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Solubility of cyclohexyl-phosphoramidic acid diphenyl ester in selected solvents

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ABSTRACT

Cyclohexyl-phosphoramidic acid diphenyl ester (CPADE) was synthesized and characterized by elemental analysis (EA), mass spectrum (MS), infrared spectroscopy (IR) and nuclear magnetic resonance (NMR). The thermostability of CPADE was measured by thermogravimetric analysis (TGA) and the melting temperature and the fusion enthalpy of CPADE were evaluated by using differential scanning calorimeter (DSC). The solubilities of CPADE in selected solvents were obtained by a gravimetric method. The experimental data were well correlated by the Wilson, nonrandom two liquid (NRTL), and universal quasichemical (UNIQUAC) equations. And the dissolution enthalpy, entropy, and the molar Gibbs energy of CPADE in the selected solvents are also calculated by the van't Hoff equation.

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1. Introduction

Organic polymer materials that greatly improve the quality of modern life are used in many fields because of their good heat endurance, chemical corrosion resistance, desired mechanical properties and so on. Unfortunately, most of the polymers are flammable, which limited their applications [1]. So the polymer materials with high heat-resistant and flame-retardant properties are urgently required. The well-known method to enhance the flame retardancy is to blend the flame retardant additives into the polymer materials. The flame retardants mainly work as two modes of actions, condensed phase and/or gas phase activities [2]. The condensed phase effects of flame retardants are relevant to a char layer which can obstruct the polymer surface from heat and air [3–5], while the gas phase effects are related to the mechanism of hydrogen and hydroxyl radical scavengers [6,7].

In general, the halogenated compounds with the antimonous oxide are often applied to give the polymers flame retardancy because of their good flame-resistant characteristics. However, this material causes environmental problems as toxic combustion products are released during combustion [8]. Hence, non-halogenated based flame retardants become increasingly popular alternatives in replacing the halogenated flame retardants. Among the available non-halogenated based flame retardants, phosphorus containing compounds are often regarded as potential candidates, because these materials, working as the modes of condensed phase action and gas phase action during the flame retardancy process, typically do not generate any toxic gas [9]. In recent years, nitrogen–phosphorus flame-retardant synergism is recognized by the researchers [10]. The compounds containing phosphorus and nitrogen are usually named intumescent flame retardants owing to a foam char layer in the condensed phase [11]. The incombustible gases without toxic smoke and fog generated from these materials can dilute the concentration of the oxygen near the flame and foam superior protective barriers to the main materials against flame and heat while heating [12,13]. Now, most of the literatures on the halogen-free retardants are deeply relevant to the phosphorus–nitrogen-based products. Furthermore, they are believed to be the biggest growing share of the flame retardant market in the future [8].

Cyclohexyl-phosphoramidic acid diphenyl ester (CPADE) ($C_{18}H_{22}O_3PN$, CAS Registry No. 6372-21-0) is one of versatile intumescent flame retardants; its chemical structure is shown in Fig. 1.

This compound has a bright future, owing to its powerful flame retardancy to the polymers. It was widely used in Ethylene-Propylene-Diene Monomer (EPDM) [14], thermoplastic polyolefin [15], poly(styrene–ethylene/butene–styrene) (SEBS) [16], polyethylene [17,18], epoxy resins [19], polycarbonate (PC) [20] etc. However, some impurities have greatly affected its thermal property and applications. Thus, the purification process employed to obtain CPADE with high purity is very significant.

In the industry, the pure production of CPADE is always obtained by crystallization which is an important separation and purification process [21]. The (solid + liquid) equilibrium (SLE) measurements of CPADE in

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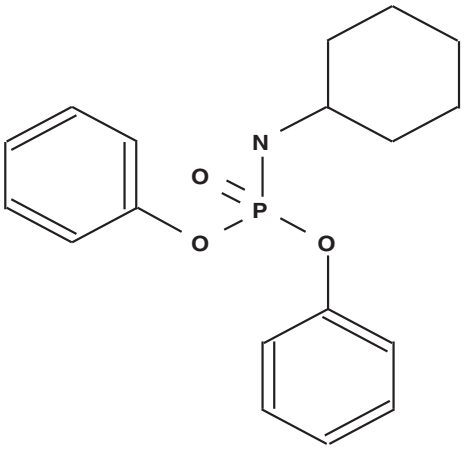

Fig. 1. Structures of the cyclohexyl-phosphoramidic acid diphenyl ester (CPADE).

organic solvents are helpful to determine and estimate some crystallization parameters and reaction kinetics or thermodynamics study. However, there has no report as to the solubilities of CPADE in selected solvents. In this work, CPADE was synthesized and characterized. To achieve more thermodynamic data on the crystallization of CPADE from some organic solvents, the solubilities of CPADE in the ten selected organic solvents were measured. The Wilson [22], nonrandom two-liquid (NRTL) [23], and UNIQUAC [24] models were employed to fit the solubility data based on the pure component thermophysical properties. Comparison and discussion of the solubility were also presented in this study. And the dissolution behaviors of CPADE in the selected solvents were also estimated by van't Hoff equation [25].

