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Thermodynamic properties and solid−liquid phase equilibrium of bisphenol A-bis (5, 5-dimethyl-1,3-dioxaphosphorinanyl-2-oxyphosphate ester) in selected solvents

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ABSTRACT

In this work, we investigated the thermodynamic properties of flame retardant bisphenol A-bis (5,5-dimethyl-1, 3-dioxaphosphorinanyl-2-oxy phosphate ester) (BADOPE), including the melting point and the enthalpy of fusion of BADOPE by differential scanning calorimeter (DSC) and the thermal stability of BADOPE by thermogravimetric analysis (TGA). BADOPE was synthesized and characterized by EA, FT-IR and 1HNMR. Using a static analytic method, solid−liquid phase equilibrium data (the solubility) of BADOPE in acetonitrile, acetone, methanol, tetrahydrofuran, ethanol, ethyl acetate, methylethylketone and 1,4-dioxane were obtained at temperatures ranging from 293 to 338 K. Several thermodynamic models, including the ideal, modified Apelblat, Wilson, NRTL, UNIQUAC and Scatchard-Hildebrand models, were applied to correlate the experimental solubility data.

Key words: Phosphorus-containing; Flame retardant; Synthesis; Solid−liquid phase equilibrium

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INTRODUCTION

Flame retardants (FRs) are considered a very important component in the transportation, building and electronic industries because they can reduce ignition and combustion in accidental fires, thereby saving lives and reducing economic loss. Over the past decade, there has been an increasing impetus for the development of novel FRs for application in polymeric systems [1]. Traditionally, halogenated compounds are used as economic and effective FRs. But halogenated flame retardants, especially brominated flame retardants (BFRs), release large amounts of smoke and toxic gas upon burning and have environmentally persistent and bioaccumulate effects, which is harmful to the environment and human health [2,3]. Therefore, halogen-free flame retardants have been becoming one of the most promising flame retardants. Among halogen-free flame retardants, intumescent flame retardants (IFRs) are well known as a new generation of environmentally-friendly flame retardants. Generally, a typical intumescent system contains three active ingredients: acid source [e.g., ammonium polyphosphate (APP)] as the catalyst, carbonization source (e.g., pentaerythritol), and blowing agent (e.g., melamine) [4].Cyclic phosphate esters can be used as effective charring agents in IFRs because they form a surface layer of char rather than yielding CO or CO2 during the process of decomposition.

Among these cyclic phosphate esters, bisphenol A-bis (5, 5-dimethyl-1, 3-dioxaphosphorinanyl-2-oxy phosphate ester) (hereafter abbreviated as BADOPE; its formula is shown in Fig. 1, CAS RN 60699-49-2) has been useful as flame retardant in polymers [5]. BADOPE shows high thermal stability due to the symmetrical structure and can provide acid source and carbonization source in the IFRs system. The scanning electron microscope (SEM) observation reveals that the puffy coking charred layers are formed by lot s of closed bubbles in the polymer filled with BADOPE after burning [6]. Synergistic effect of BADOPE and other active ingredients were crucial to fully exert the flame retardance of the IFR system. In order to utilize effectively this synergistic effect, high purity for BADOPE is required. In the industrial process and design, the knowledge of the compound solubility is very important for their preparation and purification. Experimental and theoretical study on the solubility of pharmaceuticals in the solvent has been preceded systematically by the researchers during these years [7-9]. To the best of our knowledge, the solubilities of flame retardant BADOPE in selected solvents have not been reported in the literature.

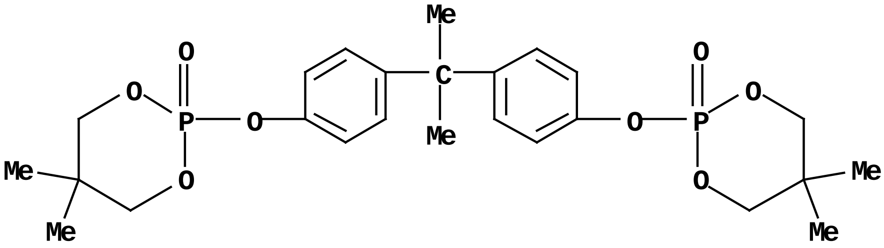

Fig.1. Structures of bisphenol A-bis (5, 5-dimethyl-1, 3-dioxaphosphorinanyl-2-oxy phosphate ester) (BADOPE)

As our continuous efforts to search for high thermally stable fire retardant, BADOPE was synthesized successfully and characterized. The solubilities of BADOPE in acetonitrile, acetone, methanol, tetrahydrofuran, ethanol, ethyl acetate, methylethylketone and 1, 4-dioxane were measured in the temperature range 293 to 338 K. The ideal, modified Apelblat, Wilson, NRTL, UNIQUAC and Scatchard-Hildebrand models were applied to represent the experimental data. Comparison and discussion of the solubility and the capability of the models were then carried out. By using the van't Hoff equation, the dissolution enthalpy, dissolution entropy, and Gibbs free energy change of BADOPE are predicted in different pure solvents.

