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Solid–Liquid Phase Equilibrium of Phosphoramidic acid, *N*,*N*′-1,2-Ethanediylbis-*P*,*P*,*P*′,*P*′-tetraphenyl Ester in Selected Solvents

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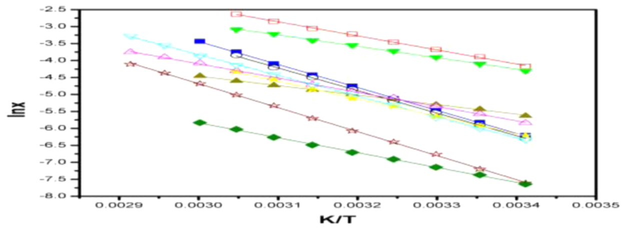
Ⓢ *Supporting Information*

ABSTRACT: Phosphoramidic acid, *N*,*N*′-1,2-ethanediylbis-*P*,*P*,*P*′,*P*′-tetraphenyl ester (PAETE) was prepared and characterized by elemental analysis (EA), mass spectra (MS), infrared spectroscopy (IR), and nuclear magnetic resonance (NMR). The thermostability of PAETE was measured via thermogravimetric analysis (TGA). The melting temperature and the fusion enthalpy of PAETE were evaluated by differential scanning calorimeter (DSC). The solubilities of PAETE in ten selected solvents were obtained using a gravimetric method. The experimental data were well correlated by the Buchowski–Ksiazczak (*λh*), Scatchard–Hildebrand, modified Apelblat model, and the ideal equations. The solubility parameter of PAETE was estimated by the Scatchard–Hildebrand Model. The dissolution enthalpy and entropy of PAETE in the ten selected solvents were also calculated by the modified Apelblat model.



■. INTRODUCTION

The high-level living standard would not be possible without the development of polymeric materials that have appeared since World War II.[1] Nowadays, polymers have been widely used in various fields, such as aerospace, mechanics, and chemistry, due to the good heat endurance and mechanical performance, small chemical corrosion resistance, and so on.[2] Unfortunately, almost all of the polymers are easily to burn, which limits their applications in electronics, transportation, cabling, construction, and so on. Flame retardancy is mandatorily required in the fields mentioned above.[3] To decrease the fire hazards and expand the range of the applications for the polymer materials, it is urgent to develop the flame retardant polymer materials. It is well know that adding the flame retardant additives into the polymer materials is an effective method to enhance the flame retardancy. Recently, some reports indicate that the flame retardant efficiency can be greatly enhanced while nitrogen and phosphorus elements are present together in the polymer systems. The synergism of phosphorus and nitrogen elements has been recognized in many research works.[4−7] Now, it is predicted that the phosphorus–nitrogen-based flame retardants will be the biggest growing share in the flame retardant market.[8]

Phosphoramidic acid, *N*,*N*′-1,2-ethanediylbis-*P*,*P*,*P*′,*P*′-tetraphenyl ester (PAETE) ($C_{26}H_{26}N_2O_6P_2$, CAS Registry No. 34670-52-5) has gained increasing attention over the past years as a versatile intumescent flame retardant because the phosphorus and nitrogen elements present in the formula. Figure 1 shows the chemical structure. PAETE possesses a bright future because of its powerful flame retardancy. It has been widely used in thermoplastic polyolefin,[9] polyethylene,[10,11] epoxy resins,[12] polycarbonate(PC),[13] and so forth.

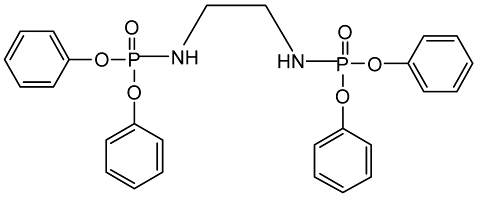


Figure 1. Structure of the phosphoramidic acid, *N*,*N*′-1,2-ethanediylbis-*P*,*P*,*P*′,*P*′-tetraphenyl ester (PAETE).

