Solubilities of Some Phosphaspirocyclic Compounds in Selected Solvents

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The solubilities of 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9- dioxide from (303.15 to 311.35) K in dichloromethane and from (298.15 to 357.65) K in acetic acid, 3,9-dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide from (309.35 to 331.55) K in acetonitrile and from (295.75 to 319.15) K in acetone, 2,4,8,10-tetraoxa-3,9-dioxide-3,9-diphosphaspiro[5.5]undecane-3,9-melamine salt from (293.15 to 343.15) K in water, and 3,9-(bis-2,2′-carboxyetheyl)-3,9-dioxo-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5] undecane from (332.15 to 342.15) K in ethyl acetate were determined using a gravimetric method. The estimated uncertainty of all the solubility values based on error analysis and repeated observations was within 2.5 %.

Introduction

It has been found that certain cyclic phosphorus compounds such as cyclic phosphonates are particularly useful as flame retardants for organic polymeric materials.[1−4] To avoid the problems of smoke, toxicity, and corrosion that were 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, polyurethanes, and polyolefins.

A phosphorus-containing molecule with a backbone of 2,4,8,-10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide (hereafter abbreviated TDUD), when the 3,9 position substituted with different groups, is widely used as a flame retardant due to its high chemical and thermal stability. Three TDUD-containing molecules, 3,9-dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5.5]undecane-3,9-dioxide (dihydroxy-TDUD) (CASRN 947-28-4) and 2,4,8,10-tetraoxa-3,9-dioxide-3,9-diphosphaspiro[5.5]-undecane-3,9-melamine salt (TDUD melamine salt) (CASRN 70776-17-9), and 3,9-(bis-2,2′-carboxyetheyl)-3,9-dioxo-2,4,8,-10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (bis-carboxyethyl-TDUD) (CASRN 149899-50-3), were all useful materials that could provide phosphorus as a component to reduce the polymers' flammability and were used in the plastics formulating art as blowing agents, char-forming additive, and the like.[3−5] The dihydroxy-TDUD and TDUD melamine salt were both synthesized from 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide **(**dichloro-TDUD) (CASRN 714-87-4). Formulas of the four phosphaspirocyclic compounds are shown in Figure 1.

It was very important to know the solubilities of these flame retardants in selected solvents for the preparation and purification of the products. But it was not available in the literature. In this work, the solubilities of these compounds in six solvents were measured.

Experimental Section

Materials. All the chemicals in the synthesis and measurement were analytical reagents purchased from Beijing Chemical Factory and were used without further purification. The mass fraction purities and physical properties for organic solvents used in the work are listed in Table 1. Double-distilled water was used. Dichloro-TDUD was synthesized by our group according to the literature.[6] In the preparation of dichloro-TDUD, it was washed by dichloromethane and then followed by a recrystallization in acetic acid. To eliminate the side products and achieve a satisfactory purity, the four phosphaspirocyclic compounds were isolated by filtration after washing with proper solvents as described in the following paragraphs. According to literature, the possible impurities in the four phosphaspirocyclic compounds were listed in Figure 2.

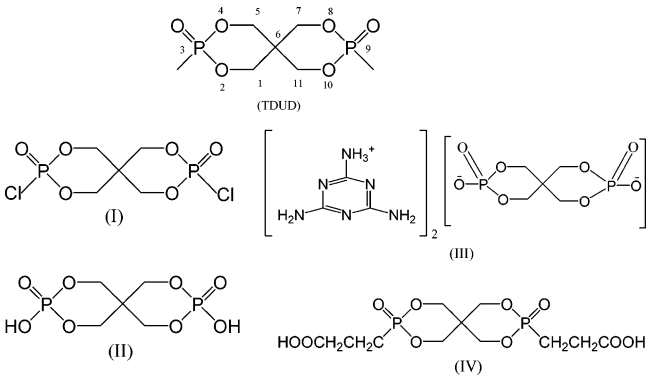

Figure 1. Formulas of the phosphaspirocyclic compounds related in this work: (I) 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide (dichloro-TDUD); (II) 3,9-dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide (dihydroxy-TDUD); (III) 2,4,8,10-tetraoxa-3,9-dioxide-3,9-diphosphaspiro[5.5]undecane-3,9-melamine salt (TDUD melamine salt); (IV) 3,9-(bis-2,2′-carboxyetheyl)-3,9-dioxo-2,4,8,-10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (bis-carboxyethyl-TDUD).