EXPERIMENTAL SECTION

1. Materials

Phosphorus oxychloride (analytical) was purchased from Tianjin Guangfu Fine Chemical Research Institute, and neopentyl glycol and bisphenol-A were purchased from Sinopharm Chemical Reagent Co.Ltd. All of the solvents were analytical grade reagents, which were purchased from Beijing Chemical Factory. Their mass fraction purities were all higher than 0.99. They were used without further purification. The water is double distilled before use.

2. Apparatus and Procedure

The melting points and enthalpy of fusion were determined with a DSC Q100 (TA Instruments) differential scanning calorimeter (DSC) in flowing nitrogen at a heating rate of 10 K· min-1. The uncertainty of DSC measurement is the same as that described in the literature [10]. Thermogravimetric analysis (TGA) was carried out with an SDT Q600 (TA Instruments) thermogravimetric analyzer at a heating rate of 10 K· min-1 under nitrogen from (298.15 to 823.15) K. The elemental analysis was performed on an ElementarVario EL element analyzer. The mass spectrometer of the BADOPE was measured with A Bruker APEX IV mass spectrometer. Fourier transform infrared (FT-IR) spectra were obtained by use of potassium bromide disks and a Perkin-Elmer 400 spectrometer. 1H NMR spectra was obtained with a Bruker ARX-400.

The setup for the solubility measurement was the same as that described in the literature [11]. A jacketed equilibrium cell was used for the solubility measurement with a working volume of 120 mL and a magnetic stirrer, and 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.

3. Synthesis of BADOPE

BADOPE was prepared according to the literature [7]. Neopentyl glycol (52.08 g, 0.5 mol) dispersed in dichloromethane (250 mL) was added in a dry 500 mL flask. Phosphorus oxychloride (80.00 g, 0.52 mol) was added dropwise to the reaction flask in an ice water bath for 1.5 h. After the addition, the reaction mixture was allowed to warm up to room temperature and refluxed for 4 h until no HCl gas could be detected. The solvent was evaporated under a vacuum and the intermediate (DOPC) precipitated in distilled water, filtered, and dried for overnight. Then a mixture of bisphenol-A (57.07 g, 0.25 mol) and the intermediate (DOPC) (96.90 g) was dissolved in dry acetonitrile (250 mL) in a 500 mL flask. Triethylamine (53.13 g) was added dropwise to the flask at 0 °Cfor 3 h. After the addition, the reaction went on at 0 °C for 6 h. After the removal of salt (Et3N HCl) by filtering and evaporation of filtrate, the crude product was purified by washing with aqueous solution of sodium bicarbonate and distilled water, and finally recrystallized from acetone to obtain the white solid (BADOPE) (101.25 g, 77 %).

4. Characterization of BADOPE

The Elemental analysis (%, calcd): C, 57.24 (57.13); H, 6.52 (6.45). MS (EI) m/z: 525.4 (M+1). FT-IR (KBr, cm-1): 3012, 1543, 1502, 1297, 1078, 967, 902. 1H NMR (CDCl3), δ (ppm): 0.91 (6H, s, CH3), 1.33 (6H, s, CH3), 1.64 (6H, s, CH3), 3.97 (2H, d, CH2), 4.02 (2H, d, CH2), 4.23 (4H, d, CH2), 7.12-7.18 (8H, m, Ar-H). Based on the above analysis, the purity of BADOPE used in this work was higher than 99.0 %. FT-IR and 1H NMR spectra of BADOPE can be seen in Figs. 2 and 3.

