Solubilities of Methyldiphenylphosphine Oxide in Selected Solvents

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Methyldiphenylphosphine oxide (MDPPO) was characterized by infrared spectroscopy (IR), nuclear magnetic resonance (^{1}H NMR and ^{31}P NMR), and a differential scanning calorimeter (DSC). Using a static analytical method, the solubilities of MDPPO were measured in benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, ethyl acetate, and binary solvent mixtures: acetone + *n*-hexane (volume ratio = 3:7) and benzene + ethyl acetate (volume ratio = 1:1). The experimental results were correlated with an empirical equation. The estimated uncertainty of all the solubility values was within 2.0 %.

Introduction

Methyldiphenylphosphine oxide (hereafter abbreviated as MDPPO; its formula is shown in Figure 1) (CASRN 2129-89-7) has been used as a ligand for many transitional metal catalysts.[1−5] The introduction of the MDPPO ligand to the Mo(VI) catalysts can not only improve the selectivity for epoxidation of olefins but also improve the solubility of the catalysts in organic solvents. The activity of the catalysts can be improved significantly. Therefore, it is important to have reliable solubility data of ligands in the selected solvents. To the best of our knowledge, no such data have been reported in the literature.

In this study, MDPPO was characterized, and its solubilities in benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, ethyl acetate, and binary solvent mixtures [acetone + *n*-hexane (volume ratio = 3:7) and benzene + ethyl acetate (volume ratio = 1:1)] were measured.

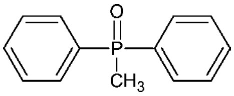

Figure 1. Structure of methyldiphenylphosphine oxide.

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

solvent	ω	ρ/g·cm^{-3}	n_D
benzene	0.995	0.879	1.5011
toluene	0.995	0.866	1.4967
ethyl acetate	0.995	0.900	1.3588
ethylbenzene	0.990	0.870	1.5009
o-xylene	0.985	0.8802	1.5055
m-xylene	0.950	0.8684	1.4972
p-xylene	0.950	0.8611	1.5004
acetone	0.995	0.788	1.3588
n-hexane	0.995	0.6594	1.3751

Experimental Section

Materials. MDPPO was purchased from Aldrich, and its mass fraction purity was higher than 0.98. All the other chemicals in the measurement were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. and were analytical grade reagents. They were used without further purification. The mass fraction purities of the organic solvents used in this work are listed in Table 1.

Apparatus. FT-IR spectra were measured on a Nicolet MAGNA 750 fitted with a Nic-plan IR microscope. ^{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}.

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.[6,7] 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 MDPPO. MW: 216.22. IR: 1438.8 (Ar−P), 1590.8, 1484.5, 741.5, 693.4 (C=C), 1170 (P=O), 1304.3 (P−CH_3). ^{1}H NMR ($CDCl_3$): δ = 7.45 to 7.74 ppm (m, 10 H), δ = 2.01 to 2.03 ppm (d, 3 H). ^{31}P NMR ($CDCl_3$): δ = 30.6446 ppm.

The results of differential scanning calorimeter (DSC) measurement of MDPPO were listed in Figure 2. The melting point and the enthalpy of fusion of MDPPO were 385.42 K and 94.21 J·g^{-1}, respectively.

Solubility Measurement. The solubilities were measured by a gravimetric method.[6] For each measurement, an excess mass of MDPPO 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 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 covered with a piece of filter paper to prevent dust

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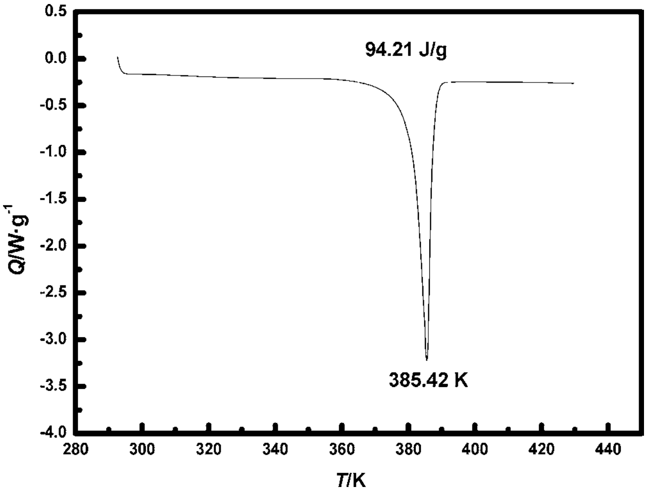

Figure 2. Experimental heat flow Q from differential scanning calorimeter (DSC) measurement of MDPPO.

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[8]

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

where M_1 is the molar mass of MDPPO 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 MDPPO; 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 MDPPO 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 observations was within 2.0 %.

Results and Discussion

Prior to the measurement, MDPPO was found to be almost insoluble in *n*-hexane but readily soluble in ethanol, formic acid, acetic acid, and acetone. In this study, the solubilities of MDPPO in benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, and ethyl acetate were measured. Considering the polarity, toxicity, price, and boiling point of the single solvent, the solubilities of MDPPPO in binary solvent mixtures acetone + *n*-hexane (volume ratio = 3:7) and benzene + ethyl acetate (volume ratio = 1:1) were also measured for comparison.