2. Experimental

2.1. Materials

Diphenyl chlorophosphate was purchased from Zhangjiagang Xinyi Chemical Co., Ltd. and purified by distillation before used. Triethylamine and cyclohexylamine were kindly supplied by Weisi Chemical Reagents Co., Ltd. All of the organic solvents used for the experiments were analytical grade reagents, which were purchased from Beijing Chemical Factory. Purities and sources of all the materials used in this study are shown in Table 1.

Table 1
The source, mass purity and purification method of the sample used in this paper.

Chemical name	Source	Mass purity	Purification method
Diphenyl chlorophosphate	Zhangjiagang Xinyi Chemical Co., Ltd	> 0.990	Distillation
Triethylamine	Weisi Chemical Reagents Co., Ltd	>0.990	None
Chloroform	Beijing Chemical Factory	>0.995	None
Cyclohexylamine	Weisi Chemical Reagents Co., Ltd	>0.990	None
Ethyl acetate	Beijing Chemical Reagents Co., Ltd	>0.995	None
Acetone	Beijing Chemical Factory	>0.995	None
Ethanol	Beijing Chemical Factory	>0.995	None
Methanol	Beijing Chemical Factory	>0.995	None
Tetrahydrofuran	Beijing Chemical Factory	>0.998	None
Dichloromethane	Beijing Chemical Factory	>0.995	None
Benzene	Beijing Chemical Factory	>0.995	None
Adipic acid	Sigma-Aldrich	>0.990	None
Toluene	Beijing Chemical Factory	>0.995	None
Acetonitrile	Beijing Chemical Factory	>0.995	None
CPADE	As prepared	>0.990	Recrystallization

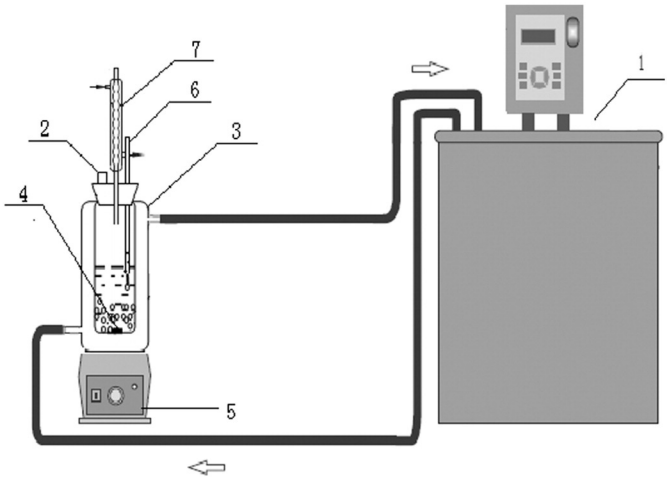

Fig. 2. Schematic diagram of the experimental apparatus: 1, thermostatic water-circulator bath; 2, sample gauge; 3, jacketed glass vessel; 4, magnetic stirrer; 5, magnetic agitator drive; 6, thermometer; 7, condenser.

2.2. Apparatus and procedure

The experimental apparatus for the solubility measurements was the same as it was described in our previous work [26]. The diagrammatic sketch of the experimental apparatus was shown in Fig. 2.

A jacketed equilibrium cell was applied for the solubility measurements 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.) with an uncertainty of ±0.01 K so that the system could reach and keep the required temperature. To prevent the evaporation of the solvent, a condenser was introduced. An analytical balance (type TG328B, Shanghai Balance Instrument Works Co., Ltd.) with an uncertainty of ±0.1 mg was used during the mass measurements.

Fourier transform infrared (FTIR) spectrum was performed on a Perkin Elmer 400 spectrometer (Connecticut, USA). The melting point and enthalpy of fusion were measured with a DSC Q100 (TA Instruments) differential scanning calorimeter (DSC) in flowing nitrogen at a heating rate of 10 $K \cdot min^{-1}$. The uncertainty of DSC measurement was the same as it was described in the literature [26]. The elemental

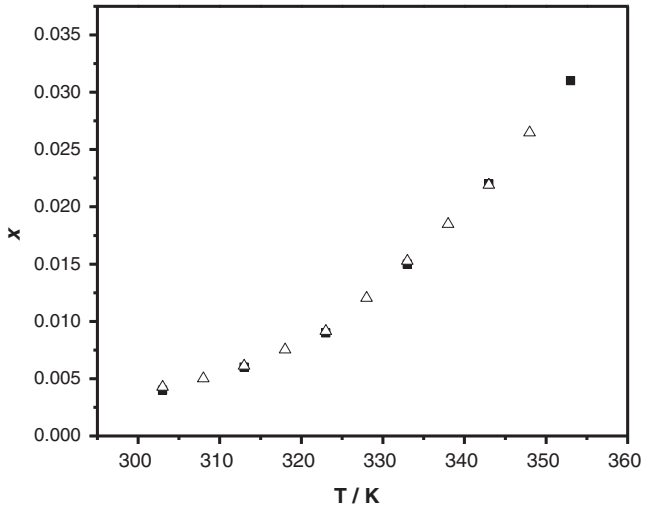

Fig. 3. Comparison of the literature and experimental mole fraction of adipic acid solubility (x) against temperature in water: ■, literature; △, this work.

analysis was performed on an Elementar Vario EL element analyzer, ^{1}H NMR and ^{13}C NMR spectra were obtained with a Bruker ARX-400. Thermogravimetric analysis (TGA) was obtained with an SDT Q600 (TA Instruments) thermogravimetric analyzer at a heating rate of 10 K·min^{-1} under nitrogen atmosphere.