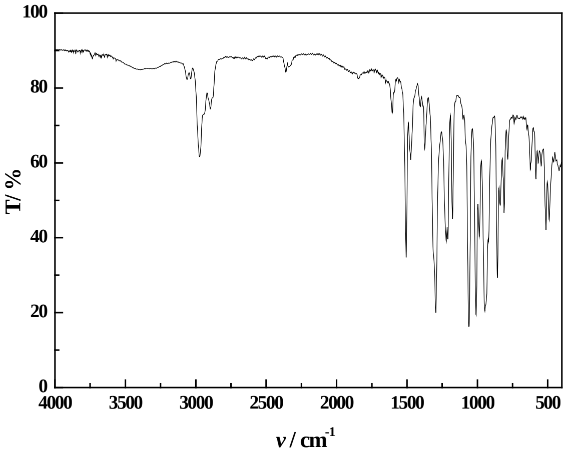

Fig. 2. FT-IR spectra of BADOPE

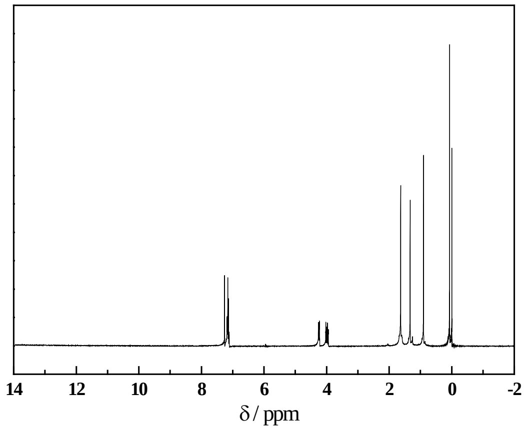

Fig. 3. 1H NMR spectra of BADOPE

5. Solid−Liquid Phase Equilibrium Measurement

The solubility of BADOPE was measured using a static method [12]. For each measurement, an excess mass of BADOPE was added to a known mass of solvent. Then the equilibrium cell was heated to a constant temperature with continuous stirring. After at least 4 h (the temperature of the water bath approached a constant value, then the actual value of the temperature was recorded), the stirring was stopped, and the solution was kept still until it was clear. A preheated on-off injector with a membrane filter withdrew 2 mL of the clear upper portion of the solution to another previously weighed measuring vial (m0). The vial was closed and weighed (m1) to determine the mass of the sample (m1 - m0). After the solvent in the vial had completely evaporated in vacuum, the vial was dried and reweighed (m2) to determine the mass of the constant residue solid (m2 - m0). Thus, the solid concentration of the sample solution in mole fraction, x1, could be determined from equation 1 [13].

$$x_1 = \frac{(m_2 - m_0)/M_1}{(m_2 - m_0)/M_1 + (m_1 - m_2)/M_2} \tag{1}$$

Different dissolution times were tested to determine a suitable equilibrium time. It was found that 5 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 estimated relative uncertainty of the solubility values based on error analysis and repeated observations was within 0.02.

RESULTS AND DISCUSSION

1. Thermodynamic Properties of BADOPE

The results of DSC and TGA measurement of BADOPE were shown in Figs. 4 and 5. The melting point of BADOPE Tm1 was 468.96 K, and the uncertainty of the melting point measurement is 0.26K. The enthalpy of fusion of BADOPE ΔfusH1 was 39.82 kJ·mol-1, and the relative uncertainty of the enthalpy of fusion of BADOPE is 0.35 %. TGA result shows that there is a one-step thermal degradation process. The entropy of fusion of BADOPE ΔfusS1 was calculated by using the following equation [14]:

$$\Delta_{fus}S_1 = \frac{\Delta_{fus}H_1}{T_{m1}} \tag{2}$$

By solving the above equation, the value of ΔfusS1 is determined to be 84.92 J/(mol·K).

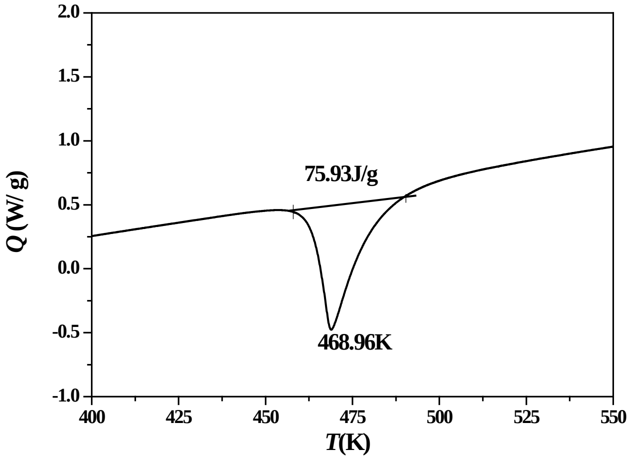

Fig. 4.Experimental heat Q flow from DSC measurement of BADOPE

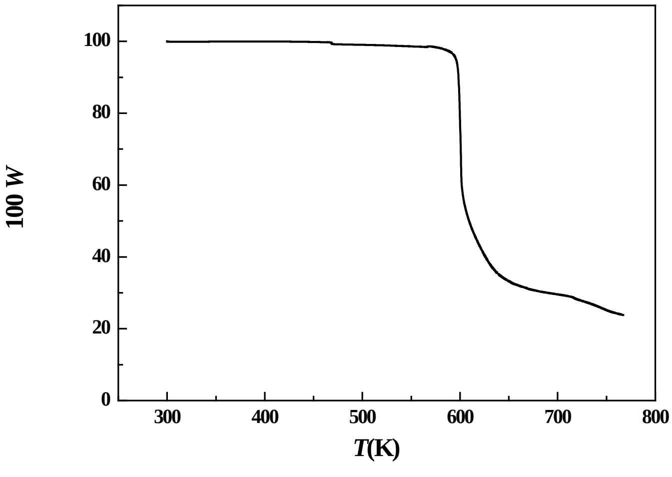

Fig. 5.TGA thermograms of BADOPE under nitrogen

2. Solid–Liquid Phase Equilibrium Data of BADOPE

The mole fraction solubilities x1 of BADOPE in selected solvents are summarized in Table 1 and plotted as lnx1 versus 1/T in Fig. 6. From Table 1 and Fig. 6, it can be found that the solubilities of BADOPE in all the investigated solvents increased with temperature in the temperature range of the measurements and the solubility in ethanol shows the strongest dependency on temperature. At a given temperature, the order of mole fraction solubility of

BADOPE in selected solvents is acetonitrile>acetone>methylethylketone>tetrahydrofuran> methanol ≈ 1,4-dioxane > ethyl acetate ≈ ethanol, which was probably related to the theory of similarity and compatibility [15-17] and the certain polarity of BADOPE.

