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Solubilities of Triphenylphosphine in Ethanol, 2-Propanol, Acetone, Benzene, and Toluene

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The solubilities of triphenylphosphine in the organic solvents ethanol, 2-propanol, acetone, benzene, and toluene were measured by a gravimetrical method from (303.2 to 333.2) K. The logarithm of the solubility data was correlated against temperature with the average absolute error less than 2 %. The solubility of triphenylphosphine in ethanol was compared with the literature data and agreed with the literature data within 1.7 %. Although ethanol is often used for recrystallization of triphenylphosphine, the solubility of triphenylphosphine in acetone was higher compared with other solvents. Knowledge of the solubility data in the organic solvents is useful in the study of the crystallization of triphenylphosphine.

Introduction

Triphenylphosphine is a common organophosphorus compound with the formula $P(C_6H_5)_3$, often abbreviated as PPh_3 or Ph_3P, which is widely used as a catalyst for organic synthesis and as an intermediate for phase-transfer catalysts and Wittig reactions.[1,2] As a ligand for many metals to form coordination compounds, it is often used to bind with most transition metals, especially those in the middle and late transition metals such as Pd, Pt, Ru, Ni, and Os.

In industry, triphenylphosphine is often purified by recrystallization from organic solvents, such as ethanol, benzene, and acetone. Thus, the solubility of triphenylphosphine in these organic solvents is of importance for the separation and purification process. To our knowledge, only the solubility of triphenylphosphine in ethanol from (297.45 to 327.65) K determined by a dynamic method has been reported.[3]

In this work, the solubilities of triphenylphosphine in the organic solvents ethanol, 2-propanol, acetone, benzene, and toluene as required in the purification process were measured by a gravimetrical method from (303.15 to 333.15) K.

Experimental Section

Chemicals. Analytical reagent triphenylphosphine (Kemiou Chemical Reagent Co., Tianjin) had a purity of 99.7 %. Ethanol, AR, 99.7 %; 2-propanol, AR, 99.7 %; benzene, AR, 99.5 %; and toluene, AR, 99.5 % were purchased from Guangcheng Chemical Reagent Co., Tianjin. Acetone (Fumin Chemical Reagent Co., Shanghai) had a purity of 99.5 %. The purities of the chemicals were checked by HPLC (LC-6A, Shimadzu Scientific Instruments) and GC (GC-960, Shanghai Haixin Chromatography Co., Ltd.). All the chemicals were used without further purification.

Apparatus and Procedures. The experiments were carried out in a magnetically stirred, jacketed equilibrium cell with a volume of 100 mL as described in the literature.[4,5] The equilibrium cell was sealed by a rubber plug to prevent evaporation of the solvent. The temperature of the equilibrium cell was controlled by circulating water from a thermostat (type 501, Shanghai Laboratory Instrument Works Co., Ltd.) within ±0.05 K. The equilibrium temperature was measured by a thermocouple immersed into the solution which was calibrated against a standard platinum resistance thermometer (SPRT) with a water bath, with an uncertainty of ±0.1 K. The sample mass was determined by an electronic balance (TG328B, Shanghai Instrument Works Co.) with an uncertainty of ±0.1 mg.

Solubility Measurements. The solubilities of triphenylphosphine in ethanol, 2-propanol, acetone, benzene, and toluene were measured by the gravimetric method.[6] To find the suitable time for the equilibrium, the test experiments were carried out over 10 h, 8 h, 6 h, 4 h, 2 h, 1 h, and 0.5 h, respectively. The solubility data that were measured over 10 h, 8 h, 6 h, 4 h, and 2 h showed a better agreement, compared with those obtained over 1 h and 0.5 h. So the equilibrium time, 2 h, was chosen in the following experiments.

For each measurement, an excess amount of triphenylphosphine was added to a known mass of solvent. Then, the equilibrium cell was heated to the required temperature with continuous stirring. After 2 h, the stirring was stopped and the solution was kept still for 30 min. Then, the excess solid could be observed in the lower part of the equilibrium cell. The sample of the upper part of the solution was withdrawn with a suitable warmed pipet to another weighed vial. The vial was closed tightly and weighed to determine the mass of the sample. Then, the vial was placed in an oven to evaporate the solvent. After the evaporation of the solvent, the vial was dried for another 2 h and reweighed to determine the mass of the solid. Thus, the solid concentration of the sample in mole fraction could be determined.[6] An average value was taken from three measurements for each temperature. The estimated uncertainty of the solubility based on an error analysis was within 2 %.

Results and Discussion

The solubilities of triphenylphosphine in ethanol, 2-propanol, acetone, benzene, and toluene were measured from (303.05 to

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Table 1. Solubilities of Triphenylphosphine in Five Organic Solvents in Mole Fraction

solvent	T/K	$10x^{\text{exptl}}$	$10^5\delta$
ethanol	303.5	0.095	1.5
	308.3	0.12	1.9
	313.3	0.16	1.0
	318.6	0.22	0.62
	323.2	0.28	1.1
	327.9	0.38	1.3
	333.0	0.50	0.61
2-propanol	303.1	0.077	1.0
	308.4	0.10	1.3
	313.3	0.14	0.64
	318.2	0.19	1.2
	322.9	0.25	0.60
	328.4	0.33	1.1
	333.2	0.45	1.1
acetone	303.2	0.89	0.63
	308.1	1.2	1.5
	313.4	1.4	1.7
	318.2	1.9	1.5
	323.5	2.5	1.9
	327.8	3.3	0.65
	333.1	4.2	1.7
benzene	303.3	0.69	0.68
	308.6	0.95	1.3
	312.9	1.2	1.8
	318.1	1.6	1.6
	323.2	2.2	1.0
	328.1	2.8	1.6
	333.2	3.7	2.2
toluene	302.4	0.50	0.61
	308.2	0.70	0.92
	313.7	1.0	1.2
	318.2	1.3	1.4
	323.3	1.8	0.64
	328.3	2.4	1.6
	333.4	3.2	0.66

333.35) K and are summarized in Table 1. The root-mean-square deviations (δ), presented in Table 1, are defined as follows:

$$\delta = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}} \qquad (1)$$

where x_i is the experimental value, $\bar{x}$ is the average value of the experimental data, and n is the number of data points for each temperature.

