Solubilities of Phosphorus-Containing Compounds in Selected Solvents

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Phosphorus-containing flame retardants (FRs) 3,9-dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5.5]-undecane-3,9-dioxide (dihydroxy-TDUD), 3,9-diphenoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5.5]-undecane-3,9-dioxide (diphenoxy-TDUD), hydroxymethylphenylphosphinic acid (HMPPA), 2-carboxyethylphenylphosphinic acid (CEPPA), tri(*p*-methoxyphenyl)phosphine (TMOPP), and tri(*p*-methoxyphenyl)phosphine oxide (TMOPPO) were characterized by elemental analysis, infrared spectroscopy, ^{1}H and ^{31}P nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Using a static analytical method, the solubilities of solutes in selected solvents were measured and correlated with an empirical equation. The estimated uncertainty of all of the solubility values based on error analysis and repeated observations was within 2.0 %.

Introduction

Flame retardants (FRs) based on organic phosphorus compounds are known to be one of the most promising candidates that can replace the halogen-based FRs.[1] These FRs are believed to be environmentally benign because they can generate less toxic gases and smoke than halogen-containing compounds.[2−4] The organic phosphorus FRs can be used in polymers to improve the fire resistance of the composites to meet the requirements in electrical engineering and the electronic, transportation, and building industries.[5,6]

Cyclic phosphorus compounds are particularly thermally stable and useful as FRs for polymeric materials.[7,8] The FRs include different derivatives from 2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5.5]undecane-3,9-dioxide (hereafter named as TDUD). 3,9-Dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5.5]-undecane-3,9-dioxide[9] (hereafter abbreviated as dihydroxy-TDUD, CAS RN 947-28-4) was synthesized from 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide. 3,9-Diphenoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5.5]-undecane-3,9-dioxide[10,11] (hereafter abbreviated as diphenoxy-TDUD, CAS RN 55120-33-7) was prepared from pentaerythritol and phenyl dichlorophosphate in the presence of pyridine.[10] Dihydroxy-TDUD and diphenoxy-TDUD were used in the plastics formulating art as blowing agents, char-forming additives, and so forth.[12−14]

Phenylphosphine and phenylphosphinic acid based derivatives are widely used as fire retardants for poly(ethylene terephthalate) (PET).[15−17] Hydroxymethylphenylphosphinic acid (HMPPA, CAS RN 61451-78-3) is a bifunctional copolymerible phosphorus monomer, and it can be synthesized from phenylphosphinic acid (PPA) and paraformaldehyde as disclosed by a U.S. patent.[17] 2-Carboxyethylphenylphosphinic acid (CEPPA, CAS RN 14657-64-8) is also a bifunctional copolymerizable phosphorus monomer as disclosed by a U.S. patent.[18,19] Both HMPPA and CEPPA can be polycondensed with ethylene glycol and terephthalic acid to produce FR-PET[17,20] and renders the alternated PET and the resulting plastics and fibers with good fire-resistance properties.

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The application of catalyst-binding phosphorus ligands is attracting more and more attention for the nature of enhancement of interfacial catalysis in a biphasic system.[21−23] In these phosphorus ligands, triphenylphosphine (TPP) and tri(*p*-hydroxyphenyl)phosphine oxide (THPPO) are the two most useful compounds. Tri(*p*-methoxyphenyl)phosphine (TMOPP, CAS RN 855-38-9) and tri(*p*-methoxyphenyl)phosphine oxide (TMOPPO, CAS RN 803-17-8) are the intermediates for preparation of THPPO.

Upon thermal decomposition of the phosphorus-containing FRs during the burning of the polymer composite, highly cross-linked P−C products which remain in the char and contribute to the fire retardancy may be produced. However, a high thermal stability will be required because the polymer composites are usually processed under high temperatures. Therefore, a high purity will be required for the FRs because the decomposition of impurities will be undesirable during the processing. For the preparation and purification of the products it is very important to know the solubilities of these FRs as a function of temperature and solvent composition in different solvents so that the condition of crystallization can be established and the lost quantity of FRs during the process can be calculated. To model these processes, the activity coefficient data are used to describe the solid−liquid equilibrium. However, only a few solubility data for these compounds were published.[9,24,25] In this study, dihydroxy-TDUD, diphenoxy-TDUD, HMPPA, CEPPA, TMOPP, and TMOPPO were characterized, and their solubilities in selected solvents were measured.