However, some impurities have greatly effects on its thermal property and the application. Hence, purifying PAETE is important to gain the product with high purity.

As the solubility of PAETE in water is very low, knowledge of (solid + liquid) equilibrium of PAETE in organic solvents is especially necessary for determining the optimal conditions in the crystallization isolation processes. Furthermore, it can also provide the database of evaluating the applications and limitations for the solution models established for predicting the thermodynamic properties.[14] However, the crystallization method of separating PAETE and the solubility data of PAETE have not been reported. In the work, PAETE was synthesized and characterized. To obtain a high yield and separation efficiency via selecting the optimal solvent, and achieve more systematic thermodynamic information on the crystallization for PAETE from some organic solvents, the solubilities of PAETE in ten selected organic solvents were measured. The modified Apelblat equation,[15] Ideal model,[16] Scatchard–

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Hildebrand,[17] and Buchowski–Ksiazczak (λh) model[18] were employed to correlate the solubility data based on the pure component with the thermophysical properties. Moreover, the activity coefficients of PAETE, the mixing enthalpies and entropies of solutions were estimated to understand the solubility behavior.

■. EXPERIMENTAL SECTION

Materials. Diphenylchlorophosphate was supplied by Xinyi Chemical Co., Ltd. (Zhangjiagang) and purified by distillation before using. Triethylamine and ethylenediamine were purchased from Weisi Chemical Reagents Co. (Beijing). All the solvents purchased from Beijing Chemical Factory were analytical grade. The mass fraction purities were all higher than 0.99 (Table 1) and used as received.

Table 1. Description of the Solute and Solvents Used in This Paper

chemical name	source	mass fraction	purification method
diphenylchlorophosphate	Zhangjiagang Xinyi Chemical Co., Ltd.	>0.990	none
triethylamine	Weisi Chemical Reagents Co., Ltd.	>0.990	none
chloroform	Beijing Chemical Factory	>0.995	none
ethanediamine	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
methyl acetate	Beijing Chemical Factory	>0.995	none
benzene	Beijing Chemical Factory	>0.995	none
toluene	Beijing Chemical Factory	>0.995	none
acetonitrile	Beijing Chemical Factory	>0.995	none
PAETE	as-prepared	>0.990[a]	recrystallization

[a] PAETE (Phosphoramidic acid, *N*,*N*′-1,2-ethanediylbis-*P*,*P*,*P*′,*P*′-tetraphenyl ester) determined by the high-performance liquid chromatography.

Apparatus and Procedure. The experimental apparatus used to measure the solubility was similar to that previously reported.[19] Figure 2 presents the setup. A jacketed equilibrium cell was used to measure the solubility. The cell was with a working volume (120 mL) and a magnetic stirrer. A circulating water bath was applied with a thermostat of 50 L, made by Shanghai Laboratory Instrument Works Co., Ltd. to keep the temperature within ± 0.05 K. A condenser was used to prevent the solvent evaporating. An analytical balance (TG328B), made by Shanghai Balance Instrument Works Co. with an uncertainty of ± 0.1 mg was used for weighing the samples.

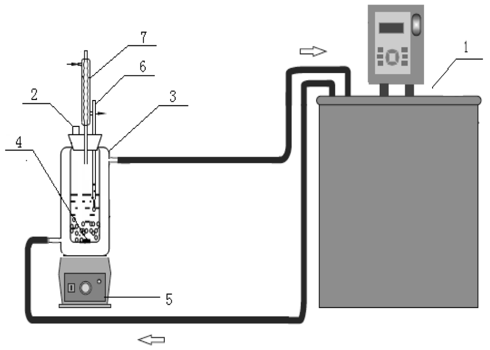

Figure 2. Schematic diagram of the experimental apparatus: 1, thermostatic water-circulator bath; 2, sample gauge; 3, jacketed glass vessel; 4, magnetic stirrer; 5, magnetic agitator drive; 6, thermometer; 7, condenser.

