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Solubilities of Dichlorophenylphosphine Sulfide and Bis(4-carboxyphenyl)phenylphosphine Oxide in Water

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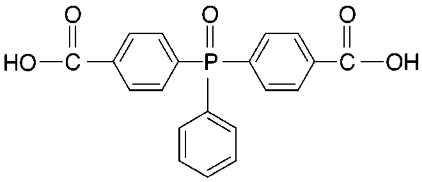
The solubilities of dichlorophenylphosphine sulfide (DCPPS) and bis(4-carboxyphenyl)phenylphosphine oxide (BCPPO) in pure water were determined. The concentration of the solution was determined by sodium hydroxide titration with phenolphthalein as indicator. The synthesis and characterization of the compounds are described. The solubilities of DCPPS were measured over the range 23 to 50 °C and the solubilities of BCPPO were measured over the range 23 to 75 °C with the uncertainty of 1.5% and 4.1% respectively.

1. Introduction

Phosphine oxide containing copolymers are of interest as a potentially important new class of flame resistant polymeric materials. The hydrolytically stable arylphosphine oxide monomer components have been chemically incorporated into various macromolecules. Many different polymeric systems with the phosphine oxide bonds have been investigated such as poly(arylene ethers),[1] polyamides,[2] and polyimide.[3] The dicarboxylic triarylphosphine oxide monomer (see substance a: bis(4-carboxyphenyl)phenylphosphine oxide, BCPPO) was prepared and subsequently incorporated into nylon 6,6 copolymers[4] and polyesters.[5]

a:

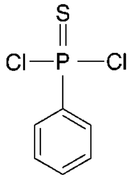


BCPPO possesses good thermal oxidative and hydrolytic stability. One of the most important polyester products is the flame retardant poly(ethylene terephthalate) (FR-PET), which can be manufactured through the direct esterification and polycondensation route of ethylene glycol (EG) and terephthalate (TPA) with BCPPO as a comonomer. FR-PET copolymers exhibit good fiber-forming properties, improved flame retarding behavior and high glass transition temperature.[5]

BCPPO was prepared by the oxidation of bis(4-methylphenyl)phenylphosphine sulfide (BMPPS). BMPPS was prepared from the Friedel-Craft reaction of toluene with DCPPS (see substance b: dichlorophenylphosphine sulfide).

The Friedel−Crafts reaction is an excellent method for preparing arylphosphonous dihalides with aluminum trichloride as catalyst. The main difficulty with this reaction is the formation of rather stable halogenophosphine−aluminum trichloride complexes. To break down these complexes, they must be hydrolyzed in water. However, the arylphosphonous dichloride is unstable in water. To improve the

b:



hydrolytic stability of the arylphosphonous dichloride, sulfur must be added to form the thiophosphoryl (P=S) group before the hydrolysis. Thus, the DCPPS is prepared by reaction of sulfur with phenylphosphonic dichloride. After the hydrolysis of the DCPPS−aluminum trichloride complexes in water, the DCPPS can be obtained by separating the organic layer and purification. In the synthesis process of DCPPS and BCPPO, their aqueous solubility must be known for the design of industrial apparatus.

2. Synthesis and Characterization of DCPPS and BCPPO

2.1. Synthesis of DCPPS and BCPPO. The procedure for the synthesis of phenylphosphonous dichloride from benzene via the Friedel−Crafts reaction, given by Wan et al.,[5] was applied without modification. The mole ratio of phosphorus trichloride, aluminum trichloride, benzene, and sulfur was 3:1:1:1. The aromatic hydrocarbon was mixed with phosphorus trichloride and heated under reflux about 8 h with stirring and exclusion of moisture.

A typical preparation was carried out using 1000 mL of PCl_3 (10.944 mol). The amount of hydrogen chloride released was absorbed in water in a flask which was weighted by an electronic balance, accurate to 0.001 g. Kinetic data including reaction time, temperature of reaction liquid, the accumulate amount, and the rate of hydrogen chloride released were recorded. The total amount of hydrogen chloride absorbed in the water after the reaction (151.97 g) is higher than the theoretical amount (133.15 g). At the final stage of the synthesis, the hydrogen chloride released from the reaction mixture and absorbed in the water in the flask did not get to zero because of the evaporation of phosphorus trichloride.