Table 1. Mole Fraction Solubilities (x1) and Activity Coefficients (γ1) of BADOPE in Selected Solvents

Solvent	T/K	x1	γ1
acetonitrile	293.12	0.00674	0.3238
	298.34	0.00878	0.3309
	303.22	0.01035	0.3634
	308.12	0.01342	0.3603
	313.23	0.01724	0.3615
	318.53	0.02118	0.3795
	323.11	0.02512	0.3960
	328.18	0.03132	0.3993
	333.28	0.03819	0.4094
	338.15	0.04541	0.4235
acetone	293.36	0.00311	0.7112
	298.58	0.00352	0.8360
	303.23	0.00455	0.8271
	308.21	0.00574	0.8463
	313.13	0.00769	0.8064
	318.24	0.00872	0.9091
	323.1	0.01024	0.9709
methanol	293.38	0.00129	1.7165
	298.25	0.00162	1.7845
	305.63	0.00241	1.7678
	308.26	0.00297	1.6397
	313.13	0.00352	1.7617
	318.22	0.00487	1.6263
	323.21	0.00642	1.5564
	328.16	0.00791	1.5797
tetrahydrofuran	293.17	0.00132	1.6580
	298.2	0.00198	1.4561
	305.22	0.00232	1.7981
	308.37	0.00351	1.3951
	313.18	0.00429	1.4490
	318.42	0.00532	1.5029
	323.16	0.00761	1.3100
	328.14	0.00916	1.3629
ethanol	293.32	0.00049	4.5040
	298.13	0.00072	3.9892
	303.26	0.00096	3.9263
	308.36	0.00143	3.4227
	313.21	0.00198	3.1441
	318.15	0.00272	2.9022
	323.18	0.00373	2.6752
	328.29	0.00442	2.8434
	333.32	0.00651	2.4060
ethyl acetate	293.28	0.00081	2.7186
	298.19	0.00108	2.6681
	303.23	0.00141	2.6690
	308.15	0.00169	2.8656
	313.19	0.00198	3.1411
	318.31	0.00279	2.8509
	323.14	0.00342	2.9123
	328.23	0.00402	3.1180
	333.16	0.00480	3.2407
methylethylketone	293.19	0.00281	0.7797
	298.39	0.00322	0.9046
	303.17	0.00391	0.9595
	308.15	0.00457	1.0597
	313.26	0.00571	1.0929
	318.32	0.00638	1.2473
	323.22	0.00832	1.2015
	328.28	0.00939	1.3378
	333.33	0.01172	1.3370
	338.4	0.01373	1.4155
1,4-dioxane	293.12	0.00138	1.5815
	298.36	0.00178	1.6337
	303.22	0.00214	1.7577
	308.34	0.00247	1.9796
	313.15	0.00282	2.2011
	318.11	0.00367	2.1469
	323.24	0.00448	2.2335
	328.17	0.00518	2.4133
	333.08	0.00586	2.6454
	338.13	0.00682	2.8176

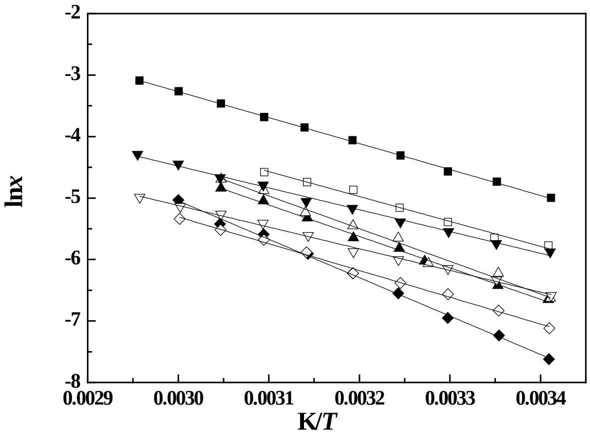

Fig. 6. Mole fraction solubilities of BADOPE in different pure solvents

Experimental data: ■, acetonitrile; □, acetone; ▲, methanol; △, tetrahydrofuran; ◆, ethanol; ◇, ethyl acetate; ▼, methylethylketone; ▽, 1,4-dioxane; – ,solubility curve calculated from the ideal model

To obtain the activity coefficients of BADOPE in the solvents from the experimental data, the following equilibrium equation for solute was derived as a fair approximation [18]:

$$\ln \frac{1}{x_1 \gamma_1} = \frac{\Delta_{fus} H_1}{R T_{m1}} \left(\frac{T_{m1}}{T} - 1 \right) \tag{3}$$

where ΔfusH1 refers to the enthalpy of fusion, Tm1 is the melting temperature, T is the absolute temperature, R is the gas constant, and x1 and γ1 refer to the mole fraction and activity coefficient of solute in the solution, respectively. With the experimental x1, T, ΔfusH1, and Tm1 values known, the activity coefficients of BADOPE in different solvents were obtained. The results are listed in Table 1.

