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Solubilities of 2-(6-Oxido-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin-6-yl)-methanol in the Selected Solvents

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The flame retardant 2-(6-oxido-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin-6-yl)-methanol (ODOPM) for epoxy resins was prepared by the reaction of 2-(2-hydroxyphenyl)phenylphosphonic acid (HBP) with paraformaldehyde. The syntheses method is simple and can lower the production costs than conventional method. The basic solubilities data of ODOPM in water (303.57 to 361.63) K as required in the new process and in *p*-xylene (302.95 to 360.65) K as in the conventional process were measured. The solubilities of ODOPM in acetone, ethyl acetate, benzene, and toluene were also measured for comparison.

Introduction

Recently organic phosphorus flame retardant has received considerable attention owing to the increasingly environment and health considerations. Generally the flame retardant character of the organic phosphorus is comparable to organic bromide and antimony oxide. However, bromine and antimony cause problems of smoke, toxicity, and corrosion that can be avoidable with organic phosphates. So the latter should be the most desirable class of flame retardant additives for polyethylene 1,4-terephthalate (PET), polyethylene 2,6-naphthalate (PEN),[1,2] aralkyl novolac,[3] poly(vinyl alcohol) (PVA).[4] For example, 2-(6-oxido-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin-6-yl)-1,4-benzenediol (ODOPB) was used as a reactive flame-retardant in *o*-cresol formaldehyde novolac epoxy resin. Owing to the rigid structure of ODOPB and the pendant phosphorus-containing group, the resultant resin provided not only a better flame retardant effect but also higher thermal stability and glass transition temperature.[5]

The compound 2-(2-hydroxyphenyl)phenylphosphonic acid (HBP) is used as an important raw material for the production of the organic phosphorus flame retardant and also is used as a raw material in production of stabilizers.[6,7] 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was prepared from the cyclizing dehydration reaction of HBP at 13.33 kPa and 403.15 K.

For epoxy resins, the flame retardant (6-oxido-6H-dibenz-[*c*,*e*][1,2]oxaphosphorin-6-yl)-methanol (ODOPM) can be prepared by the reaction of DOPO and paraformaldehyde[8] (Scheme 1). However, there exist complex steps and with xylene as solvent in the preparation procedure, the large quantity of xylene would greatly contaminate the environment. Therefore, it is interesting to find a clean and simple synthesis method. In this paper, ODOPM was directly synthesized from HBP and paraformaldehyde. (Scheme 2) In the preparation of ODOPM, we need to use HBP and paraformaldehyde in the reaction system and then wash the solid with water. Therefore, solubilities of ODOPM in water, xylene, and other selected solvents are important for its preparation and purification. The proposed method of synthesis of ODOPM from HBP and the solubility of ODOPM in water and xylene were not reported in the literature.

Experiment Section

Materials. Paraformaldehyde, xylene, acetone, ethyl acetate, benzene, and toluene were all analytical reagents from Beijing Chemical Factory. The HBP were prepared in our laboratory according to our previously report.[9] The water is double distilled for use.

Apparatus and Procedure. Melting points were obtained from an X4 micromelting point meter. The elemental analysis was performed on a Yanaco CHN FOER MT-3 element analyzer. IR spectra (Fourier transform infrared (FTIR)) were recorded on a Perkin-Elmer 2000 spectrometer using KBr pellets. Mass spectra were recorded by a TRACE-MS and nuclear magnetic resonance by a JNM-AL300.

A jacketed equilibrium cell with a working volume of 120 mL, as described by Wang,[10] was used. (The cell was sealed to prevent the evaporation of solvent.) A circulating water bath with a thermostat (type 50 L, Shanghai Laboratory Instrument Works Co. Ltd.), which is capable of maintaining the temperature within ± 0.05 K, was used. An analytical balance (type TG328B, Shanghai Balance Instrument Works Co.) with uncertainty of ± 0.1 mg was used during the mass measurements, and a magnetic stirrer was also used.