The mole fraction solubility data of MDPPO, x, in selected solvents are summarized in Table 2 and plotted as ln x vs $1/T$ in Figures 3 to 5. From these figures, it can be seen that a trend of increasing solubility with temperature is observed.

Table 2. Experimental Mole Fraction Solubilities (x) and Activity Coefficients (γ) Calculated from Equation 5 of MDPPO in the Selected Solvents

solvent	T/K	x	γ	$(x - x^{\mathrm{calcd}})/x$
benzene	288.52	0.04386	2.70	−0.026
	293.56	0.05731	2.39	0.015
	298.13	0.06975	2.23	0.012
	303.21	0.08747	2.04	0.024
	308.12	0.10233	1.98	−0.019
	312.55	0.12307	1.85	−0.010
	318.04	0.15627	1.66	0.018
	323.17	0.18304	1.61	−0.014
toluene	293.35	0.02275	5.98	0.021
	298.16	0.02870	5.42	−0.029
	303.08	0.03863	4.60	−0.012
	307.11	0.04975	3.97	0.018
	312.12	0.06500	3.46	0.016
	316.40	0.07975	3.13	−0.002
	320.95	0.09786	2.85	−0.029
	326.54	0.13478	2.36	0.017
ethylbenzene	293.35	0.01831	7.43	0.014
	298.04	0.02244	6.91	−0.030
	303.12	0.03040	5.85	0.014
	308.33	0.03929	5.19	0.013
	312.80	0.04645	4.92	−0.034
	317.51	0.06102	4.21	0.020
	321.25	0.07190	3.91	0.015
	326.39	0.08760	3.62	−0.014
m-xylene	293.75	0.01292	10.64	−0.017
	298.16	0.01665	9.34	0.013
	303.32	0.02160	8.29	0.020
	307.41	0.02582	7.72	0.004
	313.00	0.03320	6.92	−0.002
	317.53	0.03975	6.46	0.025
	320.55	0.04529	6.10	−0.026
	326.39	0.06136	5.16	0.030
p-xylene	293.65	0.01308	10.49	−0.014
	298.19	0.01751	8.89	0.028
	303.31	0.02188	8.18	−0.022
	308.42	0.02996	6.83	0.029
	313.11	0.03599	6.40	−0.022
	317.38	0.04418	5.79	−0.024
	320.55	0.05385	5.13	0.024
	326.44	0.06792	4.67	−0.015
o-xylene	293.35	0.02812	4.84	−0.020
	298.08	0.03435	4.52	0.022
	303.11	0.04065	4.38	0.027
	308.23	0.04543	4.48	−0.022
	313.09	0.05247	4.39	−0.025
	317.05	0.06028	4.21	−0.003
	321.94	0.07102	4.02	0.021
	328.07	0.08214	4.01	−0.003
ethyl acetate	293.25	0.04151	3.27	0.017
	298.46	0.04969	3.16	−0.022
	302.88	0.06177	2.86	0.016
	307.97	0.07438	2.72	0.001
	313.22	0.08851	2.61	−0.026
	317.25	0.10358	2.46	−0.017
	322.14	0.12836	2.23	0.021
	326.93	0.14980	2.14	0.008
0.3 acetone + 0.7 *n*-hexane	284.36	0.00950	10.99	−0.006
	289.11	0.01132	10.63	0.022
	293.91	0.01260	10.97	−0.014
	298.02	0.01414	10.96	−0.017
	302.85	0.01691	10.45	0.026
	308.13	0.01864	10.89	−0.020
	313.24	0.02193	10.54	0.009
0.5 benzene + 0.5 ethyl acetate	283.52	0.03441	2.96	−0.020
	288.36	0.04271	2.76	0.025
	293.43	0.05049	2.70	0.019
	298.08	0.05670	2.74	−0.018
	302.95	0.06567	2.70	−0.027
	309.07	0.08403	2.47	0.031
	313.26	0.09087	2.54	−0.015
	318.40	0.10732	2.44	0.003

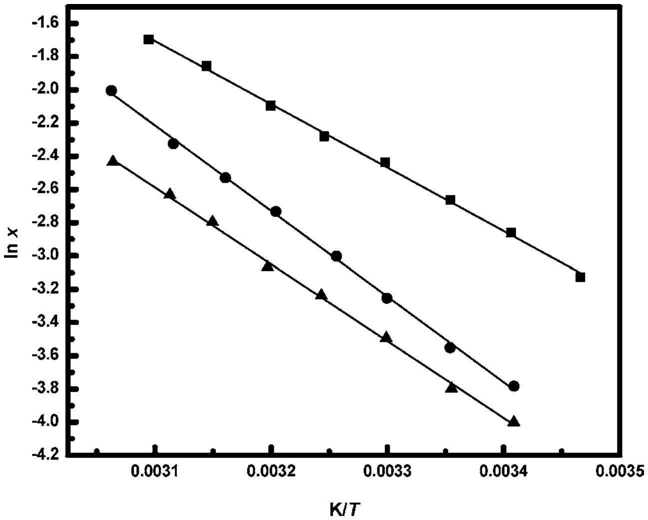

Figure 3. Mole fraction solubilities of MDPPO in: ■, benzene; ●, toluene; ▲, ethylbenzene; —, solubility curve calculated from eq 3.