Experimental Section

Materials. Dihydroxy-TDUD, diphenoxy-TDUD, HMPPA, and CEPPA were provided by Shandong Wan Zhao Co., Ltd. TMOPP and TMOPPO were prepared according to literature[26,27] in this work. The formulas of these compounds are shown in Figures 1 and 2. All of the solvents were analytical grade reagents, which were purchased from Beijing Chemical Factory. They were used without further purification. The basic physical properties and the mass fraction purities for the organic solvents used in this work are listed in Table 1. Water was deionized before use.

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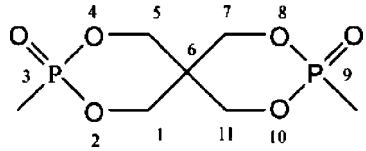

Figure 1. 2,4,8,10-Tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide (TDUD).

Apparatus and Procedure. The elemental analysis, ^{1}H and ^{31}P NMR spectra, and the IR spectra apparatus were the same as those used before.[29] The melting temperature and enthalpy of fusion of dihydroxy-TDUD, diphenoxy-TDUD, HMPPA, CEPPA, TMOPP, and TMOPPO were determined with a DSC Q100 differential scanning calorimeter (DSC) in flowing nitrogen at a heating rate of 10 K·min^{-1}, with thermogravimetric analysis (TGA) results of diphenoxy-TDUD and HMPPA, from (298.15 to 873.15) K at a scanning rate of 10 K·min^{-1} in flowing nitrogen.

The setup for the solubility measurement was the same as that described in the literature.[28,29] Figure 3 shows the schematic diagram of the experimental apparatus. A jacketed equilibrium cell was used for the solubility measurements with a working volume of 120 mL (without the jacket part) and a magnetic stirrer. A thermocouple is immersed into the solution of the measuring flask, and the uncertainty of the thermocouple is 0.01 K. A circulating water bath was used with a thermostat (type 50 L), which is capable of maintaining the temperature within ± 0.05 K. An analytical balance with an uncertainty of ± 0.1 mg was used during the mass measurements.

Characterization of Dihydroxy-TDUD. Elemental analysis (%, calcd): C, 23.26 % (23.08 %); H, 3.79 % (3.85 %). ^{1}H NMR (D_2O, ppm): δ = 4.41−4.67 (d, 8H). ^{31}P NMR (D_2O, ppm): δ = −2.263. IR (KBr): 1305 (P═O); 855 ($P(OCH_2)_2C$); 1024 (P−O−C); 1000 (P−OH) cm^{-1} [lit.[21,30] 1307 (P═O); 855.2 ($P(OCH_2)_2C$); 1024.5 (P−O−C); 1000 (P−OH) cm^{-1}]. The results show a high purity of the dihydroxy-TDUD sample as certificated by the specification. The results of DSC measurements of dihydroxy-TDUD are shown in the Supporting Information (Figure a). The melting temperature of dihydroxy-TDUD was 583.72 K [lit.[21,30] (582.15 to 585.15) K, lit.[31] 587.15 K, lit.[32] 581.15 K].

Characterization of Diphenoxy-TDUD. Elemental analysis (%, calcd): C, 49.64 % (49.52 %); H, 4.54 % (4.41 %). ^{1}H NMR (DMSO-d_6, ppm): δ = 7.27−7.47 (lit.[10] 7.30−7.50) (m, 10H); δ = 4.81−4.83 (lit.[10] 4.82) (m, 2H); δ = 4.67−4.74 (lit.[10] 4.70) (m, 2H); δ = 4.46−4.50 (lit.[10] 4.48) (m, 2H); δ = 4.41−4.45 (lit.[10] 4.42) (m, 2H). ^{31}P NMR (DMSO-d_6, ppm): δ = −7.99 (lit.[10] −7.80 ppm, s). IR (KBr, cm^{-1}): 1298.1 (P═O); 1154.7, 1030.6 (P−O−C), 1197.8, 948.3 (P−O−Ph); 1593.2−2000 (Ph−C), 763.6, 689.4 (Ph−), 911.6, 863.5, 801.6, 731.0 ($P(OCH_2)_2C$) [lit.[33] 1150, 1040 (P−O−C), 1190, 953 (P−O−Ph); 1600−2000 (Ph−C), 766, 688 (Ph−), 922, 851, 775, 685 ($P(OCH_2)_2$ C)]. The results show a high purity of the diphenoxy-TDUD sample as certificated by the specification. The results of DSC measurements of diphenoxy-TDUD were shown in the Supporting Information (Figure b). The melting temperature of diphenoxy-TDUD was 469.58 K [lit.[10] 472.65 K, lit.[34] (470.15 to 472.15) K].

