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Solubilities of 2,4,8,10-Tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dimethanol, α,α,α′,α′-tetramethyl-3,9-dioxide in Selected Solvents

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A phosphorus-containing flame retardant 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dimethanol, α,α,α′,α′-tetramethyl-3,9-dioxide (DPDM) was synthesized. The structure and the thermal stability of the compound were characterized by infrared spectroscopy (IR), nuclear magnetic resonance (^{1}H NMR), mass spectroscopy (MS), elemental analysis, and thermogravimetric analysis. Using a static analytical method, the solubilities of DPDM in acetic acid + acetone binary mixtures, water, methanol, and ethanol were determined in the temperature range from (293.14 to 338.14) K. The solubility data were correlated with an empirical equation.

Introduction

To avoid the problems of smoke, toxicity, and corrosion that are caused by organic bromide and antimony oxide, more and more organic phosphorus compounds are being used as flame retardants to reduce the flammability of organic polymers such as polyesters, polyamides, polyurethanes, and polyolefins.[1−3] For example, some phosphonates have been employed as flame retardant additives, but they have suffered from the defects of causing undesirable decomposition of the additive and crosslinking of the polymeric materials in which the phosphonates were employed. In the extrusion or spinning step, a polymer (such as polyethylene terephthalate or nylon) is molten under higher temperature. Therefore, higher stability is required for the additives. Cyclic phosphorus compounds are particularly thermally stable and useful as flame retardants for these polymeric materials.[4,5]

2,4,8,10-Tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dimethanol, α,α,α′,α′-tetramethyl-3,9-dioxide (hereafter abbreviated DPDM; its formula is shown in Figure 1) (CASRN 66063-49-8) is a bifunctional cyclic phosphorus flame retardant additive and monomer of polymer, and it can be prepared from a phosphorochloridite precursor in a reaction with formic acid and acetone as disclosed by a U.S. patent.[4] After the reaction, the DPDM was recrystallized from a glacial acetic acid and acetone mixture with a yield of 72 % and good purity. In an industrial process and in design, the knowledge of solubilities of DPDM in a binary acetic acid + acetone mixture as a function of temperature and solvent composition is necessary. In this work, these data were determined in the temperature range from (293.14 to 338.14) K at different solvent compositions. The solubilities of DPDM in ethanol, methanol, and water were also measured for comparison. The solubility data were correlated with an empirical equation. No solubility data for DPDM have been reported in the literature.

Experiment 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 the work are listed in Table 1. Their mass fraction purities were all higher than 99 %.

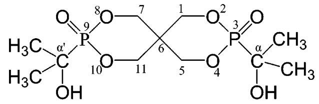

Figure 1. Structure of 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dimethanol, α,α,α′,α′-tetramethyl-3,9-dioxide.

Table 1. Mass Fraction Purity (*w*) for the Organic Solvents Used in This Work at T = 293.15 K

solvent	*w*/%	solvent	*w*/%
acetic acid	99.0	toluene	99.5
acetone	99.5	ethanol	99.7
acetonitrile	99.8	methanol	99.5

Instrumental Analysis and Apparatus. The melting point was 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 and ^{1}H NMR spectra were recorded by a BrukerARX-400. Thermogravimetric analysis (TGA) was carried out with a DuPont 2000 thermogravimetric analyzer at a heating rate of 10 K·min^{-1} under nitrogen from (298.15 to 1073.15) K.

