J. Chem. Eng. Data 2009, 54, 1382–1384

Solubilities of Triphenylphosphine Oxide in Selected Solvents

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Triphenylphosphine oxide (TPPO) was characterized by a differential scanning calorimeter (DSC) and nuclear magnetic resonance (^{1}H NMR and ^{31}P NMR). Using a static analytical method, the solubilities of TPPO were measured in benzene, toluene, ethyl acetate, and binary solvent mixtures: benzene + ethyl acetate (volume fraction = 0.5); toluene + ethyl acetate (volume fraction = 0.5); toluene + benzene (volume fraction = 0.5). The experimental results were correlated with an empirical equation. The estimated uncertainty of all the solubility values was within 2.0 %.

Introduction

Triphenylphosphine oxide (here after abbreviated as TPPO; its formula is shown in Figure 1) (CASRN 791-28-6) has been extensively employed as a ligand for many p-, d-, and f-block metals.[1] For example, it has often been chosen as a suitable ligand for complexing the oxophilic lanthanide(3+) ions and has been used in solvent extraction separation processes.[2] In addition, TPPO is a representative flame-retardant additive that is added to polymers to reduce the flammability of the base polymer.[3]

Owing to extensive application of TPPO as a ligand for many transitional metals, and our continuous efforts to search for Lewis base ligands for epoxidation of olefins using Mo(VI) compounds as catalysts, TPPO was purchased directly and characterized. To accomplish efficient epoxidation of olefins using Mo(VI) compounds as catalysts containing the TPPO ligand in suitable organic solvents, it is necessary to know reliable solubility data of the ligand in the selected solvents. Knowledge of the solubilities of TPPO in solvents is also important for its preparation and purification. To the best of our knowledge, these data were not available in the literature.

In this study, TPPO was characterized, and its solubilities in benzene, toluene, ethyl acetate, and binary solvent mixtures [benzene + ethyl acetate (volume fraction = 0.5); toluene + ethyl acetate (volume fraction = 0.5); toluene + benzene (volume fraction = 0.5)] were measured.

Experimental Section

Materials. TPPO was purchased from Alfa Aesar, and its mass fraction purity was higher than 98 %. All the other chemicals in the measurement were purchased from Beijing Chemical Reagents Company and were analytical grade reagents. They were used without further purification. The mass fraction purities for the organic solvents used in this work are listed in Table 1. Their mass fraction purities were all higher than 99 %.

Apparatus. ^{1}H NMR spectra were recorded on a Varian Unity Inova-400 spectrometer. ^{31}P NMR spectra were recorded on a JEOL JNM ECA-600 spectrometer operating at 242.95 MHz with $CDCl_3$ inside using the standard pulse sequence at room temperature. The melting points and enthalpy of fusion were determined with a DSC Q100 differential scanning calorimeter (DSC) in flowing nitrogen at a heating rate of 10 K·min^{-1}.

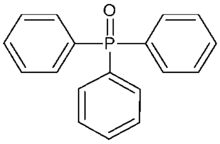

Figure 1. Structure of triphenylphosphine oxide.

Table 1. Mass Fraction Purity (ω), Density (ρ), and Refractive Index (n_D) for the Organic Solvents Used in This Work at T = 293.15 K

solvent	ω/%	ρ/g·cm^{-3}	n_D
benzene	99.5	0.879	1.5011
toluene	99.5	0.866	1.4967
ethyl acetate	99.5	0.900	1.3588

A jacketed equilibrium cell was used for the solubility measurement with a working volume of 120 mL and a magnetic stirrer, as described by Wang et al.[4,5] A circulating water bath was used with a thermostat (type 50 L), made from Shanghai Laboratory Instrument Works Co., Ltd., which is capable of maintaining the temperature within ± 0.05 K. An analytic balance (type TG328B, Shanghai Balance Instrument Works Co.) with an uncertainty of ± 0.1 mg was used during the mass measurements.

