Solubilities of 3,9-Dimethyl-3,9-dioxide-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane in Selected Solvents

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A phosphorus-containing flame retardant 3,9-dimethyl-3,9-dioxide-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5.5]undecane (PBMP) was characterized by a differential scanning calorimeter (DSC), thermo-gravimetric analysis (TGA), and nuclear magnetic resonance (^{1}H NMR and ^{31}P NMR). Using a static analytical method, the solubilities of PBMP were measured in 10 solvents and correlated with an empirical equation. The estimated uncertainty of all of the solubility values on error analysis and repeated observations was within 2.0 %.

Introduction

Flame retardants (FRs) can improve fire performance of polymers to meet the requirement in electrical engineering and the electronic, transportation, and building industries. They have been widely studied and used in polymer composites (such as polypropylene(PP)/FRs) in recent years.[1,2] Traditionally, halogenated compounds are used as economic and effective FRs in PP. However, their applications are limited because of concerns over the toxic, corrosive, and halogenated gases that might be released. In view of these concerns, there is a trend to use halogen-free FRs. In recent studies, phosphorus-containing compounds have been notably effective in providing flame retardancy for polymers. Their gas release during a fire is innocuous or less toxic to the environment. They achieve polymer flame retardancy by modifying the decomposition mode of a polymer during a fire. Cyclic phosphorus compounds are particularly thermally stable and useful as FRs for polymeric materials.

3,9-Dimethyl-3,9-dioxide-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (e.g., pentaerythritol spirobis(methyl phosphonate), hereafter abbreviated as PBMP, and its formula shown in Figure 1, with a CAS RN 3001-98-7). It is known that phosphorus compounds are often useful for conferring flame retardancy on many new polymers. PBMP and the ammonium polyphosphate combination is useful as a FR when incorporated into polyolefins, especially PP.

PBMP can be prepared from methylphosphonic dichloride in a reaction with pentaerythritol as disclosed by a U.S. patent.[3] In an industrial process and in design, the knowledge of solubilities of PBMP as a function of temperature and solvent composition is necessary. No solubility data for PBMP have been reported in the literature.

In this study, PBMP was characterized, and its solubilities in water, methanol, ethanol, acetone, benzene, and binary solvent mixtures [water + methanol (volume fraction, $\phi = 0.5$), water + ethanol ($\phi = 0.5$), methanol + benzene ($\phi = 0.5$), ethanol + benzene ($\phi = 0.5$), and water + acetone ($\phi = 0.5$)] were measured.

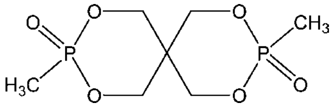

Figure 1. Structure of PBMP.

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	100ω	ρ/g·cm^{-3}	n_D
methanol	99.5	0.792	1.3301
ethanol	99.7	0.790	1.3660
benzene	99.5	0.879	1.5011
acetone	99.5	0.790	1.3590

Experimental Section

Materials. PBMP was purchased from Shunfeng Company, Shandong, and its mass fraction purity was higher than 98 %. All of 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. The water was deionized before use.

Apparatus and Procedure. ^{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 DMSO inside using the standard pulse sequence at the room temperature. The melting temperature and enthalpy of fusion were determined with a DSC Q600 differential scanning calorimeter (DSC) in flowing nitrogen at a heating rate of 10 K·min^{-1}, with thermogravimetric analysis (TGA) results of PBMP from (50 to 600) °C at a scanning rate of 10 K·min^{-1} in flowing nitrogen.

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 50L), 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 Instru-

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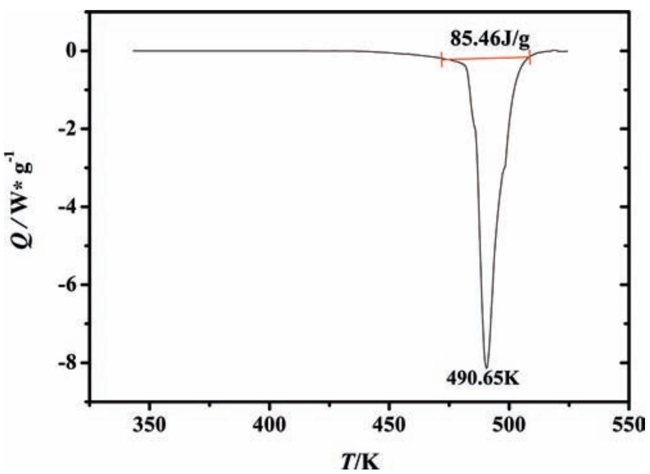

Figure 2. Experimental heat Q flow from the DSC measurement of PBMP.

