Solubilities of 2-Carboxyethylphenylphosphinic Acid and 4-Carboxyphenylphenylphosphinic Acid in Water

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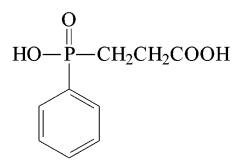
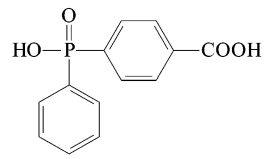
The solubilities of 2-carboxyethylphenylphosphinic acid (CEPPA) and a potential reactive flame retardant, 4-carboxyphenylphenylphosphinic acid (CPPPA), in water were measured. The concentration of the solution was determined by sodium hydroxide titration with phenolphthalein as the indicator. The solubilities of CEPPA were measured from 25.10 °C to 76.32 °C with an uncertainty of 2.2%, and the solubilities of CPPPA were measured from 26.70 °C to 94.52 °C with an uncertainty of 2.1%.

Introduction

2-Carboxyethylphenylphosphinic acid (CEPPA) is a bifunctional copolymerizable phosphorus monomer disclosed by U.S. patent.[1,2] It can be polycondensed with ethylene glycol (EG) and terephthalate (TPA) to form flame-retardant poly(ethylene terephthalate) (FR-PET)[3] and renders the alternated PET and the resulting plastics and fibers good fire-resistance properties, antistatic properties, and excellent dyeing characters. As attention was focused on a reactive phosphorus flame retardant,[4−6] a novel bifunctional copolymonomer for PET, namely, 4-carboxyphenylphenylphosphinic acid (CPPPA), in which the 2-carboxyethyl moiety of CEPPA was replaced by a 4-carboxyphenyl group, was synthesized. The melting point of CPPPA is about 90 °C higher than that of CEPPA, which might make it a potential advantageous flame retardant. In addition to the fire-resistance property, a higher melting point is favorable for spinning properties of the FR-PET.

In industry, CEPPA is obtained by hydrolyzing the acrylation intermediate prepared from dichlorophenylphosphine (DCPP) and acrylic acid, and it then crystallizes from water. The amount of water added in the preparation of CEPPA is important for its purification. According to our experiment, CPPPA was also precipitated in water. Therefore, knowledge of the solubilities of CEPPA and CPPPA in water is important for their preparation and purification. But the solubilities of CEPPA and CPPPA in water were not available in the literature. In this study, the solubilities of CEPPA and CPPPA in water were measured.

CEPPA: 

CPPPA: 

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Experimental Section

Materials. DCPP was purchased from ACROS with a purity of 97%; anhydrous $AlCl_3$, toluene, $KMnO_4$, NaOH, and phenolphthalein were all analytical reagents from Beijing Chemical Factory. The aqueous NaOH solution of $n_1 = 0.1004$ mol/L for titration of CPPPA and that of $n_2 = 1.0034$ mol/L for titration of CEPPA were prepared.

Instrumental Analysis and Measurements. Melting points (mp's) were obtained from an X4 Micromelting point meter, and the temperature was uncorrected. The C, H elemental analysis was performed on a Yanaco CHN FOER MT-3 element analyzer. IR spectra (Fourier transform infrared (FTIR)) were recorded on a Perkin-Elmer 2000 FTIR spectrometer using KBr pellets. ^{1}H NMR spectra were recorded with a Varian Unity 200 MHz spectrometer with $(CD_3)_2SO$ as the solvent. Mass spectra were obtained on a HP-5989 mass spectrometer.

Synthesis of CEPPA. CEPPA was prepared according to the literature[1,2] with a yield of 90.2%, a mp of 158 °C, and acidity of 372.71 mg NaOH/g (calculated: 373.83 mg NaOH/g, purity 99.7%).

Elemental analysis (%, calculated): C, 50.39 (50.47); H, 4.73 (5.14). IR (KBr): 3310 (O−H), 1720 (C═O), 1603, 1430 (Ar−P), 1150 (P═O) cm^{-1}. ^{1}H NMR (200 MHz, $(CD_3)_2SO$): δ13.42 (1H, s, O−H), 7.62 to 8.14 (5H, m, Ar−H), 3.0 to 4.2 (4H, m, $-CH_2CH_2-$H). MS (FAB): 213 ($M^+ - 1$).

