Solubilities of 2-(2-Hydroxyphenyl)phenylphosphonic Acid in Chlorobenzene and in Water and Partition Coefficient between Water + Chlorobenzene Mixtures

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The solubilities of 2-(2-hydroxyphenyl)phenylphosphonic acid (HBP) in chlorobenzene (300.97 to 355.30) K and in water (308.6 to 362.37) K and partition coefficient between water + chlorobenzene mixtures were measured. The partition coefficients of HBP were measured between water + chlorobenzene immiscible mixtures from (299.45 to 334.05) K.

Introduction

6-Oxo-(6*H*)-dibenz-[*c*,*e*][1,2]-oxaphosphorins (DOP) is an important additive for polymers for protection against oxidative degradation and for flame-proofing and further serves as starting materials for preparing further polymer additives.[1] The compound 2-(2-hydroxyphenyl)phenylphosphonic acid (HBP) is used as an important raw material for production of the compound DOP and also is used as a raw material in production of stabilizers and a fire retardant for organic low molecular weight and high molecular weight compounds. Furthermore, HBP is expected to extend their use soon. HBP is generally prepared from *o*-phenylphenol and phosphorus trichloride via the Fridel−Crafts reaction using zinc chloride as catalyst.[2] In the preparation of HBP we need to use an organic solvent that is insoluble in water and is inert (chlorobenzene) in the reaction system and then wash the crystal with water. Therefore, a knowledge of the solubilities of HBP in chlorobenzenes and in water and the partition coefficients of HBP between these phases is important for their preparation and crystallization. However, the solubility and partition coefficients of HBP in aqueous organic mixtures were not available in the literature.

Experimental Section

Materials. OPP (*o*-phenyl phenol) was nosocomial with a purity of 99.9 %; PCl_3, $ZnCl_2$, and C_6H_5Cl were all analytical reagents from Beijing Chemical Factory. The distilled water and HBP were prepared.

Apparatus and Procedure. Melting points 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 spectrometer using KBr pellets.

A jacketed equilibrium cell with a working volume of 120 mL, as described by Wang et al.,[3] was used. (The cell was sealed to prevent the evaporation of solvent.) A circulating water bath with a thermostat (type 50l, Shanghai Laboratory Instrument Works Co. Ltd.), which is capable of maintaining the temperature within ± 0.05 K was also used. An analytical balance (type TG328B, Shanghai Balance Instrument Works Co.) with uncertainty of ± 0.1 mg was used during the mass measurements, and a magnetic stirrer was also used.

Synthesis of HBP. The synthesis method of HBP was improved on the basis of that described by Saito et al.[4] Eight-five grams (0.5 mol) of *o*-phenylphenol and 0.8 g of zinc chloride were introduced into a 500-mL flask equipped with an agitator, a thermometer, and a reflux condenser that was connected to a gas outlet treatment equipment and gradually heated. When the temperature raised to about 323.15 K, the reactants was fused. Phosphorus trichloride, 69 g (0.5 mol), was added dropwise with a constant-pressure dropping funnel to the flask equipped at 343.15 K. When all the phosphorus trichloride had been added, the reactants were further heated to about 453.15 K, and then 21 g (total 90 g, 0.65 mol) of phosphorus trichoride was added dropwise again. The temperature of the reaction mixture was raised to 493.15 K and allowed to react at that temperature for 8 h. Generation of hydrogen chloride gas terminates, followed by cooling the condensation reaction product to 393.15 K, adding 60 g of chlorobenzene, stirring for 1 h, and further cooling the product to about 323.15 K to conduct the decoloring filtration. Into a reactor equipped with a reflux condenser and containing 200 g of water and 90 g of chlorobenzene, the above filtered fluid is gradually added with stirring. The contents is further heated, and hydrolysis occurs at condensation temperature for 4 h.