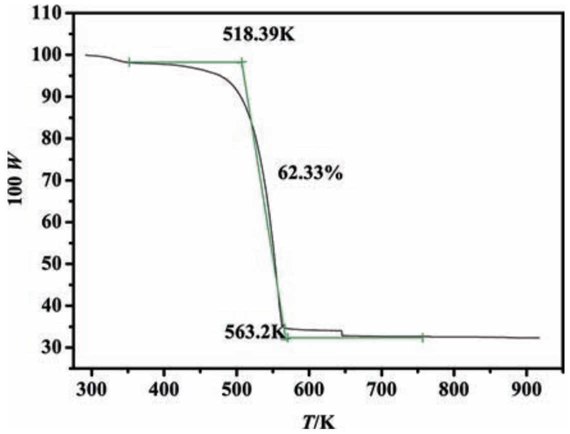

Figure 3. TGA thermograms of PBMP under N_2.

ment Works Co.) with an uncertainty of 0.1 mg was used during the mass measurements.

Characterization of PBMP. ^{1}H NMR (DMSO): $\delta = 4.20$ to 4.29 ppm (lit.,[6] 4.25 to 4.35 ppm) (m, 8H), [4.19 (m, 4H), 4.29 (m, 4H)]; $\delta = 1.42$ to 1.45 ppm (lit.,[6] 1.60 ppm) (d, 6H). ^{31}P NMR (DMSO): $\delta = 33.51$ ppm (lit.,[6] 33.22 ppm). These results show a high purity of the PBMP sample as certified by the specification. The results of DSC and TGA measurement of PBMP were shown in Figures 2 and 3. The melting point of PBMP was 490.55 K; (lit.,[3] 490.15 K; lit.,[7] 390.15 to 392.15 K). The enthalpy of fusion of PBMP was 21.88 kJ·mol^{-1} (lit.,[8] 22.03 kJ·mol^{-1}). TGA results show that there is a single-step decomposition, and no or very little residues remain for PBMP. The PBMP show better flame retardancy than phosphates.

Solubility Measurement. The solubilities were measured by a gravimetric method.[4] For each measurement, an excess mass of PBMP 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, and 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 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 PBMP 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 PBMP, M_2 and M_3 are two solvents measured, and w_2 is the mass fraction of component 2 in the solvent mixture.

Different dissolution times were tested to determine a suitable equilibrium time. It was found that 2 h was enough 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 RSD 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

In this study, PBMP was characterized, and its solubilities in water, methanol, ethanol, acetone, benzene, and binary solvent mixtures [water + methanol ($\phi = 0.5$), water + ethanol ($\phi = 0.5$), methanol + benzene ($\phi = 0.5$), ethanol + benzene ($\phi = 0.5$), and water + acetone ($\phi = 0.5$)] were measured.

The mole fraction solubility x of PBMP, in selected solvents is summarized in Table 2 and plotted as ln x versus T in Figures 4 and 5. 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

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

Parameters A and B for each solvent are listed in Table 3. The relative standard deviations (RSDs), 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.

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

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 PBMP in all of the investigated solvents increased with an increase in temperature. The solubility of PBMP in water shows the highest value from (292.95 to 363.15) K and in benzene shows the lowest value, which was probably related to the theory of similarity and compatibility and the certain polarity of PBMP. Thus, water is recommended as the best solvent for the purification of PBMP. Because of the almost moderate polarity of the selected organic solvents, however,