2.3. Synthesis and characterization of CPADE

CPADE was prepared by the method similar to our previous work [27]. To a dry chloroformic solution of $(C_6H_5O)_2P(O)Cl$, a dry chloroformic solution of cyclohexylamine and triethylamine (1:1:1.1 molar ratio) was added dropwise over a period of 1 h at 273 K. After 6 h of stirring, the solvent was removed at reduced pressure and recrystallization of the residual material after being washed with cold distilled water from acetone afforded CPADE as a white crystalline solid. The mass fraction purity of PAETE was about 0.99.

EI mass spectrum of CPADE can be seen in Fig. S1. The intensity (%) m/z of CPADE is 332.3 (M^+). Elemental analysis (%, calcd): C, 65.25% (65.37%); H, 6.69% (6.72%); N, 4.23% (4.28%). In Fig. S2, the infrared spectrum of CPADE contains characteristic absorptions at 3216 cm^{-1} for N–H stretching, 3072 cm^{-1} for aromatic –C═C–H stretching, 2933 and 2854 cm^{-1} for –HC–H stretching, ring carbon–carbon stretching vibrations occur in 1589, 1489 and 1455 cm^{-1}, 1194 cm^{-1} for the P═O stretching, 1024 cm^{-1} for the P–N stretching, 1236 cm^{-1} for the C–N stretching and 904–955 cm^{-1} for the P–O–Aryl stretching. The ^{1}H NMR spectrum of CPADE is shown in Fig. S3 of the Supporting information. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.00 (m, 10H), 3.35 (d, J = 11.9 Hz, 1H), 2.03 (d, J = 13.2 Hz, 1H), 1.80–1.22 (m, 10H). Fig. S4 presents ^{13}C NMR (400 Hz, $CDCl_3$) spectrum of CPADE. The chemical shifts of carbons with different chemical environments in CPADE structure are 25.03, 25.35, 35.50, 51.30, 120.25, 124.83, 129.67, and 151.06, respectively.

2.4. Solubility measurement

A gravimetric method [26] was used to measure the solubilities of the CPADE in methanol, acetone, acetonitrile, tetrahydrofuran, ethyl acetate, chloroform, ethanol, benzene, toluene and dichloromethane. For each measurement, an excess mass of CPADE was introduced into a known mass of solvent. Then the equilibrium cell was heated and stirred at a constant temperature. After at least 3 h (different dissolution times were tested to determine the suitable equilibrium time. It was found that 3 h was enough to reach equilibrium), the stirring was stopped, and the solution was kept still until it was clear. Then, samples of the clear saturated solution were withdrawn by a preheated injector with a cotton filter. The mass of the saturated clear solution sample was determined with the analytical balance. Each solution sample was dried in a vacuum oven for at least 3 days to evaporate all solvents. The mass of the samples was weighed repeatedly throughout the drying process to make sure that no solvent remained. The weights were recorded after the solvents have been completely evaporated. During our experiments, three parallel measurements were performed at the same composition of solvent for each temperature, and an average value is given. FTIR was used to analyze the sample to ensure that no thermal decomposition effect had occurred on PNBE and no solvate material was generated during the experiments. Finally the sample was characterized by DSC to ensure that the solute maintained the crystalline form under all the experimental conditions. Based on error analysis and repeated observations, the estimated relative uncertainty of the solubility values was $u_r(x) = 0.02$.

The solubility of adipic acid in water was obtained by using experimental apparatus and illustrated in Fig. 3. Fig. 3 showed that the experimental data agreed well with the data in the literature[28], thus the reliability of our experimental setup was verified.

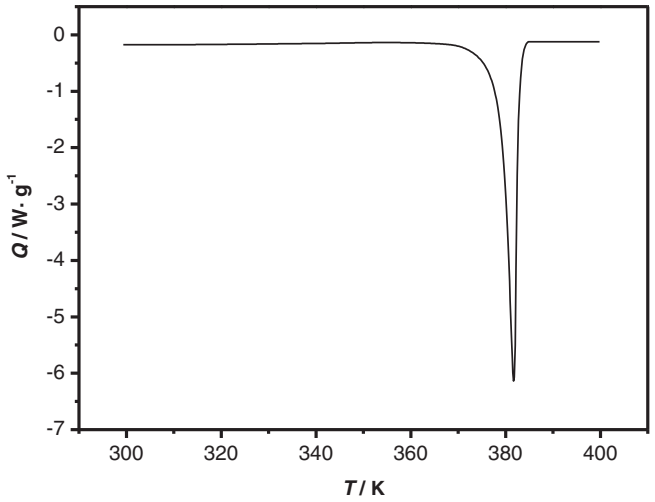

Fig. 4. Experimental heat Q flow from DSC measurement of CPADE.

