ○, measured data of TMOPP in ethanol; ●, measured data of TMOPP in methanol.

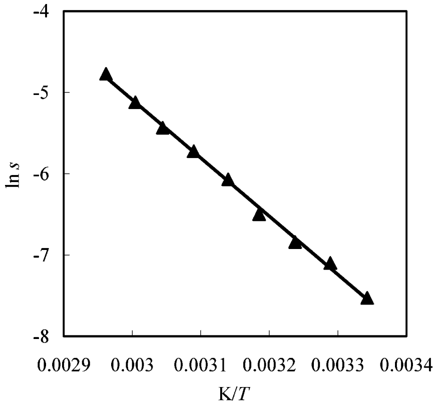

Figure 5. Temperature dependence of mole fraction solubilities of TMOPPO in Cyclohexane: —, calculated data; ▲, measured data.

ity with temperature is observed. Therefore, they were correlated as a function of temperature by

$$\ln s = a/(T/\mathrm{K}) + b \tag{1}$$

The regressed parameters *a* and *b* for PPA, HMPPA, MOPPA, MOHMPPA, TPP, TMOPP, and TMOPPO in the selected solvents are listed in Table 2. The relative deviations of the measured solubility from the smoothed data are listed in Table 1. The absolute average deviation (AAD) of the measured solubility from the smoothed data are listed in Table 2, where the AAD is defined as

$$\mathrm{AAD} = \frac{1}{N}\sum_i \left| \frac{s_i^{\mathrm{exp}} - s_i^{\mathrm{cal}}}{s_i^{\mathrm{exp}}} \right| \tag{2}$$

where $s_\mathrm{i}^{\mathrm{exp}}$ stands for experimental values, $s_\mathrm{i}^{\mathrm{cal}}$ stands for calculated values, and *N* is the number of data points.

Discussion

The solubilities of PPA from (297.79 to 312.84) K, HMPPA from (307.45 to 357.11) K, MOPPA from (303.35 to 337.35) K, and MOHMPPA from (303.95 to 346.45) K in water were measured. The concentration of the solution was determined by titration with sodium hydroxide using phenolphthalein as the indicator. The solubilities of TPP from (299.65 to 327.15) K in methanol and from (297.45 to 327.65) K in ethanol, of TMOPP from (293.35 to 322.65) K in methanol and from (298.25 to 328.15) K in ethanol, and of TMOPPO from (299.15 to 337.65) K in cyclohexane were determined using a dynamic method. The estimated uncertainty of all the solubility values based on error analysis and repeated observations was within 2.3 %.

Within the temperature range of the measurements, the mole fraction solubilities of seven organic phosphorus compounds in selected solvents showed an increased trend with temperature, and they were correlated as a linear function of inversed temperature by eq 1. Because PPA is unstable at higher temperature in air (the -P(O)-H group is easily oxidized to -P(O)-OH group by air at high temperature), the temperature range of PPA in water is limited from 297.79 K to 312.84 K.

Both PPA and HMPPA are most soluble substances in water, especially at a relatively higher temperature. The order of mole fraction solubility of these phenylphosphinic acid in water at constant temperature is PPA > HMPPA > MOPPA > MOHMPPA, as shown in Figure 3. These results indicate that the substitution of a methoxyl group to the hydrogen of benzene of PPA and HMPPA reduces their aqueous solubility, and the substitution of a hydroxymethyl group to the hydrogen of phosphorus also reduces their aqueous solubility.

Figure 4 shows that ethanol is a better solvent for TPP and TMOPP than methanol. When the para-hydrogen of benzene group of phenylphosphine is substituted by a methoxyl group, their solubility in alcohol is reduced significantly, with a similar trend as described for the MOPPA and MOHMPPA.

Figure 5 shows that cyclohexane is a good solvent for the purification of TMOPPO. The solubility in mole fraction of TMOPPO in cyclohexane increased from mole fraction 5.39×10^{-4} (mass fraction 2.36×10^{-3}) at 299.15 K to 8.48×10^{-3} (3.72×10^{-2}) at 337.65 K.

Further work is underway to measure the heat of fusion and heat capacity of these phosphorus compounds.

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