Synthesis of CPPPA. Toluene (0.4 mol) was added dropwise to 0.33 mol DCPP and 0.33 mol anhydrous $AlCl_3$ at 110 °C; the reaction went on for 8 h at 150 °C. The reaction mixture was then cooled to room temperature, hydrolyzed with 200 mL of 5 mol/L cold hydrochloric acid, and then extracted with 100 mL of toluene twice. The combined organic layer was washed with water and dried with anhydrous $CaCl_2$. The toluene was removed at reduced pressure to get the intermediate, which was then dissolved by an appropriate amount of sodium hydroxide (1 mol/L). About 1.2 mol $KMnO_4$ was added partially to the solution, and the mixture was kept at 80 °C for 8 to 10 h. An appropriate amount of sodium metabisulfite was added to decolorize the solution and then filtered. The filtrate was acidified by 2 mol/L hydrochloric acid until no further precipitation occurred and then was cooled and filtered one more time to get the solid product. The product was then dissolved in 1 mol/L sodium hydroxide and

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Table 1. Measured and Calculated Solubilities (Mole Fraction) of CEPPA and CPPPA in Water

		$10^3 s$ (measured)				
	t/°C	titration 1	titration 2	titration 3	av	$10^3 s$ (calcd)
CEPPA	25.10	1.765	1.773	1.807	1.782	1.809
	35.51	3.625	3.683	3.667	3.658	3.630
	44.92	6.756	6.656	6.706	6.706	6.811
	54.02	13.36	13.31	13.33	13.32	12.52
	64.40	24.89	24.92	24.95	24.92	25.07
	69.60	33.91	33.89	33.84	33.88	35.49
	71.91	41.18	41.22	41.22	41.21	41.42
	76.32	56.85	56.83	56.78	56.82	55.63
CPPPA	26.70	0.2223	0.2257	0.2250	0.2243	0.2325
	34.21	0.2546	0.2526	0.2513	0.2526	0.2456
	45.08	0.3030	0.3016	0.3044	0.3030	0.2958
	54.40	0.3479	0.3499	0.3499	0.3492	0.3683
	64.15	0.4734	0.4706	0.4741	0.4727	0.4732
	75.71	0.6300	0.6334	0.6306	0.6313	0.6361
	84.38	0.7934	0.7954	0.7974	0.7954	0.7857
	94.52	0.9794	0.9829	0.9843	0.9822	0.9905

reprecipitated by acidification with 2 mol/L hydrochloric acid to pH 3. The white solid was collected by filtration, washed with water until the washings were neutral, and dried to get CPPPA (37.6 g): yield, 33.1% (based on DCPP); mp, 249 to 250 °C; the acidity was 303.51 mg NaOH/g (calculated: 305.34 mg NaOH/g, purity 99.4%).

Elemental analysis (%, calculated): C, 59.07 (59.54); H, 4.43 (4.20). IR (KBr): 3180 (−OH), 1725 (C═O), 1613, 1437 (Ar−P), 1096 (P═O) cm^{-1}. ^1H NMR (200 MHz, $(CD_3)_2SO$): δ11.32, 13.15 (2H, 2s, O−H), 7.71 to 8.34 (9H, m, Ar−H). MS (FAB): 261 ($M^+ - 1$).

Apparatus for Solubility Measurement. The setup for the solubility measurement was the same as that described in the literature.[6] The equilibrium cell was a sealed 120 mL glass measuring flask. The flask was immersed in a constant-temperature water bath. The bath temperature control uncertainty is within ±0.1 °C. A magnetic stirrer was utilized for solution preparation. The precision of the analytical balance was 0.1 mg. The mass of sample of CEPPA taken for titration ranged from 5.01 g to 16.02 g, and that of CPPPA ranged from 0.31 g to 0.82 g.

Solubility Measurement. At each selected temperature, an excessive amount of CEPPA or CPPPA was added to 100 g of distilled water and constant stirring was applied. At an interval of 30 min, the stirrer was stopped and then the solution was settled for 30 min; the excess solid could be observed to settle in the lower portion of the equilibrium cell. The clear upper portion of the solution was withdrawn from the cell to another measuring flask and weighed with an analytical balance; the flask was then immersed in the same bath. 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 120 min was sufficient for CPPPA and 150 min for CEPPA 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 solubility of CEPPA in water at temperatures ranging from 25.10 °C to 76.32 °C and that of CPPPA at temperatures ranging from 26.70 °C to 94.52 °C are summarized in Table 1 and plotted in Figure 1 and Figure 2. The estimated accuracy of the solubility values, based on error analysis and repeated observations, was within 2%.