3. Results and discussion

3.1. Evaluation of pure component properties

From the results achieved by DSC and TGA analysis, as shown in Fig. 4 and Fig. 5, the melting point was 381.69 K ± 0.05 K; the enthalpy of fusion of CPADE was 27.57 kJ·mol^{-1}. TGA results illustrate that there is one single step decomposition, and about 1% char residue for CPADE which shows that the CPADE should be used as intumescent flame retardant together with the char-forming agent. The entropy of fusion of CPADE $\Delta_{fus}S$ was 72.24 J/(mol·K), which was calculated by Eq. (1).

$$\Delta_{fus}S = \frac{\Delta_{fus}H}{T_m}. \quad (1)$$

3.2. Solubility data and correlation

The measured solubility data of CPADE in acetonitrile, methanol, acetone, tetrahydrofuran, chloroform, ethyl acetate, toluene, ethanol, benzene and dichloromethane are shown in Table 2. The mole-fraction solubility data of CPADE in the selected solvents are plotted in Fig. 6.

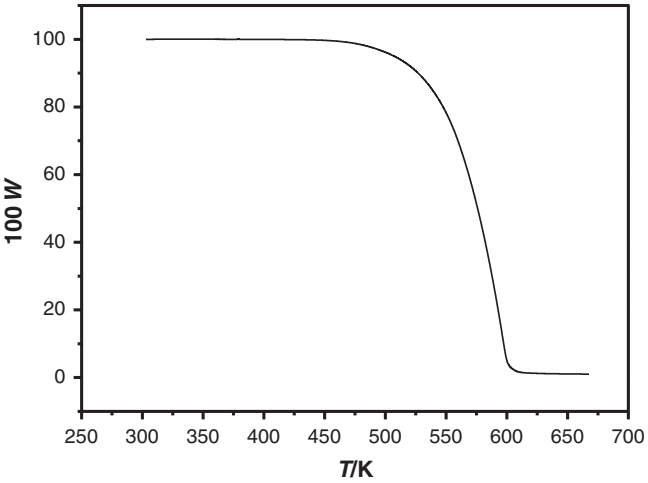

Fig. 5. TGA thermograms of CPADE under N_2.

Table 2
Mole fraction solubilities (x) and activity coefficients (γ) of CPADE in the selected solvents at temperature T and pressure $p = 0.1$ MPa.[a]

Solvent	T/K	γ	10^2x
Methanol	293.15	1.9518	4.110
	298.15	1.8203	5.328
	303.15	1.6606	7.017
	308.15	1.4566	9.553
	313.15	1.3676	12.08
	318.15	1.2122	16.10
	323.15	1.0838	21.16
	328.15	0.95454	28.09
	333.15	0.87751	35.56
Acetone	293.15	1.8259	4.394
	298.15	1.5882	6.107
	303.15	1.4629	7.965
	308.15	1.2808	10.86
	313.15	1.2369	13.36
	318.15	1.0438	18.70
	323.15	1.0013	22.90
	328.15	0.98926	27.11
Acetonitrile	293.15	6.9513	1.154
	298.15	5.6787	1.708
	303.15	4.7060	2.476
	308.15	3.7544	3.706
	313.15	3.1731	5.208
	318.15	2.5720	7.588
	323.15	2.1602	10.62
	328.15	1.8069	14.84
	333.15	1.6352	19.09
	338.15	1.3736	26.32
	343.15	1.1650	35.81
Tetrahydrofuran	293.15	0.47651	16.84
	298.15	0.50460	19.22
	303.15	0.50880	22.90
	308.15	0.51754	26.89
	313.15	0.51964	31.80
	318.15	0.52415	37.24
	323.15	0.54749	41.89
	328.15	0.53219	50.39
	333.15	0.55079	56.66
Ethyl acetate	293.15	2.6308	3.049
	298.15	2.4579	3.946
	303.15	2.1216	5.492
	308.15	1.9294	7.212
	313.15	1.7473	9.457
	318.15	1.5249	12.80
	323.15	1.3814	16.60
	328.15	1.2710	21.10
	333.15	1.1842	26.35
	338.15	1.0599	34.11
	343.15	0.98010	42.56
Chloroform	293.15	0.38795	20.68
	298.15	0.41548	23.34
	303.15	0.43873	26.56
	308.15	0.44499	31.27
	313.15	0.46890	35.24
	318.15	0.48727	40.05
	323.15	0.50015	45.85
	328.15	0.51719	51.85
Ethanol	293.15	2.2387	3.585
	298.15	1.9802	4.898
	303.15	1.8268	6.378
	308.15	1.6053	8.669
	313.15	1.4303	11.55
	318.15	1.2748	15.31
	323.15	1.1678	19.64
	328.15	1.0600	25.30
	333.15	0.9856	31.67
	338.15	0.8911	40.58
Benzene	293.15	1.0420	7.699
	298.15	0.97824	9.915
	303.15	0.92121	12.65
	308.15	0.87495	15.90
	313.15	0.84909	19.46
	318.15	0.78048	25.01
	323.15	0.78423	29.24
	328.15	0.71749	37.37
	333.15	0.68310	45.69
	338.15	0.65709	55.03
	343.15	0.65599	63.59
Toluene	293.15	1.4871	5.395
	298.15	1.4091	6.883
	303.15	1.2787	9.112
	313.15	1.0708	15.43
	323.15	0.88656	25.87
	333.15	0.76373	40.86
	343.15	0.68232	61.13
Dichloromethane	278.15	0.49305	8.840
	283.15	0.52642	10.22
	288.15	0.51063	12.91
	293.15	0.51669	15.53
	298.15	0.53811	18.02
	303.15	0.54057	21.56
	308.15	0.53439	26.04

[a] The standard uncertainties u is $u(x) = 0.0002$.