3. Correlation with the ideal and modified Apelblat Models

The ideal and modified Apelblat models were tested to fit the solubility data. The root-mean-square deviation (RSD) was used to identify the difference between the measured and calculated mole fraction solubility, and given as follows:

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

where $x_{1,i}^{\exp}$ and $x_{1,i}^{\mathrm{calc}}$ stand for the experimental mole fraction solubility and calculated value and N is the number of experimental data points.

3.1. Correlation with Ideal Model

Assuming the solution is an ideal solution (γ1 = 1), then equation 3 can be rewritten as follows:

$$\ln x_1 = a + \frac{b}{T} \tag{5}$$

where a and b are the model parameters, and x1 is the mole fraction of solubility at system temperature T. Parameters a and b for the ideal model in each selected solvent were obtained through regression of the experimental solubility data.

3.2. Correlation with Modified Apelblat Equation

The following modified Apelblat equation was used to correlate the solubility data [19]:

$$\ln x_1 = A + \frac{B}{T} + C \ln T \tag{6}$$

where x1 is the mole fraction solubility of BADOPE, T is the absolute temperature, and A, B, and C are the model parameters. The values of A and B reflect the variation in solution activity coefficients, and C denotes the effect of temperature on fusion enthalpy [20]. Parameters, RSDs, and the overall relative standard deviation of the ideal and modified Apelblat models are presented in Tables 2 and 3, respectively. For the overall relative standard deviation, the modified Apelblat equation gives better correlation results (RSD = 3.806%) compared with the ideal model in this work.

Table 2. Optimized parameters and RSDs of the ideal model for BADOPE in Selected Solvents

solvent	a	b	RSD/%
acetonitrile	9.398	-4222.654	1.783
acetone	7.985	-4049.973	4.630
methanol	10.751	-5117.343	3.289
tetrahydrofuran	11.509	-5314.827	7.906
ethanol	13.689	-6245.247	4.100
ethyl acetate	7.756	-4354.710	3.808
methylethylketone	6.165	-3548.501	3.788
1,4-dioxane	5.452	-3524.106	3.231
overall			4.067

Table 3. Optimized parameters and RSDs of modified Apelblat equation for BADOPE in Selected Solvents

solvent	A	B	C	RSD/%
acetonitrile	-7.392	-3440.246	2.487	1.766
acetone	29.593	-5038.206	-3.211	4.629
methanol	-165.607	2999.296	26.176	2.853
tetrahydrofuran	-117.138	604.291	19.095	7.736
ethanol	122.928	-11305.251	-16.195	3.907
ethyl acetate	68.254	-7156.563	-8.969	3.776
methylethylketone	-197.474	5943.821	30.156	2.548
1,4-dioxane	13.475	-3897.972	-1.188	3.233
overall				3.806

4. Correlation with the Wilson, NRTL and UNIQUAC Models

The Wilson, NRTL, and UNIQUAC activity coefficient models are applied to correlate the activity coefficients through equation 3 in this study.

4.1. Correlation with Wilson Model

The Wilson model can be expressed in the following binary form [21]:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} \right] \tag{7}$$

Where

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT} \right) = \frac{V_2}{V_1} \exp\left(-\frac{\Delta\lambda_{12}}{RT} \right)$$

$$\Lambda_{21} = \frac{V_1}{V_2} \exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT} \right) = \frac{V_1}{V_2} \exp\left(-\frac{\Delta\lambda_{21}}{RT} \right) \tag{8}$$

in which Δλ12 (= λ12 − λ11) and Δλ21 (= λ21 − λ22) are the cross interaction energy parameters, and V1 and V2 are the molar volumes of the solute and solvent, respectively. The value of molar volume of the subcooled liquid for solid solute BADOPE was estimated using advanced chemistry development (ACD/Laboratories) Software V11.02, and the values of molar volume of the solute and solvents are listed in Table 4. The values of molar volume of the solvents are obtained from the literature [22].

Table 4. Solubility Parameter (δ) , Molar Volume (V), UNIQUAC Volume Parameter (r) and Surface Parameter (q) Values for Selected Solvents22 and BADOPE

solvent	δi/(J·cm-3)1/2	106Vi/m3·mol-1	r	q
acetonitrile	24.094	52.68	1.870	1.724
acetone	19.774	73.93	2.570	2.340
methanol	29.523	40.70	1.431	1.432
tetrahydrofuran	19.129	81.94	2.942	2.720
ethanol	26.421	58.52	2.106	1.972
ethyl acetate	18.346	98.59	3.480	3.120
methylethylketone	18.796	90.20	3.250	2.880
1,4-dioxane	20.163	85.66	3.185	2.640
BADOPE	23.443	411.8	18.336	14.542

Table 5. Optimized parameters and RSDγs of Wilson model for BADOPE in Selected Solvents

solvent	α12	β12	α21	β21	RSDγ/%
acetonitrile	-4674.2	17.8	-4416.5	42	0.895
acetone	-6586	21	-26029	275	1.527
methanol	-6901	28	35004	-82	1.505
tetrahydrofuran	-6841	22	-26812	295	1.539
ethanol	-1018	13	13399	-39	3.897
ethyl acetate	-2678	4303.5	-3722.7	0.6	3.725
methylethylketone	-1341	9309	-10382	13	3.727
1,4-dioxane	-7264	15390	-10649	19	3.162
overall					2.497