Synthesis of ODOPM. Into a 1 L flask equipped with an agitator, a thermometer, and a reflux condenser were introduced 117 g (0.5 mol) of HBP and 18 g (0.6 mol) of formaldehyde. They were gradually heated under nitrogen atmosphere. When the temperature rose to about 357.15 K, the reactants were fused and the stirrer was started. Temperature fleetly rose to 380.15 K, and the reactants were boiled and allowed to react at that temperature for 4 h. Then 300 mL of water was added dropwise from a constant-pressure dropping funnel to the flask at 373.15 K. After completion of the water addition, the reaction mixture was refluxed for another 2 h, which resulted in precipitation of white solid ODOPM. Then the ODOPM was filtered and washed thoroughly with warm water of (343.15 to 353.15) K, and this operation was repeated three times. After drying, the yield of ODOPM was 96 %; melting point (431.15 to 432.15) K (literature (428.15 to 429.15) K). The IR spectrum (KBr) exhibited absorption at 1197 cm^{-1} (P=O); 945 cm^{-1} (P−O−

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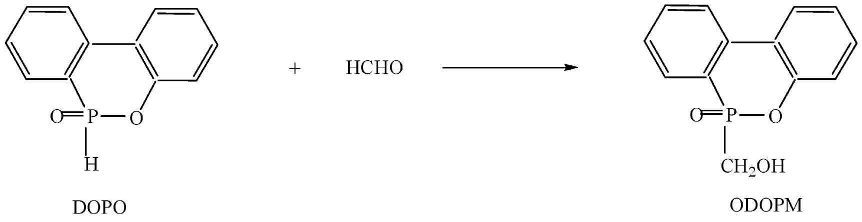
Scheme 1



Scheme 2

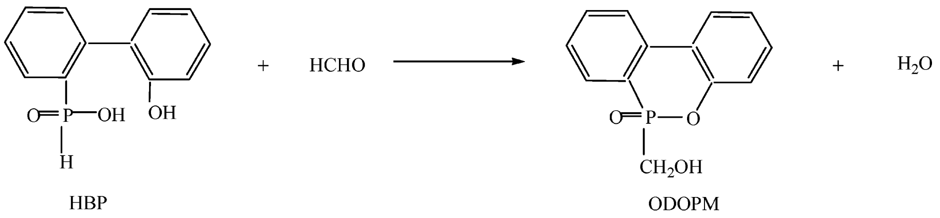


Table 1. Mole Fraction Solubilities (x) of DOPOM in the Selected Solvents

solvent	$\frac{T}{\mathrm{K}}$	$10^5\, x^{\mathrm{exp}}$	$\frac{x^{\mathrm{exp}} - x^{\mathrm{cal}}}{x^{\mathrm{exp}}}$	solvent	$\frac{T}{\mathrm{K}}$	$10^5\, x^{\mathrm{exp}}$	$\frac{x^{\mathrm{exp}} - x^{\mathrm{cal}}}{x^{\mathrm{exp}}}$
water	303.57	6.70	0.039	ethyl acetate	303.45	153.29	0.006
	307.89	7.53	−0.043		309.15	195.10	−0.004
	311.24	9.03	−0.016		315.15	244.66	−0.043
	315.31	11.22	0.013		321.35	323.86	−0.036
	320.13	14.07	0.017		327.43	440.47	0.004
	324.62	16.98	−0.03		333.85	543.16	−0.072
	328.33	21.18	0.047		338.24	708.74	0.003
	331.96	25.55	0.065		342.45	886.30	0.040
	337.65	30.16	−0.030		347.63	107.13	0.002
	342.34	37.51	−0.029		350.26	113.75	−0.055
	346.85	52.62	0.097	benzene	300.68	61.10	0.037
	351.35	62.38	0.062		307.53	77.03	−0.081
	357.60	79.56	0.018		312.27	102.50	−0.034
	361.63	87.12	−0.080		317.45	135.25	−0.020
p-xylene	302.94	0.49	0.048		322.1	179.53	0.027
	307.55	0.58	0.033		327.14	220.98	−0.021
	312.35	0.62	−0.909		332.76	315.72	0.049
	316.26	0.83	0.051		338.23	408.06	0.029
	320.95	0.91	−0.035		343.02	473.90	−0.067
	325.85	1.12	−0.027		347.82	612.30	−0.053
	331.73	1.38	−0.051		352.65	834.00	0.012
	337.25	1.78	−0.012	toluene	300.95	59.02	−0.001
	342.54	2.17	−0.024		306.25	73.10	0.017
	347.95	2.82	0.025		312.03	93.10	0.044
	351.65	3.39	0.062		317.16	107.81	0.002
	356.23	3.39	0.062		322.15	128.30	−0.009
	360.65	3.57	−0.069		327.45	161.92	0.027
acetone	302.25	292.80	0.019		332.25	184.90	−0.018
	308.85	367.10	−0.002		337.75	231.16	0.002
	314.33	459.80			342.05	265.97	−0.017
	319.36	535.00	−0.020		347.25	330.87	0.010
	322.65	618.40	0.002		351.25	354.25	−0.073
	327.78	769.85	0.028		357.35	490.98	0.030
					362.35	604.97	0.053