Characterization of TPPO. ^{1}H NMR ($CDCl_3$): δ = (7.44 to 7.69) ppm (m, 15 H). ^{31}P NMR ($CDCl_3$): δ = 29.8 ppm. These results show a high purity of the TPPO sample as certificated by Alfa Aesar. The results of differential scanning calorimeter (DSC) measurement of TPPO were shown in Figure 2. The melting point of TPPO was 431.1 K (lit. 429.0 K;[6] 431.9 K;[6,7] 429.6 K[6,8]). The enthalpy of fusion of TPPO was (23.70 ± 0.25) kJ·mol^{-1} (lit. (23.80 ± 0.24) kJ·mol^{-1};[6] (24.22 ± 0.35) kJ·mol^{-1};[6,7] (23.40 ± 0.40) kJ·mol^{-1}[6,8]).

Solubility Measurement. The solubilities were measured by a gravimetric method.[4] For each measurement, an excess mass of TPPO was added to a known mass of solvent. Then the equilibrium cell was heated to a constant temperature with continuous stirring. After at least 2 h (the temperature of the water bath approached a constant value, then the actual value of temperature was recorded), the stirring was stopped, and the solution was kept still until it was clear. A preheated on–off

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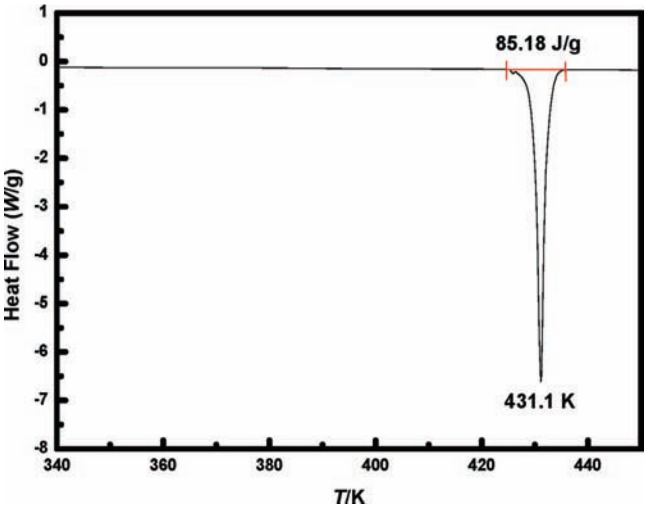

Figure 2. Experimental heat flow from differential scanning calorimeter (DSC) measurement of TPPO.

injector with a cotton filter withdrew 2 mL of the clear upper portion of the solution to another previously weighed measuring vial (m_0). The vial was quickly and tightly closed and weighed (m_1) to determine the mass of the sample ($m_1 - m_0$). Then the vial was uncovered with a piece of filter paper to prevent dust contamination. After the solvent in the vial had completely evaporated, the vial was dried and reweighed (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, x, could be determined from eq 1[9]

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

where M_1 is the molar mass of TPPO and M_2 is the molar mass of solvent.

$$x = \frac{(m_2 - m_0)/M_1}{(m_2 - m_0)/M_1 + (m_1 - m_2)w_2/M_2 + (m_1 - m_2)(1 - w_2)/M_3} \tag{2}$$

Equation 2 is for a mixed solvent, where M_1 is the molar mass of TPPO; M_2 and M_3 are two solvents measured; and w_2 is the mass of fraction of one solvent in another.

Different dissolution times were tested to determine a suitable equilibrium time. It was found that 2 h was enough for TPPO in solvent to reach equilibrium. During our experiments, three parallel measurements were performed at the same composition of solvent for each temperature, and an average value is given. The maximum standard deviation of each triplicate data is 0.25 %, and the minimum is 0.15 %. The estimated relative uncertainty of the solubility values based on error analysis and repeated observation was within 0.02.

Results and Discussion

Prior to the solubility measurement, TPPO was found to be almost insoluble in deionized water, cyclohexane, petroleum ether, and hexane but readily soluble in ethanol, formic acid, acetic acid, and dichloromethane. In this study, TPPO was characterized, and its solubilities in benzene, toluene, ethyl acetate, and binary solvent mixtures [benzene + ethyl acetate (volume fraction = 0.5); toluene + ethyl acetate (volume fraction = 0.5); toluene + benzene (volume fraction = 0.5)] were measured.