Table 1. Mass Fraction Purity *w*, Density *ρ*, and Refractive Index n_D for the Organic Solvents Used in the Work at $T = 293.15$ K

solvent	*w*/%	ρ/g·cm^{-3}	n_D
dichloromethane	99.5	1.321	1.4237
acetic acid	99.0	1.050	1.3718
acetonitrile	99.8	0.783	1.3430
acetone	99.5	0.790	1.3590
ethyl acetate	99.5	0.899	1.3719

Apparatus and Procedure. The melting point was measured with a X4 micromelting point meter, and the temperature was not corrected. The C and H elemental analyses were performed on a Vario EL III elemental analyzer. IR spectra (Fourier transform infrared (FTIR)) were recorded on a Perkin-Elmer 2000 spectrometer using KBr pellets.

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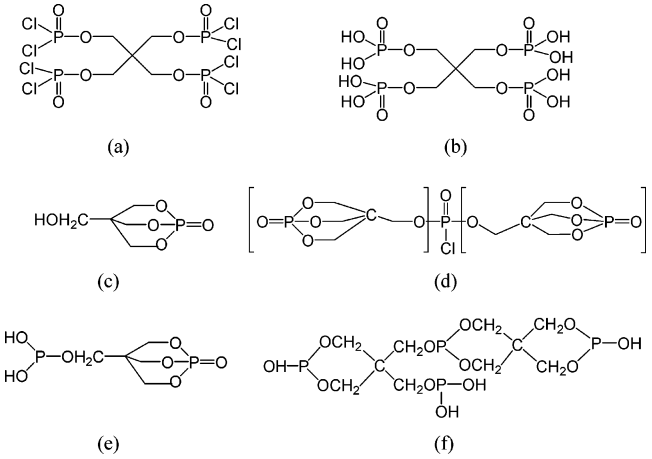

Figure 2. Possible impurities of four phosphaspirocyclic compounds used in the work: (a, b) ref 6; (c, d) refs 11 and 12; (e, f) ref 13.

A jacketed equilibrium cell with a working volume of 120 mL, as described by Wang and Shieh,[7] 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 was capable of maintaining the temperature within ± 0.1 K, was used. An analytical balance (type TG- 328B, Shanghai Balance Instrument Works Co.) with uncertainty of 0.1 mg was used.

Synthesis of 3,9-Dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide. In accordance with the literature,[6] dichloro-TDUD was prepared, and $AlCl_3$ was added in the reaction as catalyst. A yield of 82.5 % was obtained with a short reaction time and low temperature. mp (511.15 to 513.15) K: literature[6] (506.15 to 508.15) K. IR (KBr): 1300 (P═O); 864.72 ($P(OCH_2)_2C$); 1050.32 (P−O−C); 560.21 (P−Cl) cm^{-1}. The experimental mass fraction obtained by elemental analysis (calculated): C = 20.07 % (20.20 %); H = 2.73 % (2.69 %). According to the experimental and calculated results from elemental analysis, it can be estimated that the mass fraction purity was higher than 99 %.

Synthesis of 3,9-Dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide. This cyclic organic phosphorus compound was prepared as follows. A sample of 14.8 g of dichloro-TDUD was suspended in 100 mL of acetonitrile, and the suspension was warmed to 378.15 K. A total of 10 mL of distilled water was added to the mixture very slowly, and the temperature was kept at 378.15 K for 0.5 h and then filtered. A crystalline residue was obtained that was treated first with cold acetone, followed by one acetonitrile washing. The solvent treatment resulted in 10 g of crystals (79.5 % yield), mp (582.15 to 585.15) K (literature[6] 587.15 K). IR (KBr): 1307 (P═O); 855.2 ($P(OCH_2)_2C$); 1024.5 (P−O−C); 1000 (P−OH) cm^{-1}. The experimental mass fraction obtained by elemental analysis (calculated): C = 23.27 % (23.08 %); H = 3.79 % (3.85 %). Estimated by the results of elemental analysis, the product had a mass fraction purity of 99 % or higher.