Ph); 1478 cm^{-1} (P−Ph); 1428 cm^{-1} (P−C, aliphatic C); 1059, 3307 cm^{-1} (C−OH). EI mass spectrum intensity (%) m/z: 246 (M^+). The shift and splitting pattern of ^{1}H NMR spectrum: $\delta = 4.09$ to 4.36 (m, 2H), 5.58 (t, 1H), 7.23 to 7.31 (m, 2H), 7.46 (t, 1H), 7.62 (t, 1H), 7.77 (t, 1H), 8.01 (t, 1H), 8.13 to 8.23 (m, 2H). ^{31}P NMR (DMSO): a singlet peak at $\delta = 32.5$ ppm. Elemental analysis (%, calculated): C, 63.43 (63.41); H, 4.53 (4.47); O, 19.53 (19.51); P, 12.51 (12.61).

Solubility Measurement. The solubilities were measured by a gravimetric method.[11] A equilibrium cell with agitation was immersed in a constant temperature water bath. The temperature was controlled within ± 0.1 K. For determining the solubility of ODOPM in water or other solvents at different temperatures, the following procedure was applied: for each measurement, an excess amount of ODOPM was added to a certain amount of water or selected organic solvent in the equilibrium cell, and then agitation was started. After at least 2 h (the temperature of the water bath approached constant value, then the actual value of temperature was recorded), the agitation was stopped, and the solution was kept still for 3 h. And then the white solids could be observed to settle down in the lower portion of the equilibrium cell. A preheated only one-off injector with filter cotton withdrew 4 mL of the clear upper portion of the solution to another previously weighed measuring vial (m_0). The vial was quickly tightly closed and weighed (m_1) to determine the mass of the sample ($m_1 - m_0$). Then the vial was uncovered and placed in an oven at about 353 K for evaporation. The drying temperature is selected to be lower than the boiling point

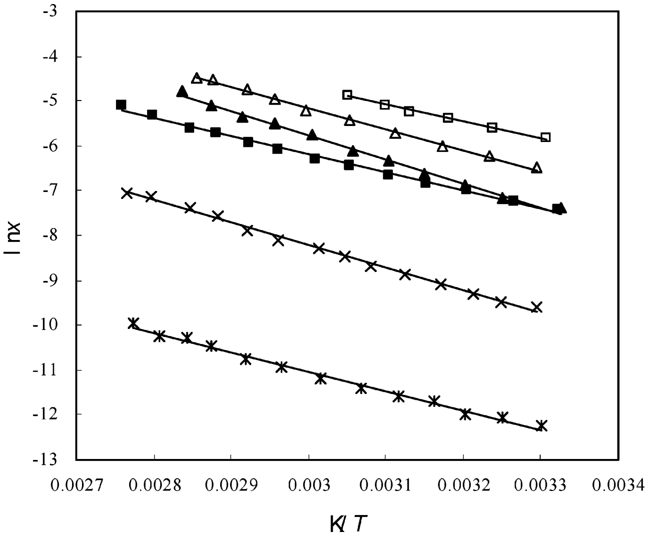


Figure 1. Solubilities (mole fraction) of ODOPM in the selected solvents: —, caculated data from eq 2; □, measured data in acetone; △, measured data in ethyl acetate; ▲, measured data in benzene; ■, measured data in toluene; ×, measured data in water; *, in water and in *p*-xylene.