Table 2. Mole Fraction Solubilities (x) and Activity Coefficients (γ) of TPPO in the Selected Solvents

solvent	T/K	x	γ	$(x - x^{\text{calcd}})/x$
toluene	294.42	0.02907	34.02	−0.008
	298.74	0.03464	28.57	0.010
	303.15	0.03960	25.00	−0.013
	308.36	0.04874	20.32	0.007
	313.53	0.05476	18.10	−0.034
	317.97	0.06657	14.90	0.036
	323.13	0.07680	12.92	0.023
	328.42	0.08823	11.25	0.005
	333.77	0.09985	9.953	−0.028
benzene	293.78	0.05504	17.97	−0.012
	303.04	0.07469	13.25	0.024
	314.12	0.09634	10.29	−0.015
	323.34	0.12254	8.098	0.005
	333.45	0.15175	6.539	−0.002
ethyl acetate	294.54	0.02297	43.06	−0.004
	299.09	0.02748	36.01	0.032
	303.30	0.03049	32.47	−0.007
	308.27	0.03485	28.42	−0.018
	313.72	0.04087	24.25	−0.031
	318.32	0.04962	19.98	0.020
	323.21	0.05547	17.89	−0.012
	328.65	0.06595	15.05	0.018
0.5 benzene + 0.5 ethyl acetate	294.07	0.04274	23.14	−0.017
	298.44	0.04856	20.38	−0.006
	303.32	0.05556	17.82	0.012
	308.27	0.06336	15.63	0.026
	313.28	0.07146	13.87	0.007
	318.45	0.07866	12.61	−0.014
	323.82	0.08838	11.23	−0.015
	327.87	0.09893	10.03	0.005
0.5 toluene + 0.5 ethyl acetate	293.32	0.03848	25.70	−0.018
	298.50	0.04479	22.09	−0.001
	303.52	0.05037	19.66	0.004
	308.31	0.05846	16.94	0.018
	312.80	0.06395	15.50	0.017
	318.23	0.07242	13.69	0.007
	323.53	0.07827	12.68	−0.029
	328.04	0.08807	11.27	0.000
0.5 toluene + 0.5 benzene	293.67	0.03793	26.07	0.021
	298.87	0.04294	23.04	0.003
	303.45	0.04796	20.64	−0.006
	308.37	0.05493	18.03	−0.014
	313.43	0.06018	16.47	−0.042
	318.08	0.07043	14.08	0.020
	322.96	0.07664	12.94	−0.014
	327.83	0.09027	11.00	0.030

The mole fraction solubility data of TPPO, x, in selected solvents are summarized in Table 2 and plotted as ln x vs $1/T$ in Figures 3 and 4. From these figures, it can be seen that a trend of increasing solubility with temperature is observed.

The solubilities were correlated as a function of temperature by

$$\ln x = A + B/(T/\text{K}) \tag{3}$$

Parameters A and B for each solvent are listed in Table 3. The relative standard deviations (RSD), defined by eq 4, are also presented in Table 3. The smoothed data calculated from eq 3 are compared with the data listed in Table 2.

$$\text{RSD} = \left[\frac{1}{N}\sum_1^n \left(\frac{x_i - x_i^{\text{calcd}}}{x_i}\right)^2\right]^{1/2} \tag{4}$$

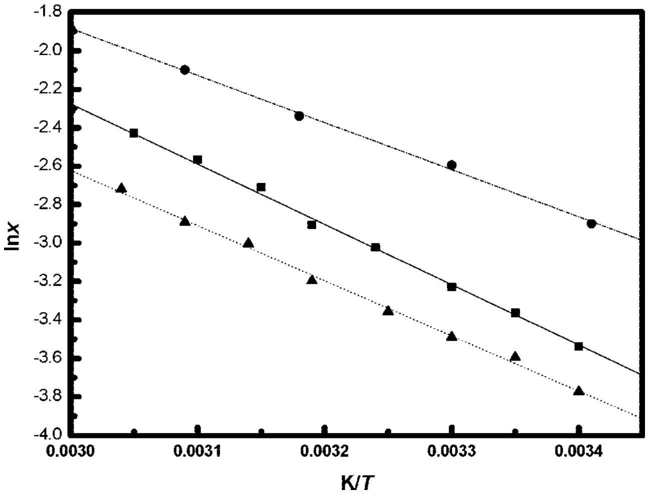

Figure 3. Mole fraction solubilities of TPPO in: (experimental) ■, toluene; ●, benzene; ▲, ethyl acetate; (calculated from eq 1) —, toluene; -•-, benzene; - - -, ethyl acetate.

