Solubilities of Diphenylphosphinic Acid in Selected Solvents

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Diphenylphosphinic acid (DPPA) was synthesized and characterized by infrared spectroscopy (IR), nuclear magnetic resonance (^{1}H NMR), mass spectroscopy (MS), and elemental analysis. The melting point and the enthalpy of fusion of DPPA were measured by a differential scanning calorimeter (DSC), and the thermal stability of DPPA was measured by thermogravimetric analysis (TGA). The solubility data of DPPA in nine solvents were measured and correlated with an empirical equation. The estimated uncertainty of all the solubility values based on error analysis and repeated observations was within 2.0 %.

Introduction

Diphenylphosphinic acid (here after abbreviated as DPPA; its formula is shown in Figure 1) (CASRN 1707-03-5) and its anhydride have been widely used as a reactive flame-retardant in epoxy resin based laminates for printed circuit boards.[1,2] Recently, it has been used as an efficient promoter for the palladium catalytic systems.[3–6] Attention has also been given to the chemistry of molecular assemblies including host−guest complexes between the DPPA derivative and amine-containing hosts.[7] In the preparation of DPPA, according to the literature,[8] the product was finally isolated from its aqueous sodium hydroxide solution by acidification with dilute hydrochloride acid and then washed with water. To improve its purity, it was necessary to carry out the recrystallization of DPPA in organic solvents. Knowledge of the solubilities of DPPA in solvents is important for its preparation and purification. These data were not available in the literature.

In this study, DPPA was synthesized and characterized. The solubilities of DPPA in different solvents as required in the purification process were measured.

Experimental Section

Materials. All the chemicals in the synthesis and measurement were analytical grade reagents, which were purchased from Beijing Chemical Factory. 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 and Procedure. 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}. The elemental analysis was performed on an Elementar Vario EL element analyzer. IR spectra (Fourier transform infrared (FTIR)) were recorded on a Magna-IR 750 using KBr pellets. Mass spectra were recorded by a VG-ZAB-HS. ^{1}H NMR and ^{31}P NMR spectra were obtained with a BrukerARX-400 and JEOL ECA-600, respectively. Thermogravimetric analysis (TGA) was carried out with an SDT Q600 thermogravimetric analyzer at a heating rate of 10 K·min^{-1} under nitrogen from (298.15 to 973.15) K.

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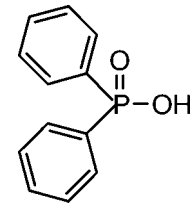

Figure 1. Structure of diphenylphosphinic acid.

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
ethanol	99.7	0.789	1.3619
isopropyl alcohol	99.7	0.785	1.3993
2-ethoxyethanol	99.5	0.929	1.4065
acetic acid	99.5	1.049	1.3718
ethyl acetate	99.5	0.900	1.3588
acetone	99.5	0.790	1.3590
benzene	99.5	0.879	1.5011
methylbenzene	99.5	0.866	1.4967

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.[9,10] 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 analytical balance (type TG328B, Shanghai Balance Instrument Works Co.) with an uncertainty of ± 0.1 mg was used during the mass measurements.

Synthesis of DPPA. DPPA was prepared according to the literature (Scheme 1).[8] The product was then purified by recrystallization from ethanol. The melting point of DPPA was 466.12 K (lit. (463.15 to 465.15) K,[11] (465.15 to 467.15) K[12]). IR (KBr): 2615 (O−H); 1129 (P═O); 964 (P−O); 1438 (P−Ph); 1589, 1485, 729, 695 cm^{-1} (Ph). MS (EI) m/z: 218(M)$^+$. ^{1}H NMR (400 MHz, DMSO) ppm: δ = 7.43 to 7.53 (m, 6H), 7.68 to 7.74 (m, 4H). ^{31}P NMR (600 MHz, DMSO-d_6) ppm: δ = 22.74 (s) (lit. 25.81[13]). Elemental analysis (%, calcd): C = 65.76 % (66.05 %); H = 5.35 % (5.09 %). Based on the above analysis, the purity of DPPA used in this work was higher than 99.0 %.