For each solvent researched, the solubility of CPADE increases as the temperature rises, but the systems behave differently. At a given temperature, the order of solubility of CPADE is as follows: chloroform > tetrahydrofuran > dichloromethane > benzene > toluene > acetone > methanol > ethanol > ethyl acetate > acetonitrile. The solubility of CPADE in acetonitrile shows the lowest value, and in chloroform gives the highest value. The higher solubility value in chloroform and dichloromethane than other solvents but tetrahydrofuran might be owing to the strong electronegativity of elemental chlorine. As there coexist both NH group and P═O group in CPADE, it can be the proton donor or acceptor. The fact that the solubility value in tetrahydrofuran is higher than that in the alcohols shows the property of the proton donor of NH group in CPADE. Accordingly, it might be the hydrogen bond between tetrahydrofuran and CPADE molecules that play an important role in contributing to the higher solubility of CPADE in tetrahydrofuran in the ten solvents. From the solubility data, tetrahydrofuran, chloroform and dichloromethane appear to be more appropriate solvents for the crystallization of CPADE. The three solvents are also suggested as the appropriate reaction solvents.

From the thermodynamic principles, solid–liquid phase equilibrium can be described as follows [29]:

$$\ln\frac{1}{x_1\gamma_1}=\frac{\Delta_{fus}H}{RT_m}\left(\frac{T_m}{T}-1\right)+\frac{\Delta_{tr}H}{RT_{tr}}\left(\frac{T_{tr}}{T}-1\right)-\frac{\Delta C_p}{R}\left(\ln\frac{T}{T_m}+\frac{T_m}{T}-1\right) \quad (1)$$

where, T_m is the melting temperature of the solute, respectively; $\Delta_{fus}H$, and ΔH_{tr} stand for enthalpy of fusion of the solute at melting temperature and enthalpy of solid–solid phase transition of the solute, respectively; T_{tr} denotes temperature of phase transition and ΔC_p denotes heat capacity of the solute at melting temperature. Here, ΔH_{tr} and ΔC_p can be neglected because no transition in CPADE solid phase occurs, which is determined by the DSC throughout the whole experiments [30]. And thus a simplified form of the solid–liquid phase equilibrium equation can be written in the following form [31]:

$$\ln\frac{1}{x_1\gamma_1}=\frac{\Delta_{fus}H}{RT_m}\left(\frac{T_m}{T}-1\right). \quad (2)$$

Based on the values of x_1, Tm and $\Delta_{fus}H$, the activity coefficients of CPADE in solid–liquid equilibrium can be calculated via Eq. (2) and are also presented in Table 2.

The solubility of CPADE varying with temperature can be correlated by the Wilson equation. In the binary system, Wilson model can be shown in the following form:

$$\ln\gamma_1 = -\ln(x_1+\Lambda_{12}x_2)+x_2\left(\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2}-\frac{\Lambda_{21}}{x_2+\Lambda_{21}x_1}\right) \quad (3)$$

$$\Lambda_{12}=\frac{v_2}{v_1}\exp\left(-\frac{\lambda_{12}-\lambda_{11}}{RT}\right)=\frac{v_2}{v_1}\exp\left(-\frac{\Delta\lambda_{12}}{RT}\right) \quad (4)$$

$$\Lambda_{21}=\frac{v_1}{v_2}\exp\left(-\frac{\lambda_{21}-\lambda_{22}}{RT}\right)=\frac{v_1}{v_2}\exp\left(-\frac{\Delta\lambda_{21}}{RT}\right). \quad (5)$$

Here, v_1 and v_2 denote the molar volumes of solute and solvent respectively. $\Delta\lambda_{11,}$ and $\Delta\lambda_{12}$ represent the cross interaction energy parameters, ($J\cdot mol^{-1}$), which can be regressed from the experimental data.

The NRTL activity coefficient model is used in this work to correlate the experimental solubility data, which has been successfully used to correlate the solid–liquid equilibrium for many nonideal solutions in wide temperature ranges [32–34]. The NRTL model which is applied to determine the activity coefficient of a solute in pure solvents can be expressed as following:

$$\ln\gamma_1 = x_2{}^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2+\frac{\tau_{12}G_{12}}{(x_2+x_1G_{12})^2}\right] \quad (6)$$

where G_{12}, G_{21}, τ_{12} and τ_{21} represent NRTL model parameters that demand to be experimentally determined by

$$G_{ij}=\exp(-a_{ij}\tau_{ij}) \quad (7)$$

$$\tau_{ij}=\frac{g_{ij}-g_{jj}}{RT}=\frac{\Delta g_{ij}}{RT}. \quad (8)$$

In which, Δg_{12} and Δg_{21} refer to the two cross interaction energy parameters ($J\cdot mol^{-1}$); a reflects the parameter related to the nonrandomness in the mixture. a is chosen to be 0.3 as usual.