Characterization of HMPPA. Elemental analysis (%, calcd): C, 41.39 % (41.86 %); H, 4.83 % (5.23 %). ^{1}H NMR (D_2O, ppm): δ = 7.41−7.67 (m, 5H, Ar−H); δ = 3.82−3.83 (2H, d,

Table 1. Mass Fraction Purity (ω), Density (ρ), and Refractive Index (n_D) for the Organic Solvents Used in This Work at T/K = 293.15[a]

solvent	ω/%	ρ / kg·m^{-3}	n_D
methanol	99.5	792	1.3301
ethanol	99.7	790	1.3660
butanone	99.5	805	1.3788
dichloromethane	99.5	1321	1.4237
toluene	99.5	866	1.4967
acetonitrile	99.8	783	1.3430
ethyl acetate	99.5	899	1.3719
chloroform	99.5	1484	1.4476
diethyl ether	99.5	714	1.3497
1,4-dioxane	99.0	1034	1.4175
pyridine	99.5	983	1.5095
tetrahydrofuran	99.0	985	1.4050
2-ethoxyethanol	99.5	929	1.4065
cyclohexane	99.5	779	1.4266
acetic acid	99.8	1049	1.3716

[a] Density and refetractive index data were taken from ref 36.

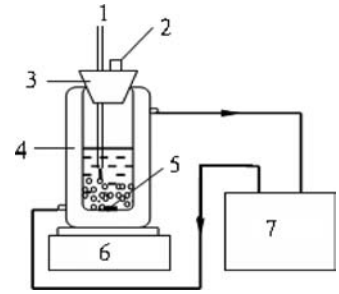

Figure 3. Schematic diagram of the experimental aparatus: 1, thermocouple; 2, sample gauge; 3, rubber plug; 4, jacket; 5, equilibrium cell; 6, magnetic stirrer; 7, water cycling bath.

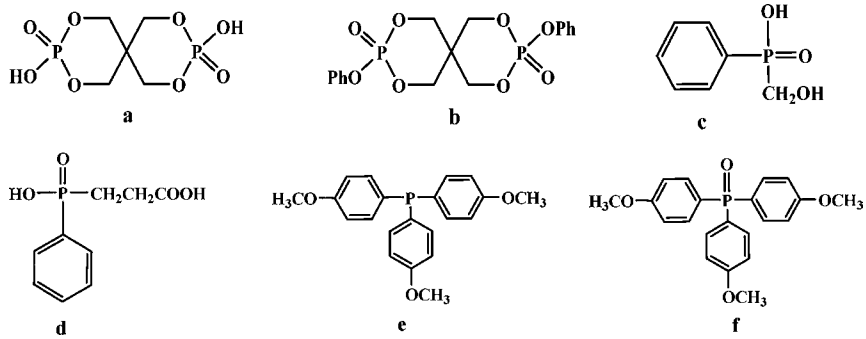

Figure 2. Formula of the organic phosphorus compounds related in this work: (a) 3,9-dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5.5]-undecane-3,9-dioxide (dihydroxy-TDUD), (b) 3,9-diphenoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5.5]-undecane-3,9-dioxide (diphenoxy-TDUD), (c) hydroxymethylphenylphosphinic acid (HMPPA), (d) 2-carboxyethylphenylphosphinic acid (CEPPA), (e) tri(*p*-methoxyphenyl)phosphine (TMOPP), (f) tri(*p*-methoxyphenyl)phosphine oxide (TMOPPO).