Thermogravimetric Analysis. An SDT Q600 Simultaneous DTA-TGA thermogravimetric analyzer was employed for

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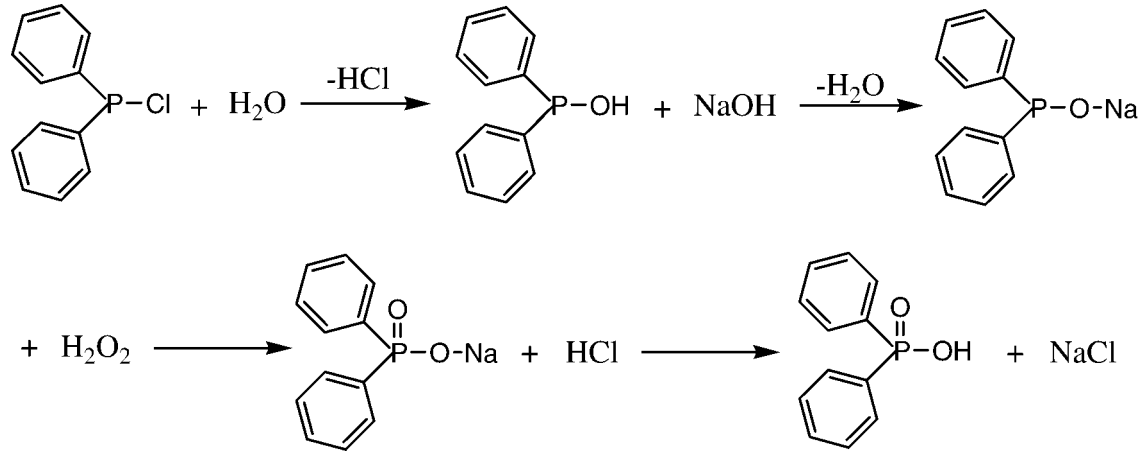
Scheme 1



thermogravimetric analysis (TGA) at a heating rate of 10 $K \cdot min^{-1}$ under nitrogen from (298.15 to 973.15) K. The thermogravimetric curve of DPPA is shown in Figure 2. The initial decomposition temperature of DPPA was around 572.98 K; the temperature at 92.63 % mass loss was 639.60 K; and the char yield at 973.15 K was 5.478 %. Figure 3 shows the results of differential scanning calorimeter (DSC) measurement

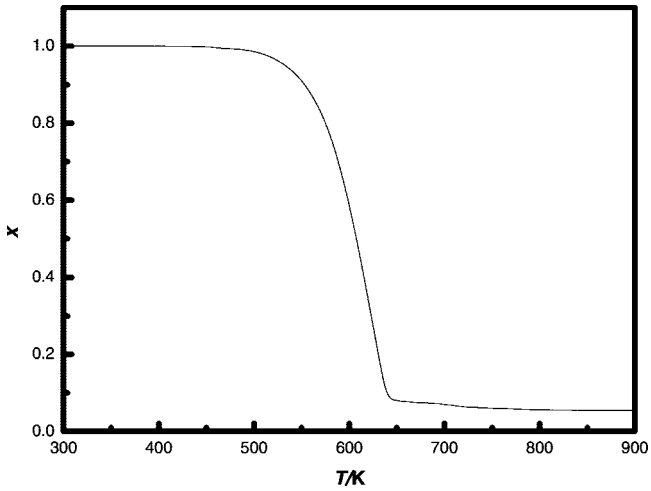


Figure 2. Experimental mass fraction x of DPPA from thermogravimetric analysis.