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

solvent	T/K	x	γ	$(x - x^{\mathrm{calcd}})/x$	solvent	T/K	x	γ	$(x - x^{\mathrm{calcd}})/x$
water	292.95	0.05524	0.4705	0.0304	water + methanol	288.5	0.00384	5.8941	−0.0130
	298.45	0.06203	0.4951	−0.0044	$\phi = 0.5$	293.15	0.00473	5.4981	0.0000
	308.05	0.07934	0.5104	−0.0091		298.15	0.00588	5.1551	0.0051
	318.95	0.10065	0.5398	−0.0384		303.15	0.00730	4.8091	0.0164
	328.15	0.12864	0.5331	−0.0033		308.25	0.00879	4.5981	0.0046
	338.05	0.16065	0.5407	0.0045		313.15	0.01061	4.3711	0.0009
	348.15	0.19717	0.5531	0.0032		318.35	0.01281	4.1371	0.0031
	358.15	0.24227	0.5567	0.0164		323.35	0.01494	4.0351	−0.0227
	363.15	0.26109	0.5721	−0.0009		328.25	0.01795	3.8071	−0.0139
benzene	293.15	0.00025	103.16	0.0009		333.15	0.02208	3.4941	0.0236
	298.15	0.00028	107.27	0.0063		338.25	0.02527	3.4331	−0.0051
	303.15	0.00032	111.21	0.0131	water + ethanol	288.55	0.00477	4.7381	0.0084
	308.15	0.00035	116.79	0.0056	$\phi = 0.5$	293.15	0.00577	4.5151	0.0243
	313.15	0.00037	125.97	−0.0302		298.25	0.00668	4.5391	−0.0179
	318.15	0.00041	128.39	−0.0092		303.15	0.00790	4.4421	−0.0316
	323.15	0.00045	133.07	−0.0081		308.25	0.00967	4.1811	−0.0062
	328.15	0.00050	137.24	−0.0023		313.35	0.01173	3.9561	0.0171
	333.15	0.00055	140.09	0.0126		318.15	0.01365	3.8821	0.0029
	338.15	0.00061	143.87	0.0203		323.15	0.01574	3.8291	−0.0146
	343.15	0.00064	152.53	−0.0045		328.15	0.01899	3.5971	0.0179
	348.15	0.00069	157.58	−0.0047		333.25	0.02146	3.5941	−0.0103
methanol	289.15	0.00360	6.4051	0.0111		338.35	0.02527	3.4331	0.0071
	294.65	0.00433	6.3281	0.0092	water + acetone	288.15	0.00300	7.5322	−0.0033
	298.65	0.00484	6.3761	−0.0103	$\phi = 0.5$	293.15	0.00385	6.7871	0.0104
	303.15	0.00560	6.2880	−0.0071		298.15	0.00493	6.1682	0.0081
	308.15	0.00649	6.2534	−0.0139		303.55	0.00631	5.6541	−0.0079
	313.15	0.00745	6.2489	−0.0242		308.15	0.00782	5.1881	−0.0013
	318.15	0.00896	5.9357	0.0156		313.25	0.00959	4.8651	−0.0261
	323.15	0.01035	5.8505	0.0203		318.45	0.01264	4.2582	0.0158
	328.15	0.01147	5.9778	−0.0131		323.25	0.01516	3.9972	0.0046
	333.15	0.01333	5.8056	0.0061	benzene + methanol	293.45	0.00053	49.627	0.0021
ethanol	288.15	0.00074	30.401	0.0166	$\phi = 0.5$	298.15	0.00073	41.624	0.0109
	293.15	0.00089	29.141	0.0078		303.65	0.00103	34.814	0.0000
	298.15	0.00108	28.081	−0.0093		308.85	0.00139	29.753	−0.0144
	303.15	0.00132	26.641	0.0000		313.15	0.00184	25.364	0.0109
	308.15	0.00155	26.181	−0.0323		318.35	0.00243	22.018	−0.0123
	313.15	0.00194	23.991	0.0103		323.65	0.00331	18.549	−0.0031
	318.15	0.00223	23.901	−0.0269		328.25	0.00424	16.231	−0.0024
	323.15	0.00272	22.261	0.0004		333.95	0.00579	13.619	0.0086
	328.15	0.00321	21.381	0.0031		338.15	0.00715	12.183	0.0056
	333.15	0.00372	20.811	−0.0108	benzene + ethanol	293.45	0.00041	64.854	0.0115
	338.15	0.00445	19.551	0.0135	$\phi = 0.5$	298.15	0.00051	60.732	−0.0115
	343.15	0.00518	18.861	0.0135		303.65	0.00066	54.324	−0.0003
acetone	288.65	0.00059	39.761	0.0033		308.85	0.00083	50.111	−0.0112
	293.67	0.00059	46.467	−0.0726		313.15	0.00103	45.278	0.0194
	298.15	0.00059	53.165	−0.1431		318.35	0.00125	42.778	−0.0160
	303.84	0.00059	62.722	−0.2361		323.65	0.00158	38.881	0.0000
	308.85	0.00059	72.183	−0.3211		328.15	0.00193	35.579	0.0155
	313.23	0.00059	81.317	−0.3981		333.95	0.00236	33.441	−0.0085
	318.36	0.00059	93.107	−0.4901		338.15	0.00280	31.141	0.0036
	323.85	0.00059	107.11	−0.5201		343.15	0.00336	29.034	0.0000

the difference among the solubility data of PBMP in these solvents is not obvious. In addition, it was found that the solubility data of PBMP in methanol and ethanol from (293.14 to 338.14) K is lower than those of 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dimethanol,α,α,α′,α′-tetramethyl-3,9-dioxide, DPDM, derived from the literature data[10] for the sake of comparison.