Thereafter, the reaction liquid mixture is allowed to stand while holding at (343.15 to 353.15) K and is separated with a water layer; 80 g of warm water of (333.15 to 343.15) K was added to an oil layer, stirred, and allowed to stand at the same temperature and separated by a washed water layer. This operation is repeated 3 times. Thereafter, 30 g of water is added to cool to 298.15 K or less, and precipitates are filtered out and washed with cold water to obtain a white crystalline, wet filtration mass. This material is identified to be HBP. It has a purity of 99.9 % or higher by liquid chromatography analysis. Yield 96 %; mp (378.15 to 379.15) K (literature (378.15 to 379.15) K). IR(KBr): 1197 cm^{-1} (P=O); 1007 cm^{-1} (P−OH); 2384 cm^{-1} (P−H); 1587 cm^{-1} (P−Ph); 3358 cm^{-1}, 1362 cm^{-1} (Ph-

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Table 1. Measured and Calculated Solubilities (Mole Fraction) of HBP in Chlorobenzene and in Water

	T			$x^{\mathrm{exp}} - x^{\mathrm{cal}}$
dissolvent	K	x^{exp}	x^{cal}	x^{exp}
chlorobenzene	300.97	$1.296 \cdot 10^{-2}$	$1.215 \cdot 10^{-2}$	0.0626
	304.47	$1.492 \cdot 10^{-2}$	$1.412 \cdot 10^{-2}$	0.0537
	308.86	$1.561 \cdot 10^{-2}$	$1.704 \cdot 10^{-2}$	−0.0917
	313.71	$1.946 \cdot 10^{-2}$	$2.099 \cdot 10^{-2}$	−0.0784
	319.15	$2.741 \cdot 10^{-2}$	$2.650 \cdot 10^{-2}$	0.0331
	325.56	$3.596 \cdot 10^{-2}$	$3.489 \cdot 10^{-2}$	0.0297
	332.40	$4.698 \cdot 10^{-2}$	$4.679 \cdot 10^{-2}$	0.0040
	338.93	$5.966 \cdot 10^{-2}$	$6.192 \cdot 10^{-2}$	−0.0378
	342.74	$7.002 \cdot 10^{-2}$	$7.291 \cdot 10^{-2}$	−0.0413
	346.96	$8.529 \cdot 10^{-2}$	$8.738 \cdot 10^{-2}$	−0.0245
	349.40	$9.742 \cdot 10^{-2}$	$9.702 \cdot 10^{-2}$	0.0040
	352.87	$11.59 \cdot 10^{-2}$	$11.26 \cdot 10^{-2}$	0.0286
	355.30	$13.11 \cdot 10^{-2}$	$12.50 \cdot 10^{-2}$	0.0468
water	308.60	$2.578 \cdot 10^{-4}$	$2.679 \cdot 10^{-4}$	−0.0390
	314.70	$3.357 \cdot 10^{-4}$	$3.145 \cdot 10^{-4}$	0.0632
	320.97	$3.957 \cdot 10^{-4}$	$3.708 \cdot 10^{-4}$	0.0628
	332.20	$4.959 \cdot 10^{-4}$	$4.983 \cdot 10^{-4}$	−0.0048
	337.70	$5.786 \cdot 10^{-4}$	$5.758 \cdot 10^{-4}$	0.0048
	342.40	$6.876 \cdot 10^{-4}$	$6.516 \cdot 10^{-4}$	0.0524
	347.77	$7.634 \cdot 10^{-4}$	$7.504 \cdot 10^{-4}$	0.0170
	352.60	$8.586 \cdot 10^{-4}$	$8.521 \cdot 10^{-4}$	0.0076
	358.30	$9.843 \cdot 10^{-4}$	$9.899 \cdot 10^{-4}$	−0.0056
	362.37	$11.49 \cdot 10^{-4}$	$11.02 \cdot 10^{-4}$	0.0412

OH). Elemental analysis (%, calculated): C, 61.54 (61.68); H, 4.71 (4.75).