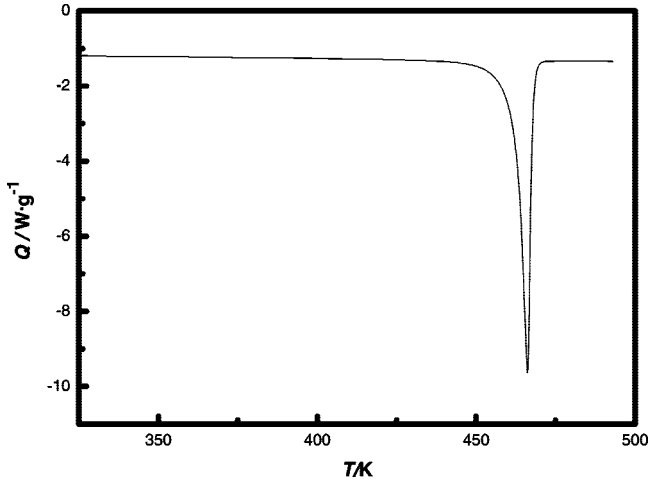


Figure 3. Experimental heat flow Q from differential scanning calorimeter (DSC) measurement of DPPA.

Table 2. Results of Differential Scanning Calorimeter Measurement of DPPA

melting point/K	466.12
enthalpy of fusion/$J \cdot g^{-1}$	100.4

of DPPA. The enthalpy of fusion of DPPA was 100.4 $J \cdot g^{-1}$. The results of DSC measurement of DPPA are summarized in Table 2.

Solubility Measurement. The solubilities were measured by a gravimetric method.[9,10] For each measurement, an excess mass of DPPA 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 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 injector 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[14]

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

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

Different dissolution times were tested to determine a suitable equilibrium time. It was found that 2 h was enough for DPPA in all solvents 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 0.02.

Results and Discussion

The mole fraction solubility data of DPPA, x, in selected solvents are summarized in Table 3 and plotted as ln x vs temperature in Figures 4 to 6. From these figures, it can be seen that a trend of

Table 3. Mole Fraction Solubilities (x) and Activity Coefficients (γ) of DPPA in the Selected Solvents

solvent	T/K	x	γ	$(x - x^{calcd})/x$	solvent	T/K	x	γ	$(x - x^{calcd})/x$
ethanol	283.15	0.00575	4.506	0.030	acetic acid	293.23	0.00426	8.374	0.011
	288.15	0.00671	4.540	0.021		303.15	0.00604	7.924	0.007
	293.10	0.00774	4.593	0.007		313.03	0.00827	7.622	−0.010
	298.07	0.00889	4.647	−0.006		323.15	0.01120	7.307	−0.022
	303.07	0.01020	4.670	−0.013		333.21	0.01510	6.937	−0.020
	308.15	0.01170	4.705	−0.022		343.04	0.02090	6.291	0.032
	313.16	0.01340	4.713	−0.026	ethyl acetate	293.06	0.00052	68.08	0.052
	318.16	0.01520	4.733	−0.032		298.15	0.00060	69.29	−0.044
	322.84	0.01730	4.712	−0.028		303.15	0.00075	63.85	−0.038
	327.94	0.01980	4.661	−0.019		308.17	0.00098	56.34	0.015
	333.10	0.02310	4.524	0.010		313.23	0.00121	52.31	0.018
	337.97	0.02640	4.441	0.027		318.04	0.00144	49.82	0.001
	342.90	0.03020	4.350	0.045		323.10	0.00176	46.59	0.001
isopropyl alcohol	288.15	0.00426	7.148	0.023		328.13	0.00208	44.68	−0.022
	293.15	0.00503	7.078	0.013		333.25	0.00247	42.50	−0.036
	297.98	0.00594	6.933	0.015		337.95	0.00318	36.91	0.048
	303.09	0.00696	6.874	0.005	acetone	293.25	0.00051	70.68	−0.015
	308.05	0.00803	6.850	−0.010		298.18	0.00068	61.20	−0.007
	313.15	0.00931	6.791	−0.020		303.12	0.00091	52.69	0.010
	318.06	0.01070	6.758	−0.032		308.23	0.00120	45.99	0.014
	323.08	0.01230	6.652	−0.033		313.19	0.00156	40.68	0.012
	328.12	0.01440	6.463	−0.019		318.21	0.00203	35.57	0.024
	332.97	0.01650	6.306	−0.010		323.24	0.00244	33.63	−0.039
	338.17	0.01890	6.218	−0.012	benzene	293.15	0.00070	51.15	0.033
	342.94	0.02230	5.882	0.030		303.19	0.00112	42.88	−0.022
	347.80	0.02570	5.690	0.048		313.17	0.00183	34.57	−0.022
2-ethoxyethanol	288.15	0.00619	4.922	0.043		322.95	0.00291	28.07	−0.011
	293.18	0.00716	4.980	0.033		333.21	0.00459	22.85	−0.001
	298.17	0.00810	5.114	0.009		343.12	0.00706	18.67	0.023
	303.04	0.00924	5.166	0.000	methylbenzene	293.15	0.00049	72.96	0.045
	308.11	0.01060	5.187	−0.003		303.16	0.00074	65.21	0.010
	313.15	0.01180	5.346	−0.032		313.18	0.00107	59.38	−0.037
	318.20	0.01350	5.353	−0.032		323.08	0.00157	52.24	−0.038
	323.16	0.01510	5.431	−0.046		333.17	0.00232	45.17	−0.016
	328.20	0.01720	5.392	−0.037		343.25	0.00326	40.58	−0.025
	332.96	0.01960	5.326	−0.024		352.95	0.00462	35.30	0.008
	338.03	0.02230	5.272	−0.012		362.65	0.00651	30.63	0.049
	343.24	0.02520	5.254	−0.008	water	303.14	0.00005	888.6	−0.045
	348.24	0.02850	5.174	0.009		313.17	0.00008	781.8	0.043
	353.25	0.03210	5.125	0.019		323.13	0.00011	760.3	0.034
	358.29	0.03600	5.068	0.031		333.00	0.00014	773.2	−0.016
	363.10	0.04010	5.013	0.042		343.05	0.00018	750.7	−0.020
						353.05	0.00023	713.0	0.001