The mole fraction solubility data in the selected solvents were also described by the UNIQUAC model in the following form:

$$\ln\gamma_1 = \ln\gamma_1{}^C + \ln\gamma_1{}^R \quad (9)$$

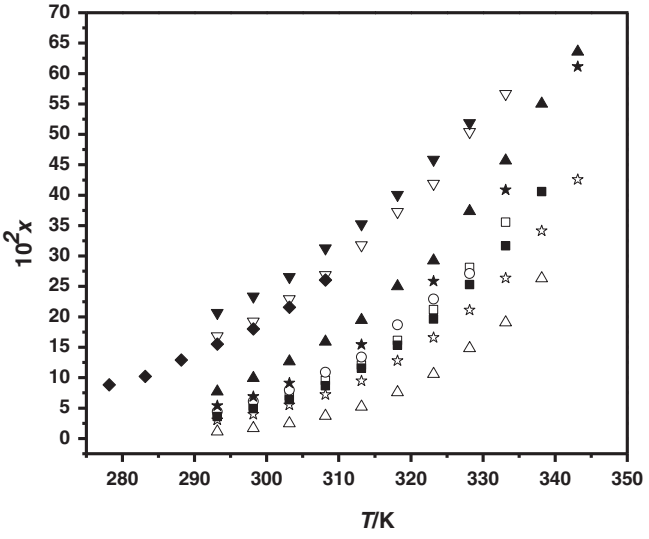

Fig. 6. Mole fraction solubility (x) data of CPADE in selected solvents: □, methanol; ○, acetone; △, acetonitrile; ▽, tetrahydrofuran; ☆, ethyl acetate; ▼, chloroform; ■, ethanol; ▲, benzene; ★, toluene; ◆,dichloromethane.

Table 3
Molar volume (V), UNIQUAC volume parameter (r), and surface parameter (q) values for selected solvents.[a]

Solvent	$10^6V_i/m^3\cdot mol^{-1}$	r	q
Methanol	40.70	1.4311	1.432
Ethanol	58.52	2.1055	1.972
Dichloromethane	64.43	2.2564	1.988
Acetonitrile	52.68	1.8701	1.724
Ethyl acetate	98.59	3.4786	3.116
Tetrahydrofuran	81.94	2.9415	2.720
Chloroform	80.66	2.8700	2.410
Benzene	89.48	3.1878	2.400
Toluene	106.6	3.9228	2.968
Acetone	73.93	2.5735	2.336
CPADE	275.9	12.326	13.09

[a] Data from Prausnitz.[26]

$$\ln\gamma_1{}^C = \ln\left(\frac{\phi_1}{x_1}\right)+\frac{z}{2}q_1\ln\left(\frac{\theta}{\phi_1}\right)+\phi_2\left(l_1-\frac{r_1}{r_2}l_2\right) \quad (10)$$

$$\ln\gamma_1{}^R = -q_1\ln(\theta_1+\theta_2\tau_{21})+\theta_2q_1\left(\frac{\tau_{21}}{\theta_1+\theta_2\tau_{21}}-\frac{\tau_{12}}{\theta_2+\theta_1\tau_{12}}\right) \quad (11)$$

$$\begin{aligned} l_1 &= \frac{z}{2}(r_1-q_1)-(r_1-1)\\ l_2 &= \frac{z}{2}(r_2-q_2)-(r_2-1)\end{aligned} \quad (12)$$

$$\tau_{12}=\exp\left(-\frac{u_{12}-u_{22}}{RT}\right)=\exp\left(-\frac{\Delta u_{12}}{RT}\right) \quad (13)$$

$$\tau_{21}=\exp\left(-\frac{u_{21}-u_{11}}{RT}\right)=\exp\left(-\frac{\Delta u_{21}}{RT}\right). \quad (14)$$

In which, $\Delta u_{12}(\Delta u_{21})$, z, Φ and θ denote two adjustable energy parameters; the coordination number usually taken as 10; the volume fraction and molecular surface fraction of solute or solvent, respectively. Parameters r and q refer to the UNIQUAC volume parameter and surface parameter of solvent and solute, which are listed in Table 3. The values of r and q of solute can be obtained from the group volume parameters (R) and surface parameters (Q) of the UNIFAC model, which are listed in Table 4.

The cross-interaction parameters of the Wilson equation ($\Delta\lambda_{12}$ and $\Delta\lambda_{21}$), the NRTL equation (Δg_{12} and Δg_{21}), and the UNIQUAC equation (Δu_{12} and Δu_{21}) are written as the following Eq. (15):

$$k_{ij}=\alpha_{ij}+\beta_{ij}T \quad (15)$$

where k stands for any interaction parameter mentioned above. α and β denote the parameters to be fitting the solubility data.

The parameters of the Wilson, nonrandom two-liquid (NRTL), and UNIQUAC model which were obtained by fitting the experimental solubility data and the relative standard deviations (RSDs) defined by

Table 4
Van der Waals group volume and surface area parameters for the UNIQUAC model.

Group	R	Q
(O–)(−O)P(=O)– [a]	1.9312	1.762
–CHNH–	0.97950	0.6240
ACH	0.53130	0.4000
AC	0.36520	0.1200
$–CH_2–$	0.67440	0.5400

[a] is taken from literature.[27] The other values in this table are from literature. [26]

Table 5
Parameters of the models and RSD% of different correlation models in ten pure solvents.