4.2. Correlation with NRTL Model

In a binary system, NRTL model can be expressed as follows:

$$\ln\gamma_2 = x_1^2\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \left(\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}}\right)^2 \qquad (9)$$

Where

$$G_{12} = \exp(-a_{12})\tau_{12}\text{,} \quad G_{21} = \exp(-a_{12})\tau_{21} \qquad (10)$$

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} = -\frac{\Delta g_{12}}{RT}\text{,} \quad \tau_{21} = \frac{g_{21} - g_{11}}{RT} = -\frac{\Delta g_{21}}{RT} \qquad (11)$$

WhereΔg12 and Δg21 are the two cross-interaction parametersin NRTL model. In the experiment, a12 was taken as an adjustable parameter, and chosen to be 0.3.

Table 6. Optimized parameters and RSDγs of NRTL model for BADOPE in Selected Solvents

solvent	α12	β12	α21	β21	RSDγ/%
acetonitrile	-12305	23	-71410	278	1.702
acetone	55022	-105	-13756	19	2.359
methanol	29426	-45	-8240	6	2.530
tetrahydrofuran	82018	-184	-16400	26	4.317
ethanol	12212	-25	-276	-3	3.916
ethyl acetate	-32	0	10059	-29	3.500
methylethylketone	-28352	91	17588	-56	2.569
1,4-dioxane	-10482	34	-430	8	3.160
overall					3.007

4.3. Correlation with UNIQUAC Model

The UNIQUAC model can be expressed in the following binary form [23,24]:

$$\ln\gamma_1 = \ln\frac{\varphi_1}{x_1} + \left(\frac{Z}{2}\right)q_1\ln\frac{\theta_1}{\varphi_1} + \varphi_2\left(l_1 - \frac{r_1}{r_2}l_2\right) - q_1\ln\left(\theta_1 + \theta_2\tau_{21}\right) + \theta_2 q_1\left(\frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1\tau_{12}}\right) \qquad (12)$$

Where

$$l_i = \frac{Z}{2}(r_i - q_i) - (r_i - 1) \quad \mathrm{Z} = 10 \qquad (13)$$

$$\theta_i = \frac{q_i x_i}{\sum\limits_j q_j x_j} \qquad \varphi_i = \frac{r_i x_i}{\sum\limits_j r_j x_j} \tag{14}$$

$$\tau_{12} = \exp\left(-\frac{\Delta u_{12}}{RT}\right) \qquad \tau_{21} = \exp\left(-\frac{\Delta u_{21}}{RT}\right) \tag{15}$$

Where Δu12 and Δu21 are UNIQUAC cross-interaction parameters; Z denotes the coordination number; θi and φi are the mean surface area and volume fraction; ri and qi are the UNIQUAC volume parameter and surface parameter for the solute and solvents, which can be calculated by van der Waals volume and van der Waals area of molecule [22]. The van der Waals volume and van der Waals area data of the solute BADOPE have not been reported in the literature, so the parameters r and q of BADOPE are calculated from the Bondi group contribution method as the sum of the group volume and area parameters [12, 25]. The values of r and q for each compound are given in Table 4.

The binary cross-interaction parameters in the Wilson equation (Δλ12 and Δλ21), NRTL equation (Δg12 and Δg21) and UNIQUAC equation (Δu12 and Δu21) are assumed to have a linear dependency on temperature, that is

$$k_{ij} = \alpha_{ij} + \beta_{ij} T \tag{16}$$

where k denotes any interaction parameter mentioned above. The parameters α and β are fitted from solubility data by minimizing the following objective function:

$$\min f = \sum_{i=1}^{N} (\ln \gamma_i^{\mathrm{exp}} - \ln \gamma_i^{\mathrm{cal}})^2 \tag{17}$$

N is the number of data points for each system. The Levenberg–Marquardt method was used as the optimization algorithm for minimizing equation 17.

The root-mean-square deviation about activity coefficient (RSDγ) were used to identify the difference between the measured and calculated data, and given as follows:

$$\mathrm{RSD}_\gamma = \left[\frac{1}{N} \sum_{i=1}^{N} \left(\frac{\gamma_{1,i}^{\mathrm{exp}} - \gamma_{1,i}^{\mathrm{calc}}}{\gamma_{1,i}^{\mathrm{exp}}} \right)^2 \right]^{1/2} \tag{18}$$

Where $\gamma_{1,i}^{\mathrm{exp}}$ and $\gamma_{1,i}^{\mathrm{calc}}$ stand for experimental value and calculated value of the activity coefficient and N is the number of experimental data points.

Tables 5-7 list the optimized parameter values for the Wilson, NRTL, and UNIQUAC models and a comparison of the correlation results by different models in terms of overall deviation. It can be seen that the Wilson model is more suitable in describing the solubility data of BADOPE, compared with NRTL and UNIQUAC models. The parameters β in Tables 5- 7 show the effect of temperature on the cross interaction energy parameters, which is helpful for selecting the solvent for the crystal procedure.