DCPPS was prepared according to the one-step method of Jensen.[6] After distilling the phosphorus trichloride at atmospheric pressure, the residue was hydrolyzed in water

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Table 1. Elemental Analysis Results of Dichlorophenylphosphine Sulfide

	elemental content,/%				
	Cl	S	C	H	P
exp value	33.94	15.01	34.31	2.55	14.28
calc value	33.64	15.16	34.12	2.37	14.66

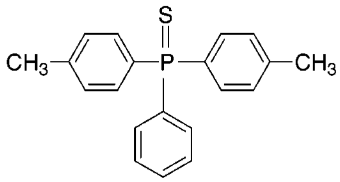
Table 2. Experimental and Smoothed Aqueous Solubility of Dichlorophenylphosphine Sulfide and Bis(4-carboxyphenyl)phenyl Phosphine Oxide

compound	t/°C	mole fraction solubility experimental (smoothed)
DCPPS	23	$1.3(1.3) \times 10^{-4}$
	32	$4.7(4.8) \times 10^{-4}$
	40	$8.5(8.2) \times 10^{-4}$
	50	$12.9(13.0) \times 10^{-4}$
BCPPO	23	$3.6(3.7) \times 10^{-6}$
	32	$5.7(5.4) \times 10^{-6}$
	40	$8.4(8.2) \times 10^{-6}$
	50	$12.5(13.3) \times 10^{-6}$
	60	$18.2(20.1) \times 10^{-6}$
	70	$29.5(28.7) \times 10^{-6}$
	75	$35.8(33.7) \times 10^{-6}$

and then the organic layer was diluted with low-boiling petroleum ether and separated. Water was again added for washing the organic phase. The low-boiling solvent was removed by distillation at atmospheric pressure. The DCPPS was then distilled under vacuum, and the boiling point temperatures are 105 °C at 267 Pa and 150 °C at 1333 Pa, respectively. The final yield of DCPPS on the basis of benzene is 80% (mole ratio of produced DCPPS and benzene is 0.8:1).

The DCPPS was identified by elemental analysis with C, H elemental analysis being performed by a mass spectrograph. The experimental and calculated results from the molecular formula are listed in Table 1. From Table 1 it can be estimated that the purity of DCPPS is higher than 98%. The density of DCPPS at 25 °C is 1.390 (g·cm^{-3}). The other materials and solvents are all analytically pure reagents as purchased from Beijing Chemical Reagent Company and were used without further purification.

The method of synthesis of BMPPS (see substance c) via Friedel−Crafts reaction was given by Wan et al.[4,5] The mole ratio of DCPPS, toluene and $AlCl_3$ was 1:2.2:1.1. The final obtained product BMPPS after purification was a white solid powder (t_m = 154.1 °C; lit. t_m = (153.5−154.0) °C).

c:


BMPPS was directly oxidized to BCPPO by using an excess of $KMnO_4$ through a two-step oxidation process. In the first step, the BMPPS was dissolved in pyridine, the oxidized product was a white solid. In the second step, this solid was dissolved in aqueous KOH and oxidized again with a slight excess amount of $KMnO_4$ at 90 °C for 6 h. After filtering the reaction mixture, the aqueous solution was acidified with HCl to precipitate a white solid. Washing by water until the HCl was completely removed yielded a white solid pure BCPPO powder.

2.2. Characterization of BCPPO. Elemental analysis, appropriate spectroscopic analyses, and melting point identified the product. The C, H elemental analysis was performed by mass spectrograph. The calculated results from the theoretical molecular formula are as follows: C, 65.58; H, 4.13. The analytical results from an AEI-MS-50 mass spectrograph are as follows: C, 65.89; H, 4.22; the theoretical and experimental acid values were 218.0 and 218.8 (mg NaOH/g), respectively.

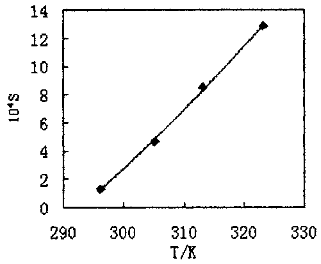


Figure 1. Plot of aqueous solubility of dichloro phenyl phosphine sulfide: ◆, experimental data; —, calculated results of eq 1.

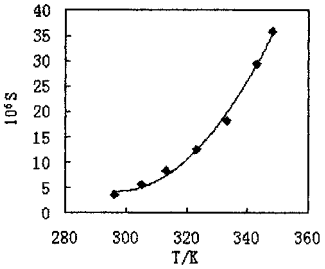


Figure 2. Plot of aqueous solubility of bis(4-carboxyphenyl)-phenylphosphine oxide: ◆, experimental data; —, calculated results of eq 2.