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

Synthesis of DPDM. DPDM was prepared according to the literature[4] with a yield of 75 %, with a melting point of (484.27 to 485.74) K (DSC) (lit. (480.15 to 482.15) K). IR (KBr): 3307 (O−H); 2990 to 2912 (C−H); 1461 (P−C); 1259 (P=O); 1151 (C−OH); 1038 (P−O−C); (665, 777, 820) cm^{-1} (loop-coil).[8] MS (EI) *m/z*: 345 (M + 1)$^+$. ^{1}H NMR (400 MHz, D$_2$O) ppm:

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Table 2. Mole Fraction Solubilities (x) of DPDM in ω Acetic Acid + (1 − ω) Acetone

ω	T/K	10^3x	$(x - x(\text{calcd}))/x$	ω	T/K	10^3x	$(x - x(\text{calcd}))/x$
0	293.60	0.582	−0.0368	0.6013	293.38	5.302	−0.0002
	298.44	0.762	0.0044		298.31	6.106	0.0132
	303.35	0.950	−0.0061		303.25	7.021	0.0247
	308.29	1.244	0.0298		308.15	7.851	0.0097
	313.27	1.587	0.0378		313.15	8.966	0.0130
	318.40	1.936	−0.0048		317.75	10.070	0.0102
	323.30	2.344	−0.0456		322.85	11.300	−0.0068
					328.07	13.310	0.0213
0.2051	293.16	1.789	0.0025	0.7981	293.20	5.946	0.0066
	298.24	2.059	−0.0102		298.15	6.821	0.0194
	303.17	2.418	0.0014		303.14	7.775	0.0250
	308.05	2.840	0.0147		308.05	8.767	0.0219
	312.95	3.247	0.0008		312.97	9.960	0.0260
	317.95	3.758	−0.0041		317.95	10.970	−0.0023
	323.04	4.340	−0.0139		323.04	12.570	0.0061
	328.05	5.168	0.0095		328.16	14.650	0.0301
0.3986	293.14	4.451	−0.0229	1	293.16	6.914	−0.0077
	298.33	5.152	−0.0074		298.15	7.803	−0.0185
	303.16	5.771	−0.0156		303.14	9.072	0.0005
	308.05	6.566	−0.0098		307.96	10.440	0.0139
	313.04	7.514	−0.0006		312.97	11.440	−0.0277
	318.03	8.444	−0.0097		318.05	13.140	−0.0228
	323.22	9.383	−0.0357		323.15	15.010	−0.0249
	328.05	10.880	−0.0092		328.05	17.320	−0.0108
					333.04	19.570	−0.0203
					338.14	23.050	0.0089

Table 3. Mole Fraction Solubilities (x) of DPDM in the Selected Solvents

solvent	T/K	10^3x	$(x - x(\text{calcd}))/x$
water	293.13	5.639	0.0108
	298.01	5.852	0.0053
	303.15	6.070	−0.0029
	308.16	6.312	−0.0074
	313.05	6.583	−0.0080
	317.89	6.916	−0.0010
	323.05	7.226	−0.0020
	328.13	7.536	−0.0044
	332.95	7.933	0.0049
	337.94	8.256	0.0013
	342.86	8.670	0.0074
methanol	293.13	5.852	0.0153
	298.15	6.646	0.0007
	302.94	7.514	−0.0122
	307.75	8.746	0.0035
	312.76	9.982	−0.0061
	317.95	11.71	0.0069
	323.05	13.56	0.0093
ethanol	294.15	1.525	−0.0638
	297.63	1.842	−0.0049
	303.05	2.310	0.0156
	307.95	2.686	−0.0190
	313.15	3.462	0.0370
	318.16	3.905	−0.0322
	322.95	4.759	−0.0157
	327.84	5.824	0.0012
	332.93	6.662	−0.0590
	337.94	8.462	−0.0082

Table 4. Parameters of Equation 3 and Root-Mean-Square Deviations of the Measured Solubility Calculated from Equation 4 for ω Acetic Acid + (1 − ω) Acetone, Water, Methanol, and Ethanol

solvent	A	B	RSD
$\omega = 0$	−21.271	0.0472	0.0289
$\omega = 0.2051$	−15.182	0.0302	0.0089
$\omega = 0.3986$	−12.779	0.0252	0.0172
$\omega = 0.6013$	−12.838	0.0259	0.0144
$\omega = 0.7981$	−12.491	0.0251	0.0198
$\omega = 1$	−12.706	0.0264	0.0176
water	−7.745	0.0087	0.0059
methanol	−13.452	0.0283	0.0090
ethanol	−17.572	0.0379	0.0330

δ = 1.401, 1.443 (d, 6H, 2CH_3), 4.482, 4.510, 4.538 (t, 8H, 4CH_2). Elemental analysis (calcd): C = 38.18 % (38.37 %); H = 6.42 % (6.40 %).