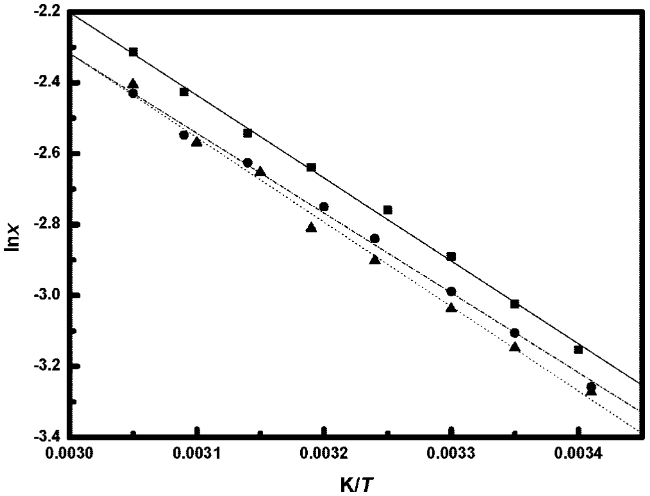

Figure 4. Mole fraction solubilities of TPPO in: (experimental) ■, 0.5 benzene + 0.5 ethyl acetate; ●, 0.5 toluene + 0.5 ethyl acetate; ▲, 0.5 toluene + 0.5 benzene; (calculated from eq 2) —, 0.5 benzene + 0.5 ethyl acetate; -•-, 0.5 toluene + 0.5 ethyl acetate; - - -, 0.5 toluene + 0.5 benzene.

Table 3. Parameters of Equation 3 and Root-Mean-Square Deviations of the Measured Solubility Calculated from Equation 4 for the Selected Solvents

solvent	*A*	*B*	RSD
toluene	7.1268	−3134.3	0.022
benzene	5.4626	−2448.8	0.014
ethyl acetate	5.9878	−2869.9	0.020
0.5 benzene + 0.5 ethyl acetate	4.8091	−2336.8	0.014
0.5 toluene + 0.5 ethyl acetate	4.4370	−2251.3	0.015
0.5 toluene + 0.5 benzene	4.8356	−2383.9	0.022

where calcd stands for the calculated values and N is the number of experimental points.

The results show that eq 3 can be used to correlate the solubility data. Within the temperature range of the measurements, the solubilities of TPPO in all of the investigated solvents increased with an increase in temperature. The solubility of TPPO in benzene shows the highest value from (293.32 to 333.77) K and in ethyl acetate shows the lowest value, which was probably related to the benzene group contained in the structure of TPPO. Thus, benzene is recommended as the best solvent for the purification of TPPO. Because of the almost moderate polarity of the selected solvents, however, the difference among the solubility data of TPPO in these solvents is unobvious. In addition, it was found that the solubility data of TPPO in benzene and toluene from (302.4 to 333.4) K is lower than those of triphenylphosphine (TPP) derived from the literature data[10] for the sake of comparison. To obtain the activity coefficients of TPPO in the solvents from the experimental data, the following equilibrium equation for solute 1 was derived as a fair approximation[9]

$$\ln \frac{1}{x_1\gamma_1} = \frac{\Delta H_f}{RT_m}\left(\frac{T_m}{T} - 1\right) \tag{5}$$

where ΔH_f refers to the enthalpy of fusion; T_m is the melting temperature; R is the gas constant; and x_1 and γ_1 refer to the mole fraction and activity coefficient of solute in the solution, respectively. With the experimental x_1, T, ΔH_f, and T_m values known, the activity coefficients of TPPO in different solvents were obtained. The results are listed in Table 2. From Table 2, it can be seen that the activity coefficients of TPPO in these selected solvents are all more than unity. For the TPPO−benzene system, relatively larger solubilities and relatively smaller activity coefficients than other systems used were obtained, which results in relatively larger deviations from the ideal behavior which corresponds to a polar or specific chemical force than other ones.

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Received for review November 10, 2008. Accepted February 1, 2009.

JE800842Z