Infrared spectra (IR) was recorded with a Perkin-Elmer 2000 FTIR spectrometer using KBr pellet, the obtained results for the measured frequencies in inverse centimeters were as follows: O−H: 2980; C=O: 1720; 1603, 1562, 1496 (C=C), 1430 (P−Ar), 1150 (P=O).

Nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a Varian Unity 200 MH2 spectrometer. The chemical shift for aromatic H was 7.62−8.14 min, and that for O−H was 13.42 s.

The melting point (t_m) and the enthalpy of fusion ($\Delta_{fus}H$) were determined by Differential Scanning Calorimeter on a DELTA Series DSC7 thermal analysis equipment at a heating rate of 20 °C/min in nitrogen. The obtained t_m is 337.4 °C (According to Morgan and Kenmore,[1] 1953, the t_m was 335 °C, prepared by hydrolysis from the corresponding dimethyl ester product; according to Thiesing and Feld,[7] 1995, the t_m was 337−341 °C, prepared via Grignard reagent type reaction). The enthalpy of fusion $\Delta_{fus}H$ of BCPPO at the melting point temperature determined by the DSC is 17.6 kJ·mol^{-1}. On the basis of the manufacture's specifications and our three parallel measurements, we estimate the uncertainty of the enthalpy of fusion measurements to be ±3%.

3. Aqueous Solubility of DCPPS and BCPPO

3.1. Aqueous Solubility Measurement. An equilibrium cell with agitation was immersed in a constant temperature water bath. The temperature was controlled within ±0.1 K. For determining the solubility of DCPPS and BCPPO in water at different temperatures, the following procedure was applied: at a constant temperature, an excess amount of DCPPS or BCPPO was added to doubly distilled water in the equilibrium cell, and then agitation was started. The agitation was stopped after different dissolution times and then the solution was kept still for 30 min. Then the solid could be observed to settle in the lower portion of the equilibrium cell because of the higher density. A known amount of the upper solution was withdrawn from the cell into a second flask in the same bath. This sample was diluted with distilled water. The concentration of the solution was determined by sodium hydroxide titration with phenolphthalein as indicator (both DCPPS and BCPPO quantitative react with sodium hydroxide). Different dissolving times were tested to determine the suitable equilibrium time. It was found that 3 h were enough for both DCPPS and BCPPO to reach equilibrium in water. The results for DCPPS in a temperature range from (23 to 50) °C and the aqueous solubility of BCPPO in a temperature range from (23 to 75) °C are summarized in Table 2. The estimated accuracy of the solubility values, based on error analysis and repeated observations, was within 2%. The hydrolysis of the DCPPS in water can be neglected because it has been shown through the titration analysis that a much higher temperature (>55 °C) is needed to detect the existence of chlorine ion in the aqueous solution.

3.2. Data Correlation. The aqueous mole fraction solubilities (S) of DCPPS and BCPPO have been correlated as a function of temperature (T/K) using following expressions:

DCPPS:

$$S \times 10^4 = 160.40 - 1.43(T/\mathrm{K}) + 3.01^{-3}(T/\mathrm{K})^2 \quad (1)$$

BCPPO:

$$S \times 10^6 = 745.55 - 5.13(T/\mathrm{K}) + 8.85^{-3}(T/\mathrm{K})^2 \quad (2)$$

The experimental aqueous solubility and the smoothed data based on eq 1 for DCPPS and eq 2 for BCPPO are listed in Table 2. The absolute average deviation (AAD%) of the measured solubilities to the smoothed data is defined as follows:

$$\mathrm{AAD\%} = \frac{1}{N}\sum_i |S^{\mathrm{exp}} - S^{\mathrm{cal}}|_i / S_i^{\mathrm{exp}} \times 100 \quad (3)$$

where the superscript exp and cal refers to the experimental and calculated values, respectively. The absolute average deviations of the measured solubilities to the smoothed data of DCPPS and BCPPO in Table 2 are 1.5% and 4.1% respectively. Figure 1 and Figure 2 are the plot of measured solubility and the calculated results of DCPPS and BCPPO. It is hoped that these data will be thermodynamic interest and valuable for the design of purification process and environmental protection.

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