Fourier transform infrared (FTIR) spectra were performed in a Nicolet 6700 Fourier-transform spectrometer in the wavenumber range of 400–4000 cm^{-1} using potassium bromide disks. A DSC Q100 (TA Instruments) differential scanning calorimeter (DSC) was used to determine the melting point and enthalpy of fusion under N_2 atmosphere at a heating rate of 10 K·min^{-1}. The uncertainty of DSC measurement was the same as that reported in our previous work.[22] An Elementar Vario EL element analyzer was used as the elemental analysis. ^{1}H NMR and ^{13}C NMR spectra were achieved by a Bruker ARX-400. An SDT Q600 (TA Instruments) thermogravimetric analyzer was applied as thermogravimetric analysis (TGA) at a heating rate of 10 K· min^{-1} in flowing N_2.

Synthesis of PAETE. PAETE was synthesized by the same method reported in our previous work.[20] To a dry chloroformic solution of $(C_6H_5O)_2P(O)Cl$, a dry chloroformic solution of ethanediamine and triethylamine (1:1:2.1 molar ratio) was added, dropwise for 1 h at 273 K. After stirring for 6 h, the solvent was removed at reduced pressure. Then, the recrystallization of the residual material was conducted by washing with cold distilled water from acetone to obtain PAETE as a white crystalline solid. The mass fraction purity of PAETE was about 0.99, which was determined by high-performance liquid chromatography made in Japan (HPLC; Shimadzu LC-10AT).

Characterization of PAETE. EI mass spectrum of PAETE is shown in Figure S1 of the Supporting Information. The intensity (%) *m*/*z* of PAETE is 525.2 (M + 1). Elemental analysis (%, calcd): C, 59.54% (60.37%); H, 5.00% (4.82%); N, 5.34% (5.28%). In Figure S2 of the Supporting Information, the infrared spectrum of PAETE contains characteristic absorptions at 3221 cm^{-1} for N—H stretching, 3058 cm^{-1} for aromatic —C═C—H stretching, 2944 and 2885 cm^{-1} for —HC—H stretching, ring carbon–carbon stretching vibrations at 1589, 1489, and 1469 cm^{-1}, 1191 cm^{-1} for the P═O stretching, 1025 cm^{-1} for the P—N stretching, 1250 cm^{-1} for the C—N stretching and 934 cm^{-1} for the P—O—aryl stretching. Figure S3 of the Supporting Information shows the ^{1}H NMR spectrum of PAETE. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.01 (m, 20H), 4.43–4.35 (t, 2H), 3.04–2.99 (m, 4H). Supporting Information Figure S4 presents ^{13}C NMR (400 Hz, $CDCl_3$) spectrum of PAETE. The chemical shifts of carbons with different chemical environments in PAETE structure are 42.95, 120.22, 129.46, 129.74 and 151.71, respectively.

Solubility Measurement. Equilibrium solubility determinations of the PAETE in chloroform, acetone, ethyl acetate, ethanol, benzene, tetrahydrofuran, methanol, acetonitrile, methyl acetate, and toluene were performed by the gravimetric method.[21] First, an excess of PAETE was put into a known mass of solvent in the equilibrium cell for each measurement. Second, the equilibrium cell was heated and stirred at a constant temperature for 8 h, long enough to achieve solid–liquid equilibrium in the equilibrium cell. The solution was settled for 5 h after the stirring was stopped. The clear upper saturated solution was withdrawn by a preheated injector with a cotton filter and then quickly transferred into a 5 cm^3 beaker with a cover to prevent solvent losing. The total mass was determined by the analytical balance immediately. The beaker must be placed into a vacuum oven at 308 K for 3 days to evaporate all solvents and then measure its mass. The mass of the samples was repeatedly weighed throughout the drying process to make sure no solvent remained. The masses were recorded when the solvents have completely evaporated. During the experiments, each experiment was repeated three times for the solvent with the same composition at each temperature, and then an average value is given. The mole fraction, x_1, was obtained from the equation as follows:

$$x_1 = \frac{w_1/M_1}{w_1/M_1 + w_2/M_2} \tag{1}$$

where w_1 and w_2 are the masses of the solute and solvent, respectively. M_1 and M_2 are molar masses of the solute and solvent, respectively.