		Methanol	Tetrahydrofuran	Ethyl acetate	Chloroform	Ethanol	Benzene	Toluene	Dichloromethane	Acetone	Acetonitrile
Wilson model	α_{12}	43802	−32071	32882	−36098	43649	95370	88233	258917	2254.4	5725.9
	β_{12}	−111.24	119.74	−76.752	136.84	−101.4	−264.39	−245.3	−804.65	−3.7491	1.5994
	α_{21}	8408.5	19681	14206	11396	15431	9696.7	13810	133.97	−12654	24918
	β_{21}	−46.539	−85.271	−56.548	−61.606	−69.862	−50.596	−59.773	−27.107	52.024	−86.848
	RSD %	1.15	1.73	1.45	0.99	1.02	1.44	1.43	1.78	1.91	1.61
NRTL model	α_{12}	−19155	7414.6	−319.16	−1365.8	−11232	164401	26065	14435	22412	32491
		79.802	−43.075	17.134	−16.062	52.198	−489.10	−93.798	−62.414	−32.097	−95.200
	α_{21}	13415	63075	5742.5	53686	12414	4065.8	74819	−25688	−15179	−6491.1
	β_{21}	−52.058	−173.12	−25.182	−148.44	−47.57	−26.682	−203.78	97.151	35.714	23.318
	RSD %	1.93	1.98	1.81	1.19	2.01	1.89	1.55	1.92	0.949	1.64
UNIQUAC model	α_{12}	2559.8	54879	−436.10	40751	1007.7	81903	80135	69621	2503.7	1958.8
	β_{12}	−13.509	−171.20	−4.7816	−130.40	−9.1657	−247.44	−239.16	−220.49	−6.2505	−9.5509
	α_{21}	30121	−3125.1	12467	−5525.5	20136	−1913.9	−3900.9	−3714.0	−4156.7	−240.30
	β_{21}	−77.537	3.7098	−26.755	10.439	−48.467	−1.8949	4.3439	6.9123	13.815	11.993
	RSD %	2.22	3.02	1.89	1.96	1.91	2.12	1.97	1.43	1.55	1.45

Table 6
The overall RSD% of different correlation models.

	Wilson model	NRTL model	UNIQUAC model
Overall RSD%	1.45	1.69	1.95

Eq. (16) were used to compare the experiment data and the calculated data by the models mentioned above.

$$\mathrm{RSD} = \left[\frac{1}{N}\sum_{i=1}^{N}\left(\frac{x_i - x_i^{cacld}}{x_i}\right)^2\right]^{\frac{1}{2}} \tag{16}$$

Herein, N, x_i and x_i^{cacld} denote the number of experimental points; the experimental solubility data and the calculated solubility data by the models, respectively.

The calculated parameters of all the models mentioned above are listed in Table 5 together with the RSDs. The overall relative standard deviations are displayed in Table 6. The results show that all the models can describe the experimental data well with the optimized parameters. The overall RSDs of the models are 1.45% (Wilson), 1.69% (NRTL) and 1.95% (UNIQUAC). For the CPADE systems, the Wilson model is better than the other models in reproducing the temperature dependence of solubility.

3.3. Calculation of dissolution enthalpy, entropy, and the molar gibbs energy

The values of standard molar dissolution enthalpy and entropy at saturation can be determined by the van't Hoff equation. The Gibbs energy of solution at saturation can be calculated by Gibbs–Helmoholtz equation,[35]

$$\ln x_1 = -\frac{\Delta H_d^0}{RT} + \frac{\Delta S_d^0}{R} \tag{17}$$

$$\Delta G_d^0 = \Delta H_d^0 - T\Delta S_d^0. \tag{18}$$

The achieved dissolution enthalpy and entropy are listed in Table 7 and the Gibbs energy is plotted in Fig. S5. From the data in Table 7, the ΔH_d^0 of CPADE in each solvent is endothermic ($\Delta H_d^0 > 0$), which explains the increasing solubility of CPADE with increasing temperature [36].

4. Conclusions

The CPADE was synthesized in this work. The solubility data of CPADE in methanol, chloroform, acetone, ethyl acetate, acetonitrile, tetrahydrofuran, ethanol, benzene, toluene and dichloromethane were obtained at different temperatures. The melting temperature and the enthalpy of fusion were measured by DSC. The order of the solubility of CPADE is: chloroform > tetrahydrofuran > dichloromethane > benzene > toluene > acetone > methanol > ethanol > ethyl acetate > acetonitrile. The experimental data were correlated with the Wilson, nonrandom two-liquid (NRTL), and UNIQUAC model. The results show that the Wilson model is more suitable in determining the solubility of CPADE compared with the other models. Based on the van't Hoff equation, the dissolution enthalpy, entropy, and molar Gibbs free energy of CPADE are calculated in different solvents.

Notes

The authors declare no competing financial interest.

Table 7
Caculated values for dissolution enthalpy and dissolution entropy of CPADE in different pure solvents.