Synthesis of 2,4,8,10-Tetraoxa-3,9-dioxide-3,9-diphosphaspiro-[5.5]undecane-3,9-melamine Salt. The preparation of the TDUD melamine salt was mainly according to the literature,[3] as an alternative embodiment, the amino-s-triazine was added to the aqueous mixture prior to the hydrolysis of dichloro-TDUD, whereupon the pentate salt was formed and precipitated as the hydrolysis proceeded. The yield was 84.3 %, mp (570.15 to 573.15) K (literature[3] 563.15 K). IR (KBr): 3110.8 (N−H); 1678 (C═N); 1231.6 (P═O); 1029.8 (P−O−C); 816.4 ($P(OCH_2)_2C$) cm^{-1}. The experimental mass fraction obtained by elemental analysis (calculated): C = 25.39 % (25.78 %); H = 4.63 % (4.30 %). The results of elemental analysis showed that the mass fraction purity was 98 % or higher.

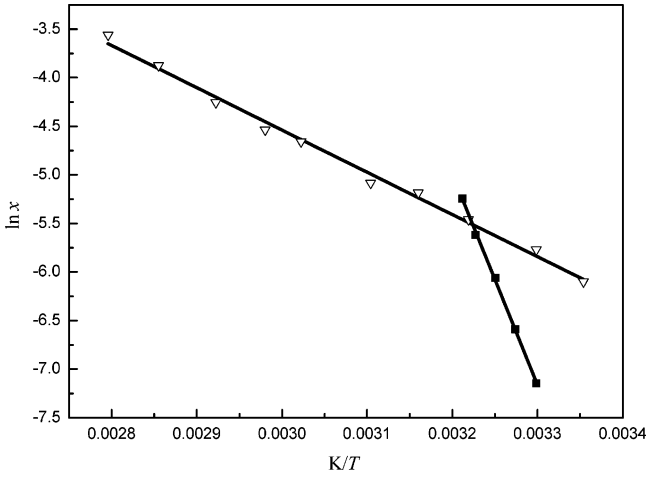

Figure 3. Temperature dependence of mole fraction solubilities of dichloro-TDUD in dichloromethane and acetic acid: —, calculated data; ■, measured data of dichloro-TDUD in dichloromethane; □, measured data of dichloro-TDUD.

Synthesis of 3,9-(Bis-2,2′-carboxyethyl)-3,9-dioxo-2,4,8,-10-tetraoxa-3,9-diphosphaspiro[5.5]undecane. The bis-carboxyethyl-TDUD was prepared according to the literature.[2] In the literature, a vacuum was applied (3.33 kPa) until all the acrylic acid and toluene had been removed by distillation, and then bis-carboxyethyl-TDUD was obtained. In this work a washing of heated ethyl acetate was used after the applying of vacuum. The yield of the bis-carboxyethyl-TDUD was 76.4 %, mp (557.15 to 559.15) K (literature[2] 553.15 K). IR (KBr): 1264.3 (P═O); 809.6 ($P(OCH_2)_2C$); 1175.6 (P−O−C); 1739.2 (C═O) cm^{-1}. The experimental mass fraction obtained by elemental analysis (calculated): C = 35.26 % (35.48 %); H = 4.72 % (4.84 %). The mass fraction purity was 98.5 % according to the results of elemental analysis.

Solubility Measurement. The solubilities were measured by a gravimetric method.[8,9] The apparatus for the solubilities measurement was the same as that described in the literature.[9] A equilibrium cell with agitation was connected with a constant temperature water bath by rubber pipe. The temperature was controlled within 0.1 K. For determining the solubilities, the following procedure was applied: for each measurement, an excess amount of solute was added to 100 g of solvent in the equilibrium cell, and then agitation was started. After at least 3 h, the agitation was stopped, and the solution was kept still for 4 h. White solids could be observed to settle down in the lower portion of the equilibrium cell. A preheated only one-off injector withdrew the clear upper portion of the solution to another previously weighed measuring vial (m_0). The vial was quickly closed and weighed (m_1) to determine the mass of 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 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 mole fraction x of the solute could be determined from eq 1:[10]

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

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

Table 2. Mole Fraction Solubilities (x) of Four Phosphaspirocyclic Compounds in Selected Solvents