■. RESULTS AND DISCUSSION

Evaluation of Pure Component Properties. On the basis of the results obtained by DSC and TGA analyses in Figures 3 and 4, the melting point (T_m) is 412.36 K with the expanded uncertainty of 0.26 K; the enthalpy of fusion ($\Delta_{fus}H$) for PAETE is 44.23 kJ·mol^{-1} with the expanded uncertainty of 0.35 kJ·mol^{-1}. TGA curves in Figure 4 illustrate that the decomposition of PAETE is one single step, and the char residue is about 27%, showing that the PAETE can be applied as intumescent flame retardant without the char-forming agent. $\Delta_{fus}S$ for PAETE calculated by eq 2 is 107.25 J/(mol·K).

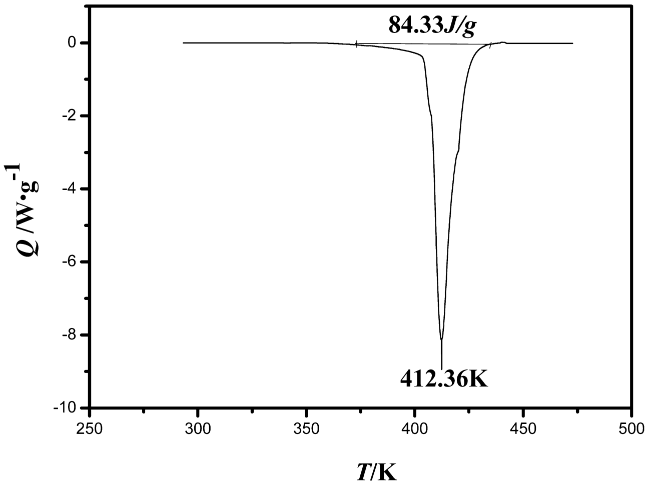

Figure 3. Experimental heat Q flow from DSC measurement of PAETE.

$$\Delta_{fus}S = \frac{\Delta_{fus}H}{T_m} \tag{2}$$

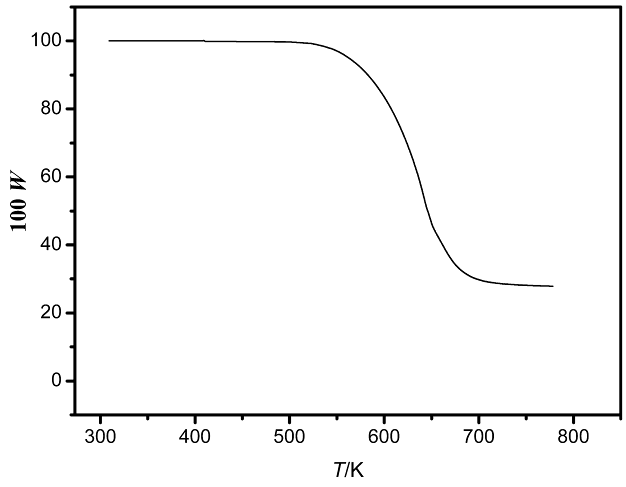

Figure 4. TGA thermograms of PAETE under N_2.