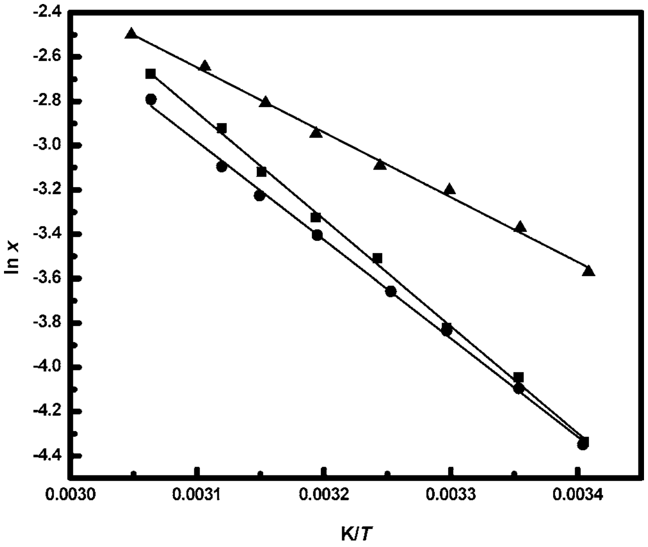

Figure 4. Mole fraction solubilities of MDPPO in: ▲, *o*-xylene; ■, *p*-xylene; ●, *m*-xylene; —, solubility curve calculated from eq 3.

The solubilities were correlated as a function of temperature by

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

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.

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

where the superscript 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 MDPPO in all of the investigated solvents increased with an increase in temperature. The solubility of MDPPO in benzene shows the highest value from (288.52 to 327.17) K, which was related to the phenyl group in the structure of MDPPO. For the binary solvent mixtures studied, it was found that the solubility of MDPPO in acetone + *n*-hexane (volume ratio = 3:7) is lower than benzene + ethyl acetate (volume ratio = 1:1), and the solubility of MDPPO in 0.3 acetone + 0.7 *n*-hexane shows the lowest value in all the selected solvents. Thus, benzene is recommended as the best solvent for the purification of MDPPO.

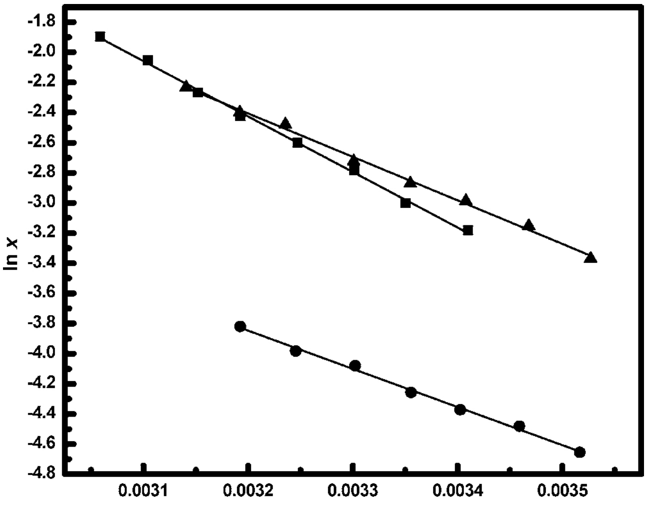

Figure 5. Mole fraction solubilities of MDPPO in: ■, ethyl acetate; ●, 0.3 acetone + 0.7 *n*-hexane; ▲, 0.5 benzene + 0.5 ethyl acetate; —, solubility curve calculated from eq 3.

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
benzene	10.1141	−3812.8	0.0181
toluene	13.7425	−5147.5	0.0199
ethylbenzene	11.7271	−4617.9	0.0208
o-xylene	6.4239	−2926.4	0.0199
m-xylene	10.7720	−4436.8	0.0196
p-xylene	12.0826	−4817.4	0.0227
ethyl acetate	9.3506	−3680.3	0.0177
0.3 acetone + 0.7 *n*-hexane	4.2595	−2533.5	0.0175
0.5 benzene + 0.5 ethyl acetate	6.8273	−2885.3	0.0213

To obtain the activity coefficients of MDPPO in the solvents from the experimental data, the following equilibrium equation for solute was derived as a fair approximation[8]

$$\ln\frac{1}{x_1\gamma_1} = \frac{\Delta H_{\mathrm{f}}}{RT_{\mathrm{m}}}\left(\frac{T_{\mathrm{m}}}{T} - 1\right) \tag{5}$$

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 MDPPO in different solvents can be obtained. The results are listed in Table 2.

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