increasing solubility with temperature is observed. The solubilities were correlated as a function of temperature by

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

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

$$\mathrm{RSD} = \left[\frac{1}{N}\sum_{i=1}^{N}\left(\frac{x_i - x_i^{\mathrm{calcd}}}{x_i}\right)^2\right]^{1/2} \quad (3)$$

where calcd stands for the calculated values and N is the number of experimental points. The results show that eq 2 can be used to correlate the solubility data. Within the temperature range of the measurements, the solubilities of DPPA in all of the investigated solvents increased with an increase in temperature. The solubility of DPPA in water shows the lowest value and in ethanol shows the higher value from (283.15 to 342.90) K. However, the solubility of DPPA in 2-ethoxyethanol at its boiling temperature (408.15 K) can be predicted from eq 2, and the result is 22.5 (g/100 g of solvent). The 2-ethoxyethanol is recommended as the best solvent for the recrystallization of DPPA. For the final stage of purification, water is recommended as solvent in order to remove the 2-ethoxyethanol from the slurry so as to quickly filtrate and dry.

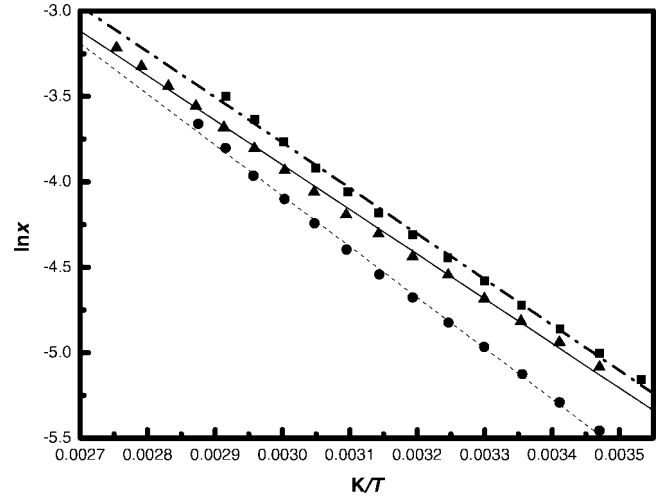


Figure 4. Mole fraction solubility of DPPA in: (experimental) ■, ethanol; ▲, 2-methoxyethanol; ●, isopropyl alcohol; (calculated from eq 2) −•−, ethanol; −, 2-methoxyethanol; - - -, isopropyl alcohol.