Solubility Measurement. The solubilities were measured by a gravimetric method.[3,5] A 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 HBP in chlorobenzene and in water at different temperatures, the following procedure was applied: for each measurement, an excess amount of HBP was added to a certain amount of solvent chlorobenzene in the equilibrium cell, and then agitation was started. After at least 2 h, the agitation was stopped, and the solution was kept still for 4 h (rather slow sedimentation rate). And then the white solids could be observed to settle down in the lower portion of the equilibrium cell. A preheated only one-off injector withdrew the clear upper portion of the solution to another previously weighed measuring vial (m_0). The vial was quickly tightly closed and weighed (m_1) to determine the mass of the sample (m_1-m_0). Then the vial was uncovered and placed in an oven at about 353 K for evaporation. The vial was covered with a piece of filter paper to prevent dust contamination. After the solvent in the vial was completely evaporated, the vial was and weighed again (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 S could be determined from eq 1:[6,7]

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

Different dissolution times were tested to determine the suitable equilibrium time. It was found that 4 h was enough for HBP in solvent to reach equilibrium. An average value is taken from three measurements at the same composition of solvent for each temperature.

With similarity method for determining the solubility of HBP in water at different temperatures, the dissimilarity: after at least 2 h, the agitation was stopped and the solution was kept still for 3 h (sedimentation rate rather rapidness)

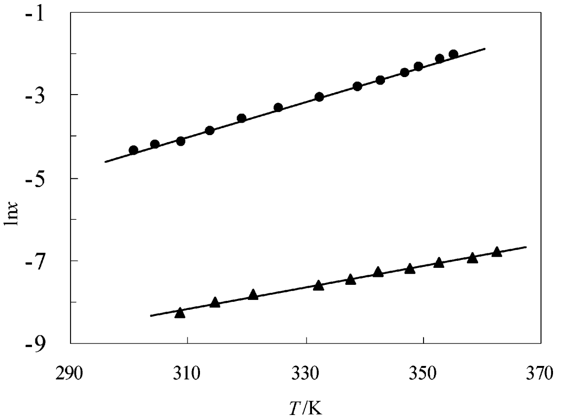

Figure 1. Solubilities (mole fraction) of HBP in chlorobenzene and in water: —, calculated from eq 3 and eq 4; ●, measured data in chlorobenzene; ▲, measured data in water.

Table 2. Measured and Calculated Partition Coefficient of HBP in Chlorobenzene + Water Mixtures

T					$D^{\mathrm{exp}} - D^{\mathrm{cal}}$
K	$x^{\mathrm{a}} \cdot 10^2$	$x^{\mathrm{b}} \cdot 10^4$	D^{exp}	D^{cal}	D^{exp}
299.45	0.4611	2.577	17.89	18.31	−0.0231
303.26	0.4166	1.987	20.97	20.68	0.0135
308.65	0.4568	1.881	24.28	24.05	0.0099
314.65	1.2352	4.494	27.49	27.79	−0.0110
318.92	1.345	4.368	30.79	30.45	0.0111
324.05	1.851	5.497	33.67	33.65	0.0007
329.23	1.731	4.701	36.82	36.88	−0.0016
334.05	1.619	4.072	39.76	39.89	−0.0032

The solubility of HBP in chlorobenzene at temperatures ranging from (300.97 to 355.30) K and that in water at temperatures ranging from (308.6 to 362.37) K are summarized in Table 1 and plotted in Figure 1. The estimated uncertainty of the solubility values based on error analysis and repeated observations was within 2 %.

Partition Coefficient Measurement. The partition coefficient of HBP in water + chlorobenzene immiscible mixtures was measured by adding a certain amount of HBP(less solubility at a temperature) in the equilibrium cell of distilled water + chlorobenzene mixtures of fixed volume ratio and then agitation was started. After at least 3 h, the agitation was stopped, and the solution was kept still for 6 h. Then the clear upper and lower portion of the solution was withdrew respectively with two preheated syringes. With similarity method of measurement of solubility, the content of HBP was measured by a gravimetric method. The effect of various temperatures on partition coefficient of HBP was investigated. Mole fractions of HBP in organic phase and water phase were x^{a} and x^{b}. For each temperature, the above operation was conducted three times, and an averaged value was taken. As intermiscibility of chlorobenzene and water was too small to be neglected,[8] the partition coefficient of HBP in these two solvents (D) could be determined from eq 2:[9,10]

$$D = \frac{x^{\mathrm{a}}}{x^{\mathrm{b}}} \tag{2}$$

The partition coefficient of HBP in water + chlorobenzene at temperatures ranging from (299.45 to 334.05) K is summarized in Table 2 and plotted in Figure 2. The estimated uncertainty of the partition coefficient values based on error analysis and repeated observations, was within 2 %.