Table 2. Compound Name, Abbreviation, Melting Temperature (K), and Melting Enthalpy (kJ·mol^{-1}) of the Organic Phosphorus Compounds Measured in This Work

compound name	abbreviation	melting temperature K	melting enthalpy kJ·mol^{-1}
3,9-dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5.5]-undecane-3,9-dioxide	dihydroxy-TDUD	583.72	22.46
3,9-diphenoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5.5]-undecane-3,9-dioxide	diphenoxy-TDUD	469.58	36.46
hydroxymethylphenylphosphinic acid	HMPPA	413.40	27.16
2-carboxyethylphenylphosphinic acid	CEPPA	432.66	33.58
tri(*p*-methoxyphenyl)phosphine	TMOPP	403.82	25.67
tri(*p*-methoxyphenyl)phosphine oxide	TMOPPO	417.84	28.52

$-CH_2$). ^{31}P NMR (D_2O, ppm): $\delta = 35.07$. IR (KBr): 3469.4 (O—H) (alcoholic); 1591.4 (O—H) (acid); 1439.3 (Ar—P); 1156.9 (P═O) cm^{-1} [lit.[24,30] 3469.35 (O—H) (alcoholic); 1591.40 (O—H) (acid); 1439.29 (Ar—P); 1156.95 (P═O) cm^{-1}]. These results show a high purity of the HMPPA sample as certificated by the specification. The results of DSC measurements of HMPPA are shown in the Supporting Information (Figure c). The melting temperature of HMPPA was 413.4 K [lit.[30] (410.15 to 413.15) K; lit.[24] (411.15 to 412.15) K].

Characterization of CEPPA. Elemental analysis (%, calcd): C, 50.39 % (50.47 %); H, 4.73 % (5.14 %). ^{1}H NMR (DMSO, ppm): $\delta = 11.521$ (2H, s, O—H); $\delta = 7.507-7.722$ (m, 5H, Ar—H); $\delta = 1.999-2.505$ (4H, m, $-CH_2CH_2-$) [lit.[25,30] $\delta = 13.42$ (1H, s, O—H); $\delta = 7.62-8.14$ (m, 5H, Ar—H); $\delta = 3.02-4.23$ (4H, m, $-CH_2CH_2-$)]. ^{31}P NMR (DMSO, ppm): $\delta = 35.79$. IR (KBr): 3310.2 (O—H); 1720.4 (C═O); 1603.3, 1430.1 (Ar—P); 1150.2 (P═O) cm^{-1} [lit.[25,30] 3310 (O—H), 1720 (C═O) 1603; 1430 (Ar—P); 1150 (P═O) cm^{-1}]. On the basis of the above analysis, the purity of CEPPA used in this work was higher than 99.0 %. The results of DSC measurements of CEPPA are shown in the Supporting Information (Figure d). The melting temperature of CEPPA was 432.66 K (lit.[25,30] 431.15 K).

Characterization of TMOPP. Elemental analysis (%, calcd): C, 68.39 % (68.41 %); H, 5.73 % (5.71 %). ^{1}H NMR (DMSO, ppm): $\delta = 6.9195-7.7658$ (m, 4H, Ar—H); $\delta = 3.8058$ (3H, s, O—CH_3) [lit.[24] (200 MHz, $CDCl_3$) (ppm) $\delta = 6.921-7.763$ (4H, m, Ar—H); 3.806 (3H, s, O—CH_3)]. ^{31}P NMR (DMSO, ppm): $\delta = 25.02$. IR (KBr): 1244.18 (C—O), 1438.78 (Ar—P), 1496.66, 1564.64, 1590.59 (C═C) cm^{-1}. These results show a high purity of the TMOPP sample as certificated by the specification. The results of DSC measurements of TMOPPO are shown in the Supporting Information (Figure e). The melting temperature of TMOPP was 403.82 K [lit.[24] (403.15 to 404.15) K].