Solubility Data and Correlation Models. The mole fraction solubility of PAETE in chloroform, acetone, ethyl acetate, ethanol, benzene, tetrahydrofuran, methanol, acetonitrile, methyl acetate, and toluene at different temperature range are presented in Supporting Informaiton Table S1. On the basis of the values of x_1, T_m, and $\Delta_{fus}H$, the activity coefficients of PAETE in solid–liquid equilibrium can be obtained by eq 3 and are also shown in Supporting Informaiton Table S1

$$\ln \frac{1}{x_1\gamma_1} = \frac{\Delta_{fus}H}{RT_m}\left(\frac{T_m}{T} - 1\right) \tag{3}$$

where T and γ_1 represent the equilibrium temperature and the activity coefficients of the solute, respectively.

The plot of the mole-fraction solubility data of PAETE is shown in Figure 5. It can be seen that the solubility of PAETE in each of the given solvents is the function of temperature. It increases with the increase of temperature. However, there are

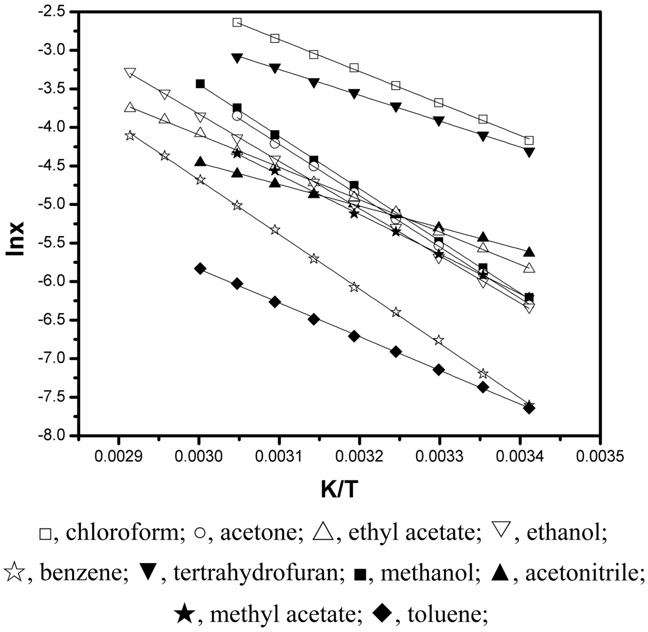

Figure 5. Mole fraction solubility (x) data of PAETE in selected solvents and modeling with the modified Apelblat model: □, chloroform; ○, acetone; △, ethyl acetate; ▽, ethanol; ☆, benzene; ▼, tetrahydrofuran; ■, methanol; ▲, acetonitrile; ★ methyl acetate; ◆, toluene;.

some differences in the increment of solubility with temperature in different solvents. At a given high temperature (above 318.15 K), the order of solubility of PAETE is as follows: chloroform > tetrahydrofuran > methanol > acetone > ethanol > ethyl acetate > methyl acetate > acetonitrile > benzene > toluene, but at low temperature (below 298.15 K), the order changes to chloroform > tetrahydrofuran> acetonitrile > ethyl acetate > acetone ≈ methyl acetate ≈ methanol ≈ ethanol > benzene > toluene. The solubility of PAETE in toluene is the lowest, whereas that in chloroform is the highest. The higher solubility in chloroform than those in the other solvents might be related to the strong electronegativity of the chlorine element. PAETE can be used as the proton donor or acceptor due to the existence of both NH and P═O groups. That the solubility in tetrahydrofuran is higher than that in alcohols shows that the PAETE is the proton donor. Accordingly, it may be that the hydrogen bonds between tetrahydrofuran and PAETE molecules contribute to the higher solubility of PAETE in tetrahydrofuran for ten solvents. It can be seen that tetrahydrofuran and chloroform are more appropriate solvents for the crystallization of PAETE from the solubility data. The two solvents are also suggested as the appropriate reaction solvents.

The solubility behaviors of the different solute in the same solvent were affected not only by the intermolecular interaction and the ability of the forming of a hydrogen bond between the solvent and the solute, but also by the molecular structure of the solute. PAETE has almost the similar molecular structure to the PAPBE,[20] but in the same selected solvents at the same condition, the solubility of PAETE is greater than that of PAPBE. For PAETE and PNBE,[22] the solubility of PNBE is greater than that of PAETE in the same selected solvents at the same condition. These phenomenona may be due to the rigid structure of the molecule of PAPBE and the molecular asymmetry of PNBE.