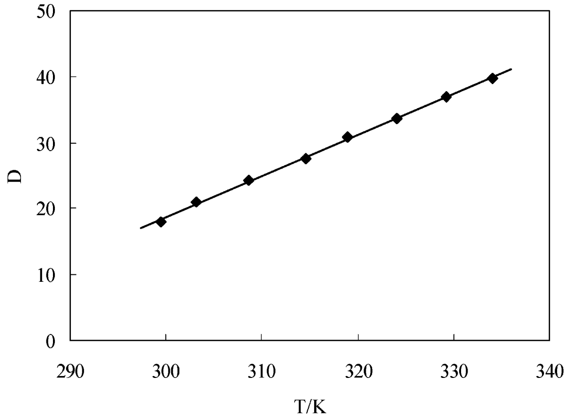

Figure 2. Partition coefficient of HBP in chlorobenzene + water mixtures: —, calculated from eq 5; ■, measured partition coefficient of HBP in mixtures.

Data Correlation

The solubility (mole fraction) of HBP in chlorobenzene was correlated as function of temperature (T/K) by adopting a logarithmic formula:

$$\ln x = 0.0429(T/\mathrm{K}) - 17.322 \qquad (3)$$

The solubility (mole fraction) of HBP in water was correlated as function of temperature (T/K) by adopting a logarithmic formula:

$$\ln x = 0.026(T/\mathrm{K}) - 16.236 \qquad (4)$$

The measured solubility and the smoothed data based on eq 3 for HBP in chlorobenzene in the temperature range of (300.97 to 355.30) K and that based on eq 4 for HBP in water in the temperature range of (308.6 to 362.37) K are presented in Table 1. The absolute average deviation (AAD) of the measured solubilities from the smoothed data is defined as

$$\mathrm{AAD} = \frac{1}{N}\sum_i \left|\frac{x_i^{\mathrm{exp}} - x_i^{\mathrm{cal}}}{x_i^{\mathrm{exp}}}\right| \qquad (5)$$

where the superscript exp stands for experimental values and cal stands for calculated values, and N stands for total number of experiment data. The AAD of the measured solubilities from the smoothed data in chlorobenzene and in water are 0.036 and 0.030.

The partition coefficient of HBP in water + chlorobenzene was correlated as function temperature (T/K) by adopting a linear formula:

$$D = 0.6237(T/\mathrm{K}) - 168.46 \qquad (6)$$

The measured partition coefficient and the smoothed data based on eq 6 for HBP between water + chlorobenzene in the temperature range of (299.45 to 334.05) K are presented in Table 2. The AAD of the measured partition coefficient of HBP from the smoothed data is defined as

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

where the superscript exp stands for experimental values and cal stands for calculated values, and N stands for total number of experiment data. The absolute average deviations of the measured partition coefficient of HBP from the smoothed data in water + chlorobenzene are 0.0093.

Conclusion

The synthesis method of HBP was improved. In the preparation of HBP decoloration was conduct by filtration and satisfying result was obtained.

Within the temperature range of the measurements, the solubilities (mole fraction) of HBP in chlorobenzene and in water showed an increased trend based on the increased temperature, but they varied greatly. The solubility in chlorobenzene increased much higher than that in water. Thus the solubility in mole fraction of HBP in chlorobenzene increased from $1.296 \cdot 10^{-2}$ at 300.97 K to $13.11 \cdot 10^{-2}$ at 355.30 K, while the solubility in mole fraction of HBP in water increased from $2.578 \cdot 10^{-4}$ at 308.60 K to $11.49 \cdot 10^{-4}$ at 362.37 K.

Within the temperature range of the measurements, the partition coefficient of HBP in water + chlorobenzene showed an increased trend based on the increased temperature. Thus the partition coefficient of HBP in water + chlorobenzene increased from 17.89 at 299.45 K to 39.76 at 334.05 K.

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