Characterization of TMOPPO. TMOPPO was prepared according to literature.[27] Elemental analysis (%, calcd): C, 68.39 % (68.41 %); H, 5.73 % (5.71 %). ^{1}H NMR (DMSO, ppm): $\delta = 7.0695-7.5058$ (m, 4H, Ar—H). $\delta = 3.8079$ (3H, s, O—CH_3) [lit.[24] (200 MHz, $CDCl_3$) (ppm) $\delta = 6.881-7.534$ (4H, m, Ar—H), 3.770 (3H, s, O—CH_3)]. ^{31}P NMR (DMSO, ppm): $\delta = 25.12$. IR (KBr): 1254.18 (C—O), 1443.25 (Ar—P), 1503.05, 1569.34, 1597.36 (C═C), 1179.73 (P═O) cm^{-1}. On the basis of the above analysis, the purity of TMOPPO used in this work was higher than 99.0 %. The results of DSC measurements of TMOPPO are shown in the Supporting Information (Figure f). The melting temperature of TMOPPO was 417.84 K [lit.[24] (416.15 to 417.15) K].

Solubility Measurements. The solubilities were measured by a gravimetric method.[28] For each measurement, an excess mass of solute was added to a known mass of solvent. Then the equilibrium cell was heated to a constant temperature with continuous stirring. After at least 2 h (the temperature of the water bath approached a constant value, then the actual value of temperature was recorded), the stirring was stopped, and the solution was kept still until it was clear. A preheated on—off injector withdrew 2 mL of the clear upper portion of the solution to another previously weighed measuring vial (m_0). The vial was quickly and tightly closed and weighed (m_1) to determine the mass of the sample ($m_1 - m_0$). Then the vial was uncovered with a piece of filter paper to prevent dust contamination. After the solvent in the vial had completely evaporated, the vial was dried and reweighed (m_2) to determine the mass of the constant residue solid ($m_2 - m_0$). Thus, the solid concentration of the sample solution in mole fraction, x, could be determined from eq 1[28]

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

where M_1 is the molar mass of solute and M_2 is the molar mass of solvent.

Different dissolution times were tested to determine a suitable equilibrium time. It was found that 2 h was enough for solute in solvent 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 maximum standard deviation of each triplicate data is 0.26 %, and the minimum is 0.12 %. The estimated relative uncertainty of the solubility values based on error analysis and repeated observations was within 0.02.

Table 3. Comparison of Thermal Degradation and Char-Forming Properties of Phosphorus-Containing FRs

compound	T_0/K	$T_{5\,\%}$/K	$T_{50\,\%}$/K	CR/%
dihydroxy-TDUD[30]	553.15	603.15	768.15	30
diphenoxy-TDUD	538.15	596.15	663.15	28
HMPPA[30]	488.15	508.15	746.15	11
CEPPA[30]	463.15	485.15	538.15	3

Results and Discussion

DSC and TGA Analysis. The melting temperature and melting enthalpy of the organic phosphorus compounds measured by DSC are listed in Table 2. Table 3 shows the comparison of the thermal stability data of diphenoxy-TDUD with the data of dihydroxy-TDUD, CEPPA, and HMPPA published in our previous paper.[30] In Table 3, T_o denotes the temperature of the onset of decomposition, and $T_{5\,\%}$ and $T_{50\,\%}$ denote the temperatures at weight loss of 5 % and 50 %, in nitrogen atmosphere, respectively. From Table 3 it can be seen that both dihydroxy-TDUD and diphenoxy-TDUD show more thermal stability than the other compounds. The initial decomposition temperature of diphenoxy-TDUD was around 577.32 K. The temperature of diphenoxy-TDUD at 71.56 % mass loss was 670.35 K, and the char yield at 873.15 K was 28.44 %. The results show that there is a single decomposition step for