Correlation. The solubility (mole fraction) of CEPPA was correlated as a function of temperature (T/K) by adopting a logarithmic formula.

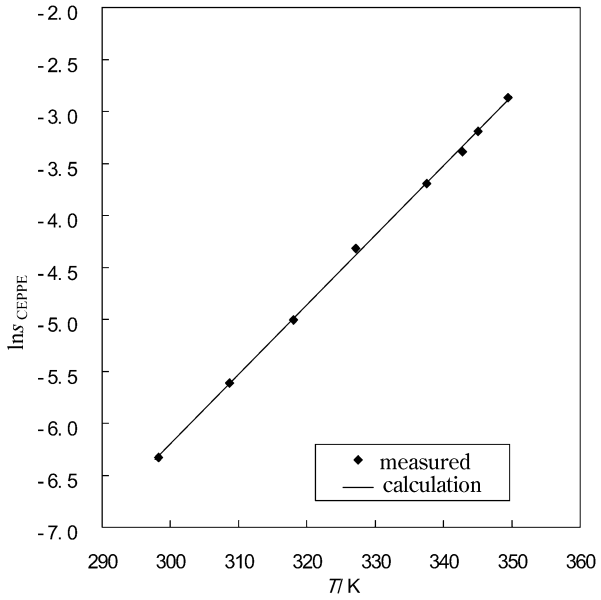

Figure 1. Solubility (mole fraction) of CEPPA in water: ◆, measured; —, calculation (eq 1).

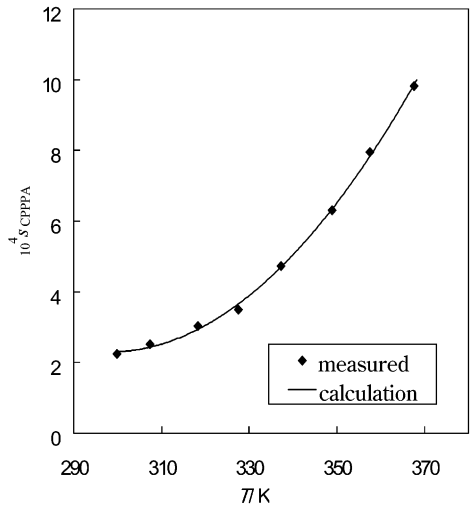

Figure 2. Solubility (mole fraction) of CPPPA in water: ◆, measured; —, calculation (eq 2).

$$\ln s_{\mathrm{CEPPA}} = -26.2623 + 6.6882 \times 10^{-2}(T/\mathrm{K}) \quad (1)$$

The solubility (mole fraction) of CPPPA was correlated as a function of temperature (T/K) by adopting a second-order polynomial:

$$s_{\mathrm{CPPPA}} = 1.4128 \times 10^{-2} - 9.3254 \times 10^{-5}(T/\mathrm{K}) + 1.5644 \times 10^{-7}(T/\mathrm{K})^2 \quad (2)$$

The measured solubility and the smoothed data based on eq 1 for CEPPA in the temperature range of 25.10 to 76.32 °C and that based on eq 2 for CPPPA in the temperature range of 26.70 to 94.52 °C are presented in Table 1. The absolute average deviation (AAD%) of the measured solubilities from the smoothed data is defined as

$$\mathrm{AAD\%} = \frac{1}{N}\sum_i |s_i^{\mathrm{exptl}} - s_i^{\mathrm{calcd}}|/|s_i^{\mathrm{exptl}}| \times 100$$

where the superscript exptl stands for experimental values and calcd stands for calculated values. The absolute average deviations of the measured solubilities from the smoothed data of CEPPA and CPPPA are 2.2% and 2.1%, respectively.

Discussion

Within the temperature range of the measurements, the solubilities (mole fraction) in water of both CEPPA and CPPPA showed an increased trend based on the increased temperature, but they varied greatly. The solubility for CEPPA increased more quickly than that of CPPPA. Because the up-trends were different, a logarithmic equation was used to correlate the sharply increased solubility data for CEPPA, and a polynomial equation was used to correlate the gently increased solubility data of CPPPA. The solubility of CEPPA is much higher than that of CPPPA, showing that CEPPA is readily dissolvable in water, especially in heated water. Thus the solubility in mole fraction of CEPPA in water increased from 1.782×10^{-3} at 25.10 °C to 5.682×10^{-2} at 76.32 °C, while the solubility in mole fraction of CPPPA in water increased from 0.2243×10^{-4} at 26.70 °C to 0.9822×10^{-4} at 94.52 °C.

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