Table 7. Optimized parameters and RSDγs of UNIQUAC model for BADOPE in Selected Solvents

solvent	α12	β12	α21	β21	RSDγ/%
acetonitrile	2147.6	-6.6	-3534.5	14.2	1.591
acetone	1785.1	2	-1858.9	1.7	4.089
methanol	1268	-3.4	-2548.8	13.3	2.588
tetrahydrofuran	1862.4	1.5	-1309.1	-0.1	6.559
ethanol	1015.4	-5.7	-473.7	11.2	3.854
ethyl acetate	-174.2	-2.1	-208.4	6.9	3.731
methylethylketone	-403.0	-5.7	-459.4	611.7	5.546
1,4-dioxane	-564.5	-4.5	3167.7	493.7	3.424
overall					3.923

5. Correlation with Scatchard-Hildebrand Model and Prediction of Solubility Parameter of BADOPE

The Scatchard-Hildebrand activity coefficient model for regular solution [26] will be used to correlate the activity coefficients listed in Tables 1. On the basis of this model and a further simplification, the activity coefficient model used for the correlation in this paper can be expressed as

$$RT\ln\gamma_1 = V_1\Phi_2^2(\delta_1-\delta_2)^2 \tag{19}$$

Whereγ1 is the activity coefficient of solute; V1 is the molar volume of the subcooled liquid of pure solid solute; δ1 and δ2 are the solubility parameters of the solute and solvent; R is the gas constant; T is the absolute temperature; and Φ_2 refers to the volume fraction of the solvent. The solubility parameters δ2 of the solvents are obtained from the literature [22] and listed in Table 4. A residual function Y can be rearranged from equation 19 [27].

$$Y = \frac{RT\ln\gamma_1}{V_1\Phi_2^2} - \delta_2^2 = -2\delta_2\delta_1 + \delta_1^2 \tag{20}$$

equation 20 shows that there is a linear relation between Y and the solvent solubility parameter δ2 for a given solvent and temperature T. The value of the solute solubility parameter δ1 can be obtained from the slope of this line. The linear dependence between Y and δ2 at 298.15 K was displayed in Fig. 7. Values of solubility parameter of BADOPE from 293 to 323 K given in Table 8 indicate that δ1 approaches to a constant in the range of temperature studied. The average value of the solute solubility parameter δ1 is 23.443 (J·cm-3)1/2. The result is also listed in Table 4.

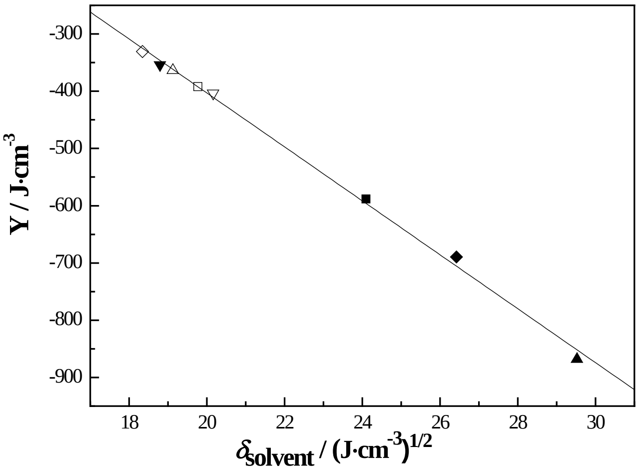

Fig. 7. Residual function Y for BADOPE versus solvent solubility parameters δ solvent: ■, acetonitrile; □, acetone; ▲, methanol; △, tetrahydrofuran; ◆, ethanol; ◇, ethyl acetate; ▼, methylethylketone; ▽, 1,4-dioxane; –, regression line

Table 8. Solubility Parameter δ (J/cm)1/2 of BADOPE

T/K	δ from intercept	δ from slope	R2
293.15	23.21	23.54	0.9967
298.15	23.22	23.56	0.9969
303.15	23.25	23.58	0.9969
308.15	23.28	23.62	0.9969
313.15	23.30	23.63	0.9971
318.15	23.33	23.66	0.9972
323.15	23.34	23.68	0.9971

Table 9. Dissolution Enthalpy ΔHd, Dissolution Entropy ΔSd, and Gibbs Free Energy Change ΔGd of BADOPE in Different Pure Solvents