Table 4. Mole Fraction Solubilities (x) and Activity Coefficients (γ) of Solute in the Selected Solvents

solute	solvent	T/K	x	γ	$(x - x^{calcd})/x$	T/K	x	γ	$(x - x^{calcd})/x$
dihydroxy-TDUD	acetone[9]	295.75	0.0040	2.700	0.018	307.95	0.0049	3.167	0.025
		297.55	0.0041	2.767	0.008	309.15	0.0050	3.211	0.006
		299.85	0.0043	2.855	0.002	313.35	0.0053	3.380	0.018
		301.45	0.0044	2.913	0.001	317.15	0.0057	3.536	0.019
		303.15	0.0045	2.982	0.012	319.15	0.0058	3.621	0.010
		305.35	0.0047	3.065	0.005				
	butanone	293.16	0.0006	15.619	0.015	318.18	0.0013	16.212	0.006
		298.17	0.0007	15.822	0.008	323.16	0.0015	16.211	0.011
		303.16	0.0008	16.468	−0.026	328.16	0.0016	16.669	−0.012
		308.17	0.0010	16.459	−0.020	333.17	0.0018	16.449	0.007
		313.16	0.0011	16.082	0.001				
	chloroform	293.16	0.00046	21.631	0.023	318.18	0.00114	17.997	−0.012
		298.17	0.00054	21.639	−0.024	323.16	0.00137	17.120	−0.001
		303.16	0.00067	20.002	0.010	328.16	0.00163	16.338	0.007
		308.17	0.00081	19.153	0.009	333.17	0.00192	15.655	0.013
		313.16	0.00094	18.996	−0.025	338.15	0.00222	15.301	−0.001
	acetonitrile[9]	309.35	0.0006	27.314	0.078	321.55	0.0017	13.049	0.020
		311.25	0.0007	23.940	0.060	323.25	0.0020	11.908	0.030
		313.25	0.0009	20.187	0.009	325.75	0.0025	10.209	0.016
		315.45	0.0010	18.346	0.026	327.45	0.0028	9.2599	0.016
		317.35	0.0012	16.736	0.033	329.45	0.0032	8.661	0.066
		319.55	0.0015	14.103	0.014	331.55	0.0038	7.691	0.069
	dichloromethane	291.16	0.00027	35.169	−0.005	303.19	0.00045	30.398	0.0019
		295.18	0.00032	33.086	0.009	305.2	0.00048	29.831	−0.002
		299.16	0.00037	32.014	−0.005	309.15	0.00056	28.508	0.001
	diethyl ether	291.16	0.00053	17.699	−0.022	303.19	0.00124	10.893	0.004
		295.18	0.00073	14.592	0.014	305.20	0.00140	10.226	−0.006
		299.16	0.00096	12.454	0.020				
	1,4-dioxane	293.16	0.00025	40.254	0.012	318.18	0.00045	45.894	0.012
		298.17	0.00028	42.202	−0.007	323.16	0.00050	46.934	0.013
		303.16	0.00031	43.805	−0.017	328.16	0.00055	48.024	0.013
		308.17	0.00035	44.641	−0.010	333.17	0.00060	50.501	−0.015
		313.16	0.00040	45.115	0.005	338.15	0.00066	51.232	−0.007
	ethyl acetate	293.16	0.00078	12.846	0.002	318.18	0.00177	11.607	0.008
		298.17	0.00092	12.678	−0.006	323.16	0.00204	11.503	−0.001
		303.16	0.00109	12.375	−0.001	328.16	0.00229	11.626	−0.029