The solute−solvent intermolecular interaction can be estimated by the solute activity coefficients γ_i in a saturated solution. $\gamma_i < 1$ means that the solutions positively deviate from Raoult's law and repulsive interactions exist between PAETE and the solvent molecules. The systems of chloroform and tetrahydrofuran exhibit positive deviations from ideality, whereas the others exhibit negative deviations deviations from ideality.

The relationship between temperature and mole fraction solubility in the selected solvents can be calculated by the ideal model, the modified Apelblat equation and the λh equation.

The temperature dependence of the solubility for PAETE in the selected solvents can be represented by the following ideal model

$$\ln x_1 = A + \frac{B}{T} \tag{4}$$

where T represents the equilibrium temperature in kelvin; A and B refer to the parameters of the equation, respectively.

The correlation of the solubility and the temperature can be expressed by the modified Apelblat equation as follows:

$$\ln x_1 = A + \frac{B}{T} + C\ln(T) \tag{5}$$

Herein, A, B, and C refer to empirical constants. The values of A and B are the variation in the solution activity coefficient. The C value discloses the effect of temperature on the fusion enthalpy.

The experimental data of solubility can be described by the λh equation as follows

$$\ln\left[1 + \frac{\lambda(1 - x_1)}{x_1}\right] = \lambda h\left(\frac{1}{T} - \frac{1}{T_m}\right) \tag{6}$$

Herein, λ and h denote two model parameters. λ discloses the nonideality of the solution. h reflects the excess mixing enthalpy of solution.

The ideal model, modified Apelblat equation, and λh model parameters could be obtained via fitting the experimental solubility data and minimizing the following objective function:

$$F_{obj} = \sum_{j=1}^{N_p} (x_1^{\exp,i} - x_1^{cal,i})^2 \tag{7}$$

where $x_1^{\exp,i}$, $x_1^{cal,i}$, N_p refer to the experimental value, the calculated value, and the number of data points, respectively. The difference between the measured and calculated data was identified by the relative standard deviations (RSDs), defined by eq 9

$$\mathrm{RSD} = \left[\frac{1}{N - 1}\sum_{i=1}^{N}\left(\frac{x_i - x_i^{calcd}}{x_i}\right)^2\right]^{1/2} \tag{8}$$

where N denotes the total number of experimental points; x_i and x_i^{calcd} refer to the experimental solubility and the calculated solubility, respectively.

The corresponding results of the parameters and rmsds of the five models mentioned above are shown in Tables 2, 3, 4,

Table 2. Regressed Parameters and RSDs for the Ideal Model

solvent	A	B	RSD%
methanol	16.877	−6772.6	1.58
acetone	16.419	−6657.9	1.47
tetrahydrofuran	7.1522	−3354.7	1.26
ethyl acetate	8.5029	−4200.2	1.75
chloroform	9.9938	−4146.2	1.42
ethanol	14.572	−6132.8	1.84
benzene	16.532	−7071.5	1.94
toluene	7.3119	−4383.5	1.60
methyl acetate	11.346	−5148.6	1.59
acetonitrile	3.9404	−2800.2	1.16
overall			1.56

Table 3. Regressed Parameters and RSDs for the Modified Apelblat Equation

solvent	A	B	C	RSD%
methanol	−101.26	−1302.3	17.515	0.89
acetone	4.1156	−6092.0	1.8263	1.47
tetrahydrofuran	106.72	−7935.4	−14.779	0.90
ethyl acetate	12.080	−4367.9	−0.52913	1.75
chloroform	71.163	−6959.9	−9.0797	1.32
ethanol	−25.112	−4273.0	5.8707	1.73
benzene	64.835	−9336.2	−7.1455	1.77
toluene	−73.874	−625.38	12.037	1.31
methyl acetate	−81.456	−878.90	13.775	1.35
acetonitrile	33.021	−4146.3	−4.3117	1.12
overall				1.36