Within the temperature range of the measurements, the mole fraction solubilities of triphenylphosphine in the organic solvents increased with an increase in temperature. Because the solubility data of triphenylphosphine in ethanol and 2-propanol were less than those in acetone, benzene, and toluene, the logarithms of the mole fraction solubilities against temperature are shown in Figures 1 and 2, respectively, which show good linearity. The solubility of triphenylphosphine in ethanol was compared with the literature data[3] with the absolute average deviation of 1.7 %, as shown in Figure 1, in which the slope of the solubility line of triphenylphosphine in ethanol is slightly larger than that of the literature data.[3] At temperatures of 302.25 K and 323.05 K, the solubility of triphenylphosphine in ethanol has absolute average deviations of 3.1 % and 0.52 %, respectively, compared with the reference data.[3]

The solubilities (x) of triphenylphosphine were correlated as a function of temperature as follows:

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

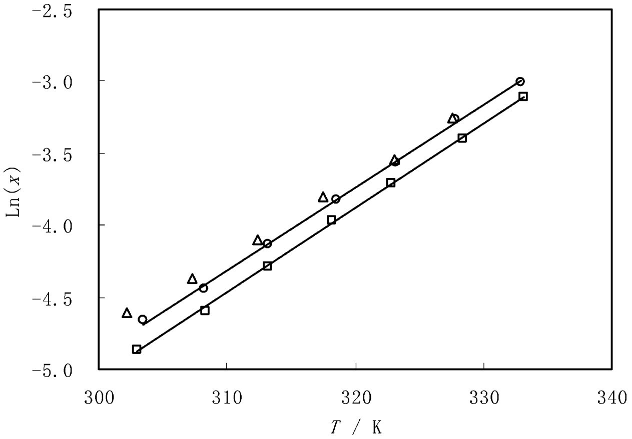

Figure 1. Solubilities of triphenylphosphine in ethanol and 2-propanol in mole fraction vs temperature: ○, solubility in ethanol; □, solubility in 2-propanol; Δ, literature data from ref 3; —, correlated data from eq 2.

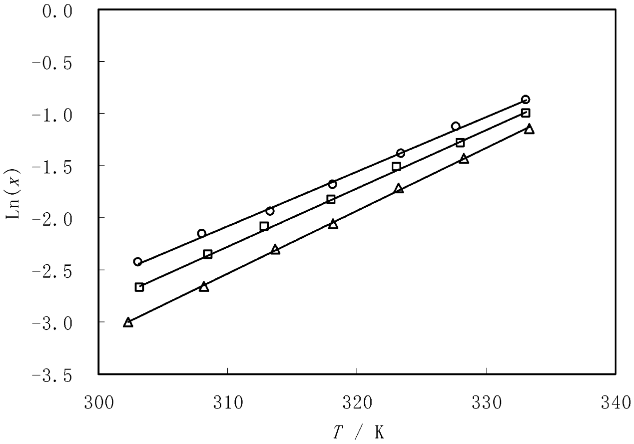

Figure 2. Solubilities of triphenylphosphine in acetone, benzene, and toluene in mole fraction vs temperature: ○, solubility in acetone; □, solubility in benzene; Δ, solubility in toluene; —, correlated data from eq 2.

Table 2. Regressed Parameters *A* and *B* and the Absolute Average Deviation (AAD) of the Measured Solubility from the Calculated Results of Equation 2

solvent	A	B	100 AAD
ethanol	−22.0697	0.0573	1.78
2-propanol	−22.7152	0.0589	1.82
acetone	−18.2441	0.0521	2.35
benzene	−19.4887	0.0555	1.61
toluene	−21.2389	0.0603	1.42

The parameters A and B for the solvents are listed in Table 2. The absolute average deviations (AADs) of the measured solubility from the correlated data are also listed in Table 2. The AAD is defined as

$$\text{AAD} = \frac{1}{N}\sum_i \left|\frac{x_i^{\text{exptl}} - x_i^{\text{cal}}}{x_i^{\text{exptl}}}\right| \qquad (3)$$

where the superscript exptl stands for the experimental data, cal stands for the correlated values, and N is the number of data points. The results showed that the solubilities of triphenylphosphine in the organic solvents could be correlated by eq 2 with the overall absolute average deviation of 1.8 %, within the temperature range of the measurement.

Although ethanol is often used to recrystallize triphenylphosphine from solutions, the solubility of triphenylphosphine in ethanol was slightly higher than in 2-propanol, as listed in Table 1. The solubility of triphenylphosphine in acetone showed a higher value than those in the other solvents, as shown in Figure

2. Thus, acetone should be a better solvent to separate and purify triphenylphosphine from solutions.

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