		308.17	0.00129	12.082	0.004	333.17	0.00271	11.144	−0.002
		313.16	0.00152	11.795	0.009	338.15	0.00315	10.781	0.015
	acetic acid	293.16	0.00017	58.022	−0.019	318.18	0.00048	42.928	0.017
		298.17	0.00022	53.631	0.003	323.16	0.00057	41.325	0.007
		303.16	0.00026	51.449	−0.010	328.16	0.00067	39.652	0.002
		308.17	0.00032	48.138	0.004	333.17	0.00078	38.790	−0.022
		313.16	0.00040	44.763	0.025	338.15	0.00092	36.675	−0.009
	benzene	293.16	0.00031	32.806	−0.010	318.18	0.00088	23.402	0.022
		298.17	0.00038	30.274	0.005	323.16	0.00103	22.657	−0.000
		303.16	0.00047	28.916	−0.012	328.16	0.00123	21.725	−0.012
		308.17	0.00059	26.369	0.019	333.17	0.00146	20.588	−0.010
		313.16	0.00070	25.507	−0.006	338.15	0.00176	19.289	0.005
	toluene	293.16	0.00046	21.547	−0.017	318.18	0.00122	16.861	−0.024
		298.17	0.00059	19.569	0.025	323.16	0.00146	15.758	−0.002
		303.16	0.00071	18.975	0.005	328.16	0.00176	15.086	−0.003
		308.17	0.00086	18.138	−0.001	333.17	0.00209	14.391	0.002
		313.16	0.00104	17.208	0.003	338.15	0.00248	13.678	0.011
	cyclohexane	293.16	0.00016	60.543	0.004	318.18	0.00032	63.388	0.001
		298.17	0.00019	61.612	−0.004	323.16	0.00037	63.112	0.013
		303.16	0.00022	61.896	0.000	328.16	0.00041	64.317	0.002
		308.17	0.00025	62.569	−0.002	333.15	0.00046	65.311	−0.006
		313.16	0.00028	63.367	−0.007	338.15	0.00052	65.409	−0.001
diphenoxy-TDUD	acetone	293.17	0.00237	1.533	−0.002	313.24	0.00421	2.246	0.001
		298.16	0.00275	1.696	−0.002	318.07	0.00479	2.445	0.001
		303.26	0.00322	1.855	0.007	323.25	0.00542	2.693	−0.007
		308.57	0.00371	2.068	−0.002	328.36	0.00622	2.898	0.004
	butanone	293.15	0.00399	0.909	0.011	313.16	0.00638	1.479	−0.013
		298.16	0.00446	1.046	−0.007	318.19	0.00733	1.605	0.012
		303.17	0.00506	1.174	−0.005	323.15	0.00809	1.796	0.002
		308.18	0.00575	1.309	−0.000				
	chloroform	293.25	0.00224	1.625	−0.012	318.25	0.01062	1.110	−0.008
		298.17	0.00319	1.459	0.014	323.04	0.01386	1.045	−0.012
		303.25	0.00436	1.367	0.000	328.35	0.01882	0.958	0.006
		308.56	0.00611	1.253	0.009	333.13	0.02336	0.934	−0.031
		313.25	0.00806	1.175	0.006				
	tetrahydrofuran	293.53	0.00524	0.705	0.000	313.35	0.00996	0.954	0.003
		298.16	0.00615	0.758	0.004	318.31	0.01154	1.024	0.003
		303.49	0.00727	0.830	−0.004	323.35	0.01334	1.098	0.002
		308.25	0.00845	0.893	−0.005	328.46	0.01533	1.180	−0.002