Thermogravimetric Analysis. A DuPont 2000 thermogravimetric analyzer was employed for thermogravimetric analysis at a heating rate of 10 K·min^{-1} under nitrogen from (298.15 to 1073.15) K. A 5 % decomposition temperature was around 473.15 K; a 50 % decomposition temperature was around 730.15 K; and the char yield at 1073.15 K was 35.9 %.

Procedure. The solubilities were measured by a gravimetric method.[9,10] For each measurement, an excess mass of DPDM 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 for 1 h. 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 and placed in an oven at about 333 K for evaporation. The vial was covered 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 or eq 2[10,11]

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

Equation 1 is for a mixed solvent, where M_1, M_2, and M_3 are the molar masses of the DPDM, acetic acid, and acetone and w_2 is the mass fraction of acetic acid in the solvents.

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

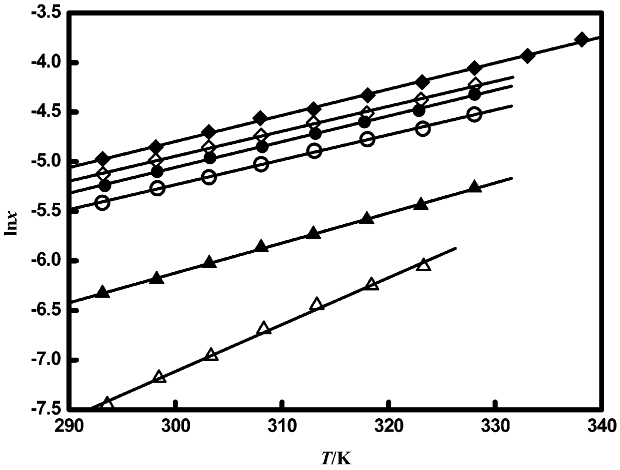

Figure 2. Mole fraction solubilities of DPDM in ω acetic acid + $(1 - \omega)$ acetone: △, $\omega = 0$; ▲, $\omega = 0.2051$; ○, $\omega = 0.3986$; ●, $\omega = 0.6013$; ◇, $\omega = 0.7981$; ◆, $\omega = 1$; −, solubility curve calculated from eq 3.

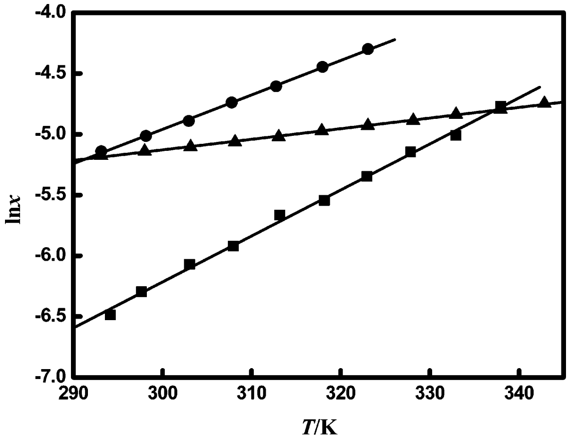

Figure 3. Mole fraction solubilities of DPDM in: ▲, water; ●, methanol; ■, ethanol.

Equation 2 is for pure solvent, where M_1 is the molar mass of DPDM 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 DPDM in all solvents to reach equilibrium. An average value was taken from three measurements at the same composition of solvent for each temperature. The estimated uncertainty of the solubility values based on error analysis and repeated observations was within 2 %.