solute	solvent	T/K	$10^3\,x^{exp}$	$\lvert(x^{exp} - x^{cal})/x^{exp}\rvert$
dichloro-TDUD	dichloromethane	303.15	0.79	0.0112
		305.45	1.37	0.0044
		307.65	2.32	0.0244
		309.85	3.62	0.0313
		311.35	5.27	0.0075
	acetic acid	298.15	2.25	0.0206
		303.15	3.12	0.0644
		310.65	4.26	0.0318
		316.45	5.61	0.0490
		322.15	6.19	0.0990
		330.85	9.49	0.0215
		335.55	10.72	0.0877
		342.15	14.21	0.0534
		350.25	20.76	0.0322
		357.65	28.44	0.0863
dihydroxy-TDUD	acetonitrile	309.35	0.59	0.0779
		311.25	0.71	0.0595
		313.25	0.89	0.0089
		315.45	1.04	0.0255
		317.35	1.20	0.0328
		319.55	1.51	0.0142
		321.55	1.72	0.0200
		323.25	1.97	0.0301
		325.75	2.45	0.0155
		327.45	2.82	0.0163
		329.45	3.17	0.0657
		331.55	3.76	0.0694
	acetone	295.75	3.99	0.0180
		297.55	4.12	0.0080
		299.85	4.28	0.0023
		301.45	4.40	0.0007
		303.15	4.52	0.0123
		305.35	4.69	0.0048
		307.95	4.89	0.0253
		309.15	4.99	0.0062
		313.35	5.33	0.0184
		317.15	5.65	0.0193
		319.15	5.82	0.0104
TDUD melamine salt	water	293.15	0.69	0.0626
		298.35	0.80	0.0453
		303.15	0.87	0.0345
		308.25	1.04	0.0326
		313.15	1.27	0.0055
		318.45	1.33	0.1341
		323.15	1.71	0.0347
		328.15	2.10	0.0069
		333.15	2.65	0.0693
		338.45	3.06	0.0350
		343.15	3.47	0.0031
bis-carboxyethyl-TDUD	ethyl acetate	332.15	0.82	0.0012
		334.25	1.08	0.0492
		336.05	1.51	0.0153
		338.35	2.23	0.0519
		340.15	2.90	0.0506
		342.15	3.48	0.0705

Different dissolution times were tested to determine the suitable equilibrium time. It was found that 3 h was enough for the dissolution to reach equilibrium. An average value was taken from three measurements at the same position of solvent for each temperature.

Results and Data Correlation

In this work, the solubilities of dichloro-TDUD from (303.15 to 311.35) K in dichloromethane and from (298.15 to 357.65) K in acetic acid, dihydroxy-TDUD from (309.35 to 331.55) K in acetonitrile and from (295.75 to 319.15) K in acetone, TDUD melamine salt from (293.15 to 343.15) K in water, and bis-carboxyethyl-TDUD from (332.15 to 342.15) K in ethyl acetate were determined using a gravimetric method.

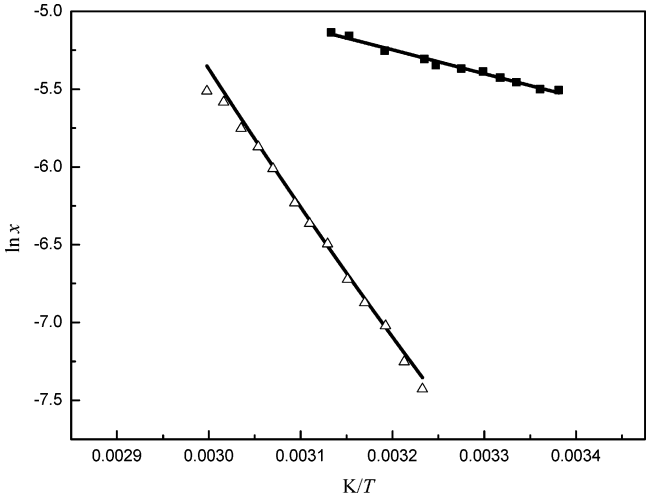

Figure 4. Temperature dependence of mole fraction solubilities of dihydroxy-TDUD in acetonitrile and acetone: —, calculated data; △, measured data of dihydroxy-TDUD in acetonitrile; ■, measured data of dihydroxy-TDUD in acetone.