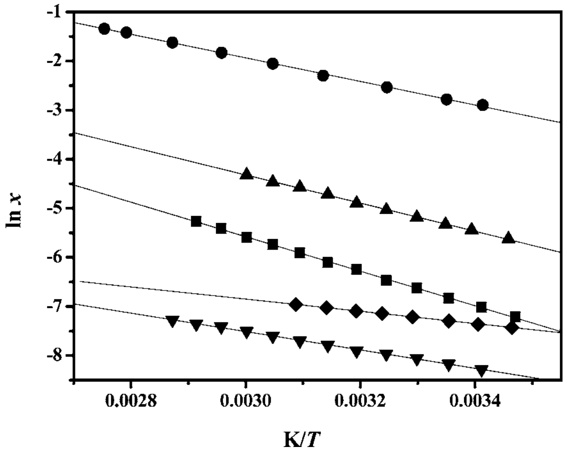

Figure 4. Mole fraction solubilities of PBPM in: ●, water; ▲, methanol; ■, ethanol; ◆, acetone; ▼, benzene (experimental); solid line, solubility curve calculated from eq 3.

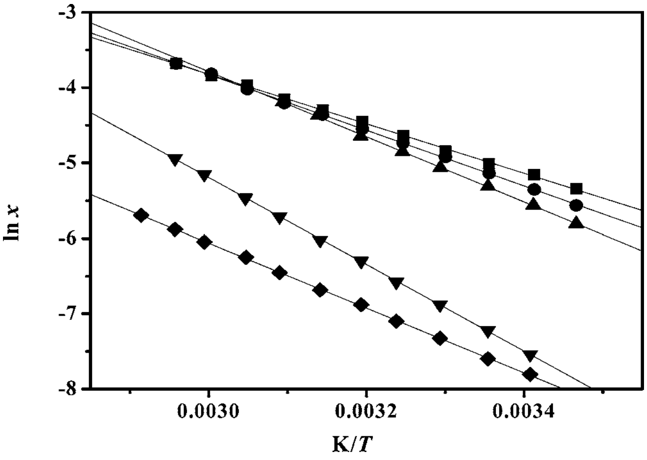

Figure 5. Mole fraction solubilities of PBPM in volume fraction $\phi = 0.5$ of various solvent mixtures: ■, water + ethanol; ●, water + methanol; ▲, water + acetone; ▼, benzene + methanol; ◆, benzene + ethanol; (experimental); solid line, solubility curve calculated from eq 3.

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
water	5.2724	−2401.9	0.0199
methanol	4.3080	−2875.7	0.0154
ethanol	4.9683	−3515.5	0.0159
benzene	−1.8895	−1873.6	0.0138
acetone	−3.1189	−1243.7	0.0040
water + methanol, $\phi = 0.5$	7.2685	−3698.2	0.0142
water + ethanol, $\phi = 0.5$	6.0436	−3288.4	0.0182
water + acetone, $\phi = 0.5$	9.1967	−4327.8	0.0139
benzene + methanol, $\phi = 0.5$	12.087	−5759.9	0.0096
benzene + ethanol, $\phi = 0.5$	6.8392	−4301.2	0.0115

To obtain the activity coefficients of PBMP in the solvents from the experimental data, the following equilibrium equation for solute 1 was derived as a fair approximation:[9]

$$\ln \frac{1}{x_1 \gamma_1} = \frac{\Delta_{\mathrm{fus}} H}{R T_{\mathrm{m}}} \left(\frac{T_{\mathrm{m}}}{T} - 1 \right) \qquad (5)$$

where $\Delta_{\mathrm{fus}}H$ 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, $\Delta_{\mathrm{fus}}H$, and T_{m} values known, the activity coefficients of PBMP in different solvents were obtained. The results are listed in Table 2. From Table 2, it can be seen that the activity coefficients of PBMP in these selected organic solvents are all more than unity. For the PBMP−water system, relatively larger solubilities and relatively smaller activity coefficients than other systems used were obtained, which corresponds to a polar or specific chemical force than other ones.

Supporting Information Available:

^{1}H NMR and ^{31}P NMR spectra of PBMP. This material is available free of charge via the Internet at http://pubs.acs.org.

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