Results and Discussion

The mole fraction solubility data of DPDM, x, in selected solvents are summarized in Table 2 and in Table 3 and plotted as ln x vs temperature in Figure 2 and in Figure 3. In both Table 2 and Figure 2, the composition of the solvent is given as the mass fraction of acetic acid in the solution on a solute-free basis. The mole fraction 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 4. The smoothed data calculated from eq 3 are listed in Table 2. The relative standard deviations (RSD), defined by eq 4, are also presented in Table 4.

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

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 DPDM in all of the investigated solvents increased with an increase in temperature. The solubility of DPDM in pure acetic acid shows the highest value, and it decreases with the increasing concentration of acetone in the mixed acetic acid + acetone solvent at a constant temperature. The compound DPDM is a diol, and its solubility is related to the polarity of the solute and solvent. The polarity of DPDM is high; there exists hydrogen bonding between the hydrogen atom of DPDM and the carbonyl oxygen of acetic acid, so it is very soluble in the highly polar acetic acid.

Note Added after ASAP Publication. Changes were made to row 1 of Tables 2 and 3 and to eq 4. This paper was published ASAP May 31, 2007; the corrected version was published June 13, 2007.

Literature Cited

(1) Lin, C.-H.; Wu, C.-Y.; Wang, C.-S. Synthesis and properties of phosphorus-containing advanced epoxy resins. *J. Appl. Polym. Sci.* **2000**, *78*, 228−235.
(2) Wang, L.-S.; Wang, X.-L; Yan, G.-L. Synthesis, characterization and flame retardance behavior of poly(ethylene terephthalate) copolymer containing triaryl phosphine oxide. *Polym. Degrad. Stab.* **2000**, *69*, 127−130.
(3) Wang, C.-S.; Lin, C.-H. Synthesis and properties of phosphorus containing polyarylates derived from 2-(6-oxido-6*H*-dibenz[c,e][1,2]-oxaphosphorin-6-yl)-1,4-dihydroxy phenylene. *Polymer* **1999**, *40*, 4387−4398.
(4) Gail, H. B. Hydrogen phosphonates and polymer compositions containing them as flame retardants. U.S. Patent 4,070,336, 1978.
(5) William, G.; Gianluigi, L.; Antonio, R.; Carlo, N. New pentaerythryl phosphonates containing self-extinguishing thermoplastic compositions. U.S. Patent 5,338,787, 1994.
(6) Wang, L.-S.; Liu, Y.; Wang, R. Solubilities of some phosphaspirocyclic compounds in selected solvents. *J. Chem. Eng. Data* **2006**, *51*, 1686−1689.
(7) Wang, Z.-W.; Sun, Q.-X.; Wu, J.-S.; Wang, L.-S. Solubilities of 2-carboxyethyl-phenylphosphinic acid and 4-carboxyphenylphenylphinic acid in water. *J. Chem. Eng. Data* **2003**, *48*, 1073−1075.
(8) Rudi, R.; Orville, J. S. Some chemical reactions of 3,9-dichloro-2,4,8,-10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-dioxide. *J. Org. Chem.* **1963**, *28*, 1608−1602.
(9) Wang, L.-S.; Wang, S.-B. Solubilities of 2-(6-Oxido-6*H*-dibenz[*c*,*e*]-[1,2]oxaphosphorin-6-yl)-methanol in the selected solvents. *J. Chem. Eng. Data* **2006**, *51*, 749−752.
(10) Long, B.-W.; Wang, L.-S.; Wu, J.-S. Solubilities of 1,3-benzenedicarboxylic acid in water + acetic acid solutions. *J. Chem. Eng. Data* **2005**, *50*, 136−137.
(11) Zhu, M. Solubility and density of disodium salt hemiheptahydrate of ceftriaxone in water + ethanol mixtures. *J. Chem. Eng. Data* **2001**, *46*, 175−176.

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