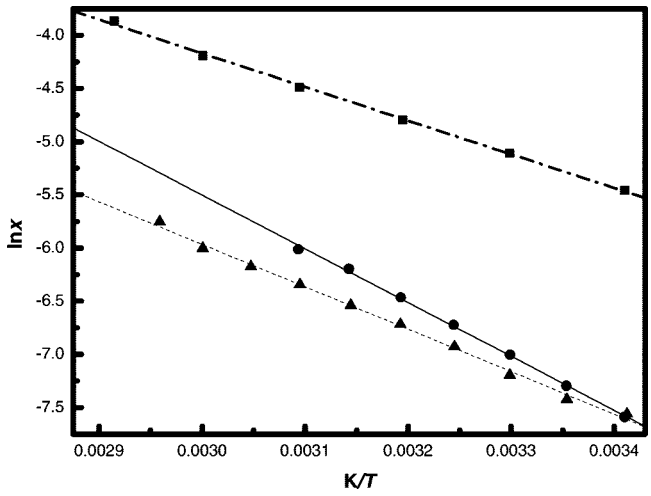


Figure 5. Mole fraction solubility of DPPA in: (experimental) ■, acetic acid; ●, acetone; ▲, ethyl acetate; (calculated from eq 2) − · −, acetic acid; −, acetone; - - -, ethyl acetate.

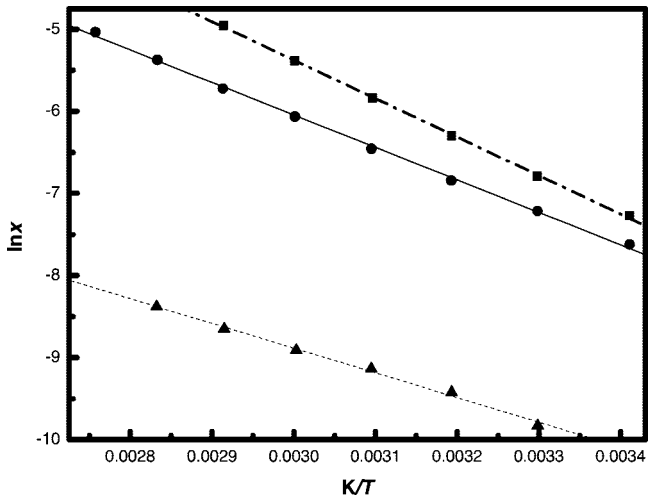


Figure 6. Mole fraction solubility of DPPA in: (experimental) ■, benzene; ●, methylbenzene; ▲, water; (calculated from eq 2) − · −, benzene; −, methylbenzene; - - -, water.

Table 4. Parameters of Equation 3 and Root-Mean-Square Deviations of the Measured Solubility Calculated from Equation 4 for Ethanol, Isopropyl Alcohol, and 2-Ethoxyethanol

solvent	*A*	*B*	RSD
ethanol	4.2261	−2665.7	0.024
isopropyl alcohol	4.8420	−2974.8	0.024
2-ethoxyethanol	3.9303	−2610.5	0.028
acetic acid	5.3416	−3170.1	0.019
ethyl acetate	6.0228	−3995.9	0.033
acetone	9.6676	−5056.6	0.020
benzene	8.6762	−4684.5	0.021
methylbenzene	5.8252	−3956.6	0.032
water	0.1434	−3009.5	0.031

To obtain the activity coefficients of DPPA in the solvents from the experimental data, the following equilibrium equation for solute 1 was derived as a fair approximation[15]

$$\ln \frac{1}{x_1\gamma_1} = \frac{\Delta H_f}{RT_m}\left(\frac{T_m}{T} - 1\right) \quad (4)$$

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 DPPA in different solvents were obtained. The results are listed in Table 3. From Table 3 it can be seen that the activity coefficients of DPPA in different solvents are all more than unity. For the DPPA−water system, very small solubilities and very large activity coefficients were obtained, and this results in great deviations from the ideal behavior.

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