T/K	ΔHd(J/mol)	ΔSd(J/mol·K)	ΔGd(J/mol)
acetonitrile			
293.12	35107.14	78.14	12203.15
298.34	35107.14	78.14	11795.27
303.22	35107.14	78.14	11413.95
308.12	35107.14	78.14	11031.07
313.23	35107.14	78.14	10631.78
318.53	35107.14	78.14	10217.65
323.11	35107.14	78.14	9859.77
328.18	35107.14	78.14	9463.61
333.28	35107.14	78.14	9065.10
338.15	35107.14	78.14	8684.57
acetone			
293.36	33671.47	66.39	14196.47
298.58	33671.47	66.39	13849.93
303.23	33671.47	66.39	13541.24
308.21	33671.47	66.39	13210.63
313.13	33671.47	66.39	12884.01
318.24	33671.47	66.39	12544.78
323.1	33671.47	66.39	12222.14
methanol			
293.38	42545.59	89.38	16322.19
298.25	42545.59	89.38	15886.90
305.63	42545.59	89.38	15227.24
308.26	42545.59	89.38	14992.16
313.13	42545.59	89.38	14556.87
318.22	42545.59	89.38	14101.90
323.21	42545.59	89.38	13655.88
328.16	42545.59	89.38	13213.43
tetrahydrofuran			
293.17	44187.47	95.69	16134.91
298.2	44187.47	95.69	15653.61
305.22	44187.47	95.69	14981.89
308.37	44187.47	95.69	14680.47
313.18	44187.47	95.69	14220.22
318.42	44187.47	95.69	13718.82
323.16	44187.47	95.69	13265.26
328.14	44187.47	95.69	12788.74
ethanol			
293.32	51922.99	113.81	18539.04
298.13	51922.99	113.81	17991.59
303.26	51922.99	113.81	17407.73
308.36	51922.99	113.81	16827.27
313.21	51922.99	113.81	16275.28
318.15	51922.99	113.81	15713.03
323.18	51922.99	113.81	15140.55
328.29	51922.99	113.81	14558.96
333.32	51922.99	113.81	13986.48
ethyl acetate			
293.28	36205.06	64.49	17292.30
298.19	36205.06	64.49	16975.67
303.23	36205.06	64.49	16650.66
308.15	36205.06	64.49	16333.38
313.19	36205.06	64.49	16008.36
318.31	36205.06	64.49	15678.19
323.14	36205.06	64.49	15366.72
328.23	36205.06	64.49	15038.48
333.16	36205.06	64.49	14720.56
methylethylketone			
293.19	29502.23	51.26	14473.81
298.39	29502.23	51.26	14207.27
303.17	29502.23	51.26	13962.25
308.15	29502.23	51.26	13706.99
313.26	29502.23	51.26	13445.06
318.32	29502.23	51.26	13185.69
323.22	29502.23	51.26	12934.52
328.28	29502.23	51.26	12675.16
333.33	29502.23	51.26	12416.30
338.4	29502.23	51.26	12156.42
1,4-dioxane			
293.12	29299.41	45.33	16013.57
298.36	29299.41	45.33	15776.07
303.22	29299.41	45.33	15555.79
308.34	29299.41	45.33	15323.72
313.15	29299.41	45.33	15105.70
318.11	29299.41	45.33	14880.89
323.24	29299.41	45.33	14648.37
328.17	29299.41	45.33	14424.91
333.08	29299.41	45.33	14202.36
338.13	29299.41	45.33	13973.47

6. Prediction of Dissolution Enthalpy, Dissolution Entropy, and Gibbs Free Energy Change

The van't Hoff equation (equation 21) expresses the relationship between the mole fraction solubility of a solute and the temperature by taking the solvent effect into account.

$$\ln x_1 = -\frac{\Delta H_d}{RT} + \frac{\Delta S_d}{R} \qquad (21)$$

where x1 is the mole fraction solubility of solute in the solvent; T is the absolute temperature; ΔHd and ΔSd denote the standard enthalpy and entropy of dissolution, respectively.

Using the data in Fig. 6, a plot of lnx1 versus 1/T gives the values of the dissolution enthalpy and entropy of BADOPE from the slope and the intercept, respectively. The changes of Gibbs free energy ΔGd for the dissolution of BADOPE in different solvents were calculated by the following equations [28]:

$$\Delta G_d = \Delta H_d - T\Delta S_d \qquad (22)$$

The calculated dissolution enthalpy, entropy, and Gibbs free energy change are shown in Table 9.

From the data in Table 9, it can be seen that the ΔHd, ΔSd, and ΔGd values are positive in all solvents and the values of the change of Gibbs free energy decrease with the increasing temperatures in all the solvents. It indicates that the dissolution process of BADOPE in these solvents is endothermic, entropically driven, and not spontaneous. The endothermic process of dissolution means that the interactions between BADOPE molecule and solvent molecules are more powerful than those between solvent molecules. These results are critical for the optimization of the dissolution and crystallization processes of BADOPE.

CONCLUSION

The phosphorus-containing flame retardant (BADOPE) was synthesized successfully in high purity and its chemical structure was confirmed by EA, MS, FT-IR, and 1H NMR. The solid−liquid phase equilibrium data (solubilities) of BADOPE in acetonitrile, acetone, methanol, tetrahydrofuran, ethanol, ethyl acetate, methylethylketone and 1,4-dioxane were measured by a static analytic method and the results were compared. The experimental results show that acetonitrile has the highest solubility at a constant temperature. The solubilities of BADOPE in all the investigated solvents increase with temperature in the temperature range of the measurements. The measured solubility data were correlated by the ideal, modified Apelblat, Wilson, NRTL, UNIQUAC and Scatchard-Hildebrand models. The calculated results show that all the models can reproduce the experimental results well with the optimized parameters. By using the van't Hoff equation, the dissolution enthalpy, dissolution entropy, and Gibbs free energy change of BADOPE are predicted in different pure solvents.

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