Table 4. Regressed Parameters and RSDs for the λh Equation

solvent	λ	h	RSD%
methanol	0.61682	11089	1.86
acetone	0.50725	13223	1.52
tetrahydrofuran	0.15234	22623	1.14
ethyl acetate	0.071191	59571	1.75
chloroform	0.40749	10555	1.35
ethanol	0.28911	21435	2.05
benzene	0.20405	34805	1.85
toluene	0.013401	327516	1.61
methyl acetate	0.12129	42691	1.63
acetonitrile	0.021744	129660	1.16
overall			1.59

respectively. From Tables 2–4, the calculated data of PAETE in the ten selected pure organic solvents agree well with the experimental data. The order of the overall RSDs of the three models mentioned above is as follows: the λ h eq (1.59%) > the ideal model (1.56%) > the modified Apelblat eq (1.36%). Compared with the ideal model and the λ h equation for these systems, the modified Apelblat equation is more accurate because the modified Apelblat equation was proposed by taking the complex formed by the solute and solvent molecules into account. The parameter λ is approximately considered as the mean association number of solute molecules in solution for the λ h equation. In Table 4, it can be seen that there is no obvious association when the PAETE dissolves in these solvents.

Evaluation of the Solubility Parameter δ_1 of PAETE. The Scatchard–Hildebrand activity coefficient model, used to describe the binary system, can be shown as follows:

$$RT\ln \gamma_1 = V_1\varphi_2^{\,2}(\delta_1 - \delta_2)^2 \tag{9}$$

$$\varphi_2 = \frac{x_2V_2}{x_2V_2 + x_1V_1} \tag{10}$$

Here, δ_1 (δ_2), ϕ_2, and V_1 (V_2), denote the solubility parameters of the solute (solvent), the volume fraction of solvent in the binary mixture, the molar volume of the subcooled liquid of pure solid solute (solvent), respectively.

The solubility parameter δ_1 of PAETE was obtained from the slope of the equation as follows and can be rearranged from Scatchard–Hildebrand model

$$Y = \frac{RT\ln \gamma_1}{V_1\varphi_2^{\,2}} - \delta_2^{\,2} = -2\delta_1\delta_2 + \delta_1^{\,2} \tag{11}$$

Based on the above equation, the linear dependence between Y and δ_2 at 298.15 K is presented in Figure 6. The molar volume of PAETE is estimated to be 401.00 $cm^3 \cdot mol^{-1}$ by the advanced chemistry development (ACD/Laboratories) Software V11.02 at 293.15 K (press: 760 Torr) and is listed in Table 5. The solubility parameters of the solvent can be gotten from the literature[22] and are also listed in Table 5. The obtained parameter δ_1 of PAPBE is 23.27$(J \cdot cm^{-3})^{1/2}$ and is also showed in Table 5.

Thermodynamic Properties for the Solution. According to the modified Apelblat equation, the dissolution enthalpy ΔH_d and the dissolution entropy ΔS_d at saturation can be calculated by the equations as follows:

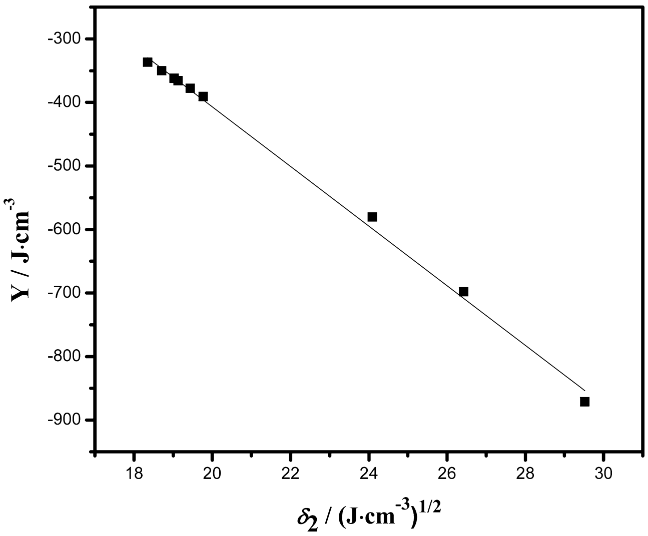

Figure 6. Residual function Y for PAETE versus solvent solubility parameters δ_2. ■, experiment data; —, regression line to experimental data, $Y = -46.939\delta_2 + 531.9$ ($R^2 = 0.9971$).

Table 5. Solubility Parameter, δ, for Selected Solvents and PAETE

solvent	δ_i	10^6V_i
	$(J \cdot cm^{-3})^{1/2}$	$m^3 \cdot mol^{-1}$
methanol	29.52	40.70
ethanol	26.42	58.52
methyl acetate	19.44	81.50
acetonitrile	24.09	52.68
ethyl acetate	18.35	98.59
tetrahydrofuran	19.13	81.94
chloroform	19.03	80.66
benzene	18.71	89.48
toluene	18.35	106.60
acetone	19.77	73.93
PAETE	23.27	401.00

$$\Delta H_d = RT\left[\frac{\partial \ln x_1}{\partial \ln T}\right] = R(-B + CT) \tag{12}$$

$$\Delta S_d = R\left[\frac{\partial \ln x_1}{\partial \ln T} + \ln x_1\right] = R[A + C(1 + \ln T)] \tag{13}$$

The values of ΔH_d and ΔS_d of solutions at measured solubility points were calculated and listed in Supporting Informaiton Table S2. The calculated values $\Delta H_d > 0$ means that the dissolving process of PAETE is endothermic. Additionally, the entropy increases in the dissolving process for the experimental temperature range. The endothermic process of dissolution indicates that the interactions between PAETE molecule and solvent molecules are stronger than those between the solvent molecules. The positive ΔH_d and ΔS_d in the systems show that the processes involved in dissolving PAETE in the selected solvents are endothermic, entropy-driven, and not spontaneous.[23]

■ CONCLUSIONS

The PAETE was synthesized in the work. The solubility data of PAETE in chloroform, acetone, ethyl acetate, ethanol, benzene, tetrahydrofuran, methanol, acetonitrile, methyl acetate, and

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toluene were determined at different temperatures. The chloroform, acetone, ethyl acetate, ethanol, benzene, tetrahydrofuran, methanol, acetonitrile, methyl acetate, and toluene and the melting temperature were measured by DSC. At a given high temperature (above 318.15 K), the order of solubility for PAETE is as follows: chloroform > tetrahydrofuran > methanol > acetone > ethanol > ethyl acetate > methyl acetate > acetonitrile > benzene > toluene, and at low temperature (below 298.15 K) the order changes to chloroform > tetrahydrofuran> acetonitrile > ethyl acetate > acetone ≈ methyl acetate ≈ methanol ≈ ethanol > benzene > toluene. The experimental data were correlated with the modified Apelblat equation, Ideal model, Scatchard−Hildebrand model, and Buchowski−Ksiazczak model. The results show that, compared with the other models, the modified Apelblat equation is more suitable in determining the solubility of PAETE. Based on the modified Apelblat model, the dissolution enthalpy and entropy of PAETE are determined in different solvents at saturation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

MS spectra of PAETE, IR spectra of PAETE, ^{1}H NMR spectra of PAETE, ^{13}C NMR spectra of PAETE, mole fraction solubilities and activity coefficients of PAETE, and calculated values for dissolution enthalpy and dissolution entropy of PAETE in different pure solvents. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/je5010565.

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Notes

The authors declare no competing financial interest.

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