Solvent	ΔH_d (K J/mol)	ΔS_d (J/(mol × K))
Methanol	44.2	124.1
Acetone	42.2	118.2
Acetonitrile	57.5	159.1
Tetrahydrofuran	25.1	70.7
Ethyl acetate	44.5	122.7
Chloroform	21.3	59.3
Ethanol	44.6	124.3
Methyl acetate	35.6	100.3
Toluene	41.2	116.2
Dichloromethane	25.8	72.4

Appendix A. Supplementary data

Supplementary data of MS spectra of CPADE, IR spectra of CPADE, ^{1}H NMR spectra of CPADE, ^{13}C NMR spectra of CPADE associated with this article can be found, in the online version, at

References

[1] A.R. Horrocks, D. Price, Fire Retardant Materials, CRC Press, New York, 2001.
[2] M.W. Beach, N.G. Rondan, R.D. Froese, B.B. Gerhart, J.G. Green, B.G. Stobby, A.G. Shmakov, V.M. Shvartsberg, O.P. Korobeinichev, Polym. Degrad. Stab. 93 (2008) 1664–1673.
[3] Y. Tang, Q.L. Zhao, K. Zeng, P.K. Miao, K. Zhou, W.R. Tang, H.F. Zhou, T. Liu, Y.P. Wang, G.C. Yang, Chem. Lett. 18 (2007) 973–976.
[4] G.H. Hsiue, Y.L. Liu, J. Tsiao, J. Appl. Polym. Sci. 78 (2000) 1–7.
[5] N.N. Ghosh, B. Kiskan, Y. Yagci, Prog. Polym. Sci. 32 (2007) 1344–1391.
[6] B.N. Jang, C.A. Wilkie, Thermochim. Acta 433 (2005) 1–12.
[7] S.Y. Lu, I. Hamerton, Prog. Polym. Sci. 27 (2002) 1661–1712.
[8] M. Rakotomalala, S. Wagner, M. Doring, Materials 3 (2010) 4300–4327.
[9] W. Zhao, B. Li, M. Xu, J.K. Yang, L. Li, Fire Mater. 33 (2012) 351–359.
[10] T. Tsutomu, K. Takehiro, A. Tarek, Polym. J. 40 (2008) 1121–1131.
[11] L.j. Chen, L. Song, P. Lu, G.X. Jie, Q.l. Tai, W.Y. Xing, Y. Hua, Prog. Org. Coat. 70 (2011) 59–66.
[12] B.K. Kandola, A.R. Horrocks, Polym. Degrad. Stab. 54 (1996) 289–303.
[13] R. Sarawut, T. Nuttiwan, S. Nitinat, J. Chanchira, T. Tsutomu, T. Sunan, J. Appl. Polym. Sci. 130 (2013) 1074–1083.
[14] Y.M. Liu, D.M. Hao, C.W. Chen, L. Yin, T. Chen, Z.S. Lin, CN Patent 101,928,431 (2012)
[15] D.M. Hao, Y.M. Liu, C.W. Chen, Z.S. Lin, L. Yin, T. Chen, CN Patent 101,824,182 (2010)
[16] D.M. Hao, Y.M. Liu, C.W. Chen, T. Chen, L. Yin, Z.S. Lin, CN Patent 101,469,100 (2009)
[17] Y.M. Liu, D.M. Hao, L.Yin, C.W. Chen, CN Patent 101,434,723 (2009)
[18] D.M. Hao, Y.M. Liu, L. Yin, C.W. Chen, CN Patent 101,343,387 (2009)
[19] Y.M. Liu, D.M. Hao, L. Yin, C.W. Chen, CN Patent 101,200,573 (2008)
[20] T. Masuda, S. Morishita, T. Kawada, N. Kano, JP Patent 154,277 (2000)
[21] D.W. Wei, K.X. Jin, J. Chem. Thermodyn. 41 (2009) 145–149.
[22] D.S. Abrams, J.M. Prausnitz, AICHE J. 21 (1975) 116–128.
[23] G.M. Wilson, J. Am. Chem. Soc. 86 (1964) 127–130.
[24] H. Renon, J.M. Prausnitz, AICHE J. 14 (1968) 135–144.
[25] N. Aldabaibeh, M.J. Jones, A.S. Myerson, Cryst. Growth Des. 9 (2009) 3313–3317.
[26] X.Z. Shao, L.S. Wang, M.Y. Li, Ind. Eng. Chem. Res. 51 (2012) 5082–5089.
[27] C.M. Qi, L.S. Wang, J.C. Du, G.M. Yu, G.Q. Sun, Fluid Phase Equilib. 360 (2013) 343–350.
[29] D.W. Wei, Y.H. Pei, Ind. Eng. Chem. Res. 47 (2008) 8953–8956.
[30] L.Q. Yang, Q.X. Yin, B.H. Hou, Y.L. Wang, Y. Bao, J.K. Wang, H.X. Hao, Ind. Eng. Chem. Res. 52 (2013) 2477–2485.
[31] R.Y. Li, H. Yan, Z. Wang, J.B. Gong, Ind. Eng. Chem. Res. 51 (2012) 8141–8148.
[32] W. Zou, Q. Xia, W. Zhao, F.B. Zhang, G.L. Zhang, J. Chem. Thermodyn. 70 (2014) 239–244.
[33] A.G. Gilani, H.G. Gilani, F. Amouzadeh, J. Chem. Thermodyn. 71 (2014) 103–111.
[34] R.M. Shah, R. Anantharaj, T. Banerjee, G. Yadav, J. Chem. Thermodyn. 62 (2013) 142–150.
[35] J.M. Prausnitz, R.N. Lichtenthaler, E.G. Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria, 3rd ed. Prentice Hall, New York, 1999.
[36] N. Wang, Q. Fu, G.D. Yang, Fluid Phase Equilib. 324 (2012) 41–43.