Table 2. Regressed Parameters *a* and *b*, Relative Standard Deviation (RSD) of the Measured Solubility from Calculated Results of Equation 2, and Experimental Uncertainties for the Different Binary Mixtures

solvent	temperature range/K	*a*	*b*	RSD
water	303.57 to 361.63	−5076.5	7.0111	0.048
p-xylene	302.95 to 360.65	−4313.3	1.8973	0.048
acetone	302.25 to 327.78	−3711.3	6.4236	0.018
ethyl acetate	303.45 to 350.26	−4693.9	8.9241	0.036
benzene	300.68 to 352.65	−5398.0	10.437	0.044
toluene	300.95 to 362.35	−4034.1	5.9129	0.031

of the solvent. The vial was covered with a piece of filter paper to prevent dust contamination. After the solvent in the vial was completely evaporated, the vial was weighed again (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:[12]

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

where the M_1 is the molecular weight of ODOPM and M_2 is the molecular weight of the solvent.

Different dissolution times were tested to determine the suitable equilibrium time. It was found that 3 h was enough to reach equilibrium. For convenience, the solubilities of ODOPM in acetone, ethyl acetate, benzene, and toluene were measured in a similar method.

During our experiments, three parallel measurements were performed at each temperature, and an average value is given. The maximum standard deviation of each triplicate data is 0.27 %, and the minimum is 0.12 %.

The solubilities of ODOPM in some solvents determined in this work are summarized in Table 1 and plotted in Figure 1. The estimated uncertainty of the solubility values based on error analysis and repeated observations was within 2 %.

Data Correlation

Upon comparison the experimental Figure 1, a trend of increasing solubility with temperature is observed. The logarithm of the mole fraction solubilities determined that the temperature shows good linearity. Therefore, they were correlated as a function of temperature by

$$\ln x = a/(T/\mathrm{K}) + b \tag{2}$$

The regressed parameters *a* and *b* for the solubilities (mole fraction) of ODOPM in the selected solvents are listed in Table 2. The smoothed data calculated from eq 2 are listed in Table 1. The relative standard deviation (RSD) of the measured solubilities from the smoothed data is defined as

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

where the superscript exp stands for experimental values, the superscript cal stands for calculated values, and N stands for the total number of experimental data. The RSD of the measured solubilities from the smoothed data in the selected solvents are listed in Table 2.

Conclusion

In this paper the synthesis method of ODOPM was improved, and the ODOPM was directly prepared from HBP and paraformaldehyde. In the purification process, water was used as solvent instead of xylene; therefore, a contaminate factor to environment is eliminated. From Figure 1 it can be seen that the order of the weight fraction solubility in the selected solvents is acetone > ethyl acetate > benzene > toluene > water > xylene.

The solubility in mole fraction of ODOPM in water increased from $6.700 \cdot 10^{-5}$ at 303.57 K to $8.712 \cdot 10^{-4}$ at 361.03 K, while the solubility in mole fraction of ODOPM in xylene increased from $4.880 \cdot 10^{-6}$ at 302.95 K to $4.712 \cdot 10^{-5}$ at 360.65 K. It has been found that solubility of ODOPM in water is higher than in xylene, and using water as a solvent hardly influences the yield of product. Within the temperature range of the measurements, the solubilities of ODOPM in water showed an increased trend based on the increased temperature. Owing to solubilities of paraformaldehyde and HBP, much higher than solubilities of ODOPM in water at about 343.15 K, ODOPM can be purified by warm water and satisfactory purity can be achieved.

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