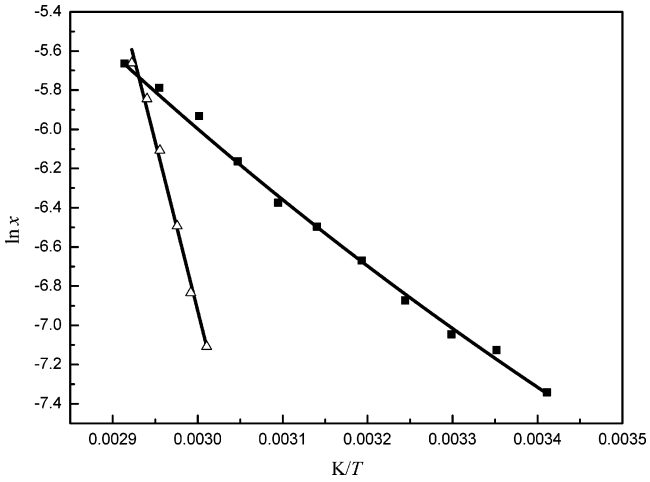

Figure 5. Temperature dependence of mole fraction solubilities of TDUD melamine salt in water and bis-carboxyethyl-TDUD in ethyl acetate: —, calculated data; ■, measured data of TDUD melamine salt in water; △, measured data of bis-carboxyethyl-TDUD in ethyl acetate.

As shown in Figures 3 to 5, the logarithm of the mole fraction solubilities x determined in this work plotted against the inverse temperature showed good linearity. A trend of increasing solubility with temperature was observed. Therefore, they were correlated as a function of temperature by

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

The measured solubilities of the solutes in the selected sol-

Table 3. Regressed Parameters (a and b), the Absolute Average Deviation (AAD) of the Measured Solubilities from Calculated Results of Equation 2, and the Experimental Uncertainties for the Different Binary Mixtures

solute	solvent	a	b	AAD/%	uncertainty/%
dichloro-TDUD	dichloromethane	−21646.2	64.270	1.58	2.1
	acetic acid	−4351.1	8.515	5.46	2.5
dihydroxy-TDUD	acetonitrile	−8311.1	19.476	3.63	2.3
	acetone	−1523.6	−0.373	1.14	2.2
TDUD melamine salt	water	−3433.6	4.319	4.21	1.9
bis-carboxyethyl-TDUD	ethyl acetate	−17226.7	44.754	3.98	2.5

vent and the smoothed data based on eq 2 are presented in Table 2. The estimated uncertainty of all the solubility values based on error analysis and repeated observations was within 2.5 %. The uncertainty for the different binary mixtures is listed in Table 3.

The regressed parameters a and b for dichloro-TDUD, dihydroxy-TDUD, TDUD melamine salt, and bis-carboxyethyl-TDUD in the selected solvents are listed in Table 3. The absolute average deviation (AAD) of the measured solubilities from the smoothed data are also listed in Table 3, where the AAD is defined as

$$\mathrm{AAD} = \frac{1}{N}\sum_{i}\left|\frac{x_i^{\mathrm{exp}} - x_i^{\mathrm{cal}}}{x_i^{\mathrm{exp}}}\right| \qquad (3)$$

where x_i^{exp} stands for experimental values, x_i^{cal} stands for calculated values, and N is the number of data points.

Conclusions

Within the temperature range of the measurements, the mole fraction solubilities x of the four phosphaspirocyclic compounds in the selected solvents showed an increased trend with temperature. They can be correlated as a linear function of inversed temperature by eq 2.

Figure 3 shows that the solubility of dichloro-TDUD in acetic acid increased with the temperature from $x = 2.246 \times 10^{-3}$ at 298.15 K to $x = 2.844 \times 10^{-2}$ at 357.65 K. The results indicated that acetic acid was a good solvent for the crystallization of dichloro-TDUD. From Figure 3, it can be seen that the solubility of dichloro-TDUD in dichloromethane was $x = 0.789 \times 10^{-3}$ at 303.15 K, and it increased greatly with the temperature. However, due to the boiling point of dichloromethane is 314.15 K, the temperature range of the measurement was limited. Thus, at low temperature, using dichloromethane as a washing solvent hardly influenced the yield.

Figure 4 shows that acetone was a better solvent for dihydroxy-TDUD than acetonitrile at a low temperature (below 319.15 K). Thus, the solubility of dihydroxy-TDUD in acetone increased from $x = 3.989 \times 10^{-3}$ at 295.75 K to $x = 5.820 \times 10^{-3}$ at 319.15 K, while the solubility of dihydroxy-TDUD in acetonitrile increased from $x = 0.594 \times 10^{-3}$ at 309.35 K to $x = 3.762 \times 10^{-3}$ at 331.55 K.

Figure 5 shows that the solubilities of TDUD melamine salt in water and bis-carboxyethyl-TDUD in ethyl acetate were both very low at lower temperature. Using water and ethyl acetate as insert solvents in the purification or suspending media in the reaction for TDUD melamine salt and bis-carboxyethyl-TDUD, respectively, did not significantly reduce the yields.

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