Table 4. Continued

solute	solvent	T/K	x	γ	$(x - x^{calcd})/x$	T/K	x	γ	$(x - x^{calcd})/x$
	pyridine	293.43	0.00813	0.452	0.000	313.35	0.01141	0.833	0.007
		298.35	0.00885	0.532	−0.001	318.31	0.01231	0.960	0.006
		303.51	0.00964	0.627	−0.003	323.35	0.01316	1.113	−0.002
		308.35	0.01045	0.725	−0.002	328.45	0.01414	1.279	−0.004
	dichloromethane	293.16	0.00103	3.542	0.007	303.86	0.00146	4.229	−0.010
		299.22	0.00127	3.894	0.003	307.60	0.00167	4.396	0.006
	diethyl ether	291.95	0.00179	1.865	−0.002	299.26	0.00234	2.120	−0.006
		295.37	0.00204	1.955	0.006	303.55	0.00275	2.254	0.002
	1,4-dioxane	293.26	0.00132	2.773	0.013	318.36	0.00294	4.036	0.015
		298.45	0.00152	3.110	−0.019	323.35	0.00335	4.381	0.001
		303.26	0.00181	3.321	−0.010	328.23	0.00383	4.688	−0.002
		308.67	0.00214	3.599	−0.009	333.36	0.00438	5.027	−0.006
		313.24	0.00253	3.745	0.018	338.25	0.00499	5.330	−0.003
	water	293.18	0.00014	25.496	0.007	338.36	0.00148	14.931	0.010
		298.77	0.00020	23.881	−0.010	343.26	0.00188	14.227	0.002
		308.37	0.00030	21.691	0.001	348.35	0.00241	13.388	0.009
		313.56	0.00037	20.709	−0.002	353.24	0.00295	13.157	−0.029
		318.25	0.00050	19.356	−0.004	358.25	0.00371	12.471	−0.027
		323.24	0.00064	18.391	−0.014	363.36	0.00477	11.508	0.003
		328.43	0.00086	16.888	0.009	368.25	0.00591	11.052	−0.008
		333.45	0.00116	15.579	0.026				
	ethyl acetate	293.25	0.00107	3.4133	0.004	318.35	0.00281	4.211	0.011
		298.46	0.00132	3.580	0.005	323.35	0.00334	4.388	0.009
		303.27	0.00158	3.775	−0.006	328.26	0.00392	4.580	0.003
		308.66	0.00193	3.982	−0.013	333.37	0.00459	4.802	−0.007
		313.27	0.00230	4.119	−0.009	338.26	0.00539	4.941	−0.001
	benzene	293.17	0.00119	3.062	0.002	323.24	0.00136	10.745	0.006
		298.16	0.00121	3.844	0.001	328.43	0.00138	13.069	0.004
		304.76	0.00124	5.162	−0.006	333.46	0.00141	15.659	0.006
		308.37	0.00127	5.997	−0.003	338.34	0.00143	18.697	0.000
		313.55	0.00129	7.425	−0.004	343.26	0.00145	22.175	−0.002
		318.26	0.00133	8.900	0.002	348.35	0.00147	26.381	−0.007
	acetonitrile	293.31	0.00156	2.341	0.017	323.36	0.00438	3.348	−0.027
		298.17	0.00187	2.494	0.009	328.27	0.00522	3.442	−0.008
		303.26	0.00223	2.682	−0.008	333.35	0.00614	3.583	−0.002
		308.57	0.00273	2.804	0.004	338.56	0.00738	3.651	0.024
		313.35	0.00318	2.987	−0.010	343.44	0.00841	3.852	0.013
		318.24	0.00375	3.147	−0.014				
	toluene	298.17	0.00115	4.055	0.013	323.37	0.00352	4.171	−0.005
		303.25	0.00143	4.173	−0.013	328.25	0.00424	4.233	−0.018
		308.56	0.00185	4.136	−0.002	333.34	0.00536	4.105	0.015
		313.34	0.00229	4.157	−0.005	338.56	0.00646	4.171	0.001
		318.26	0.00285	4.145	−0.000	343.45	0.00781	4.155	0.006
	methanol	293.24	0.00271	1.344	0.008	313.23	0.00401	2.360	−0.003
		298.24	0.00298	1.573	−0.004	318.16	0.00443	2.653	0.005
		303.16	0.00329	1.808	−0.006	323.15	0.00483	3.008	0.002
		308.17	0.00365	2.061	−0.001				
	ethanol	298.16	0.00136	3.423	0.005	323.16	0.00288	5.043	0.002
		303.15	0.00157	3.775	−0.011	328.17	0.00329	5.443	−0.004
		308.16	0.00187	4.023	0.005	333.16	0.00383	5.712	0.015
		313.14	0.00218	4.328	0.008	338.16	0.00426	6.229	−0.006
		318.16	0.00246	4.769	−0.014	343.15	0.00485	6.611	−0.002
	2-ethoxyethanol	293.24	0.00325	1.122	0.022	333.16	0.01224	1.785	0.004
		298.24	0.00392	1.193	0.022	338.17	0.01396	1.902	−0.011
		303.16	0.00455	1.306	−0.008	343.16	0.01608	1.994	−0.011
		308.17	0.00543	1.383	−0.007	348.17	0.01846	2.087	−0.010
		313.23	0.00637	1.484	−0.020	353.16	0.02145	2.147	0.006
		318.16	0.00756	1.553	−0.012	358.16	0.02436	2.247	0.004
		323.18	0.00897	1.622	−0.001	363.17	0.02771	2.339	0.006
		328.15	0.01041	1.716	−0.007	368.16	0.03186	2.396	0.022
HMPPA	acetone	288.15	0.0013	24.34	0.024	308.14	0.0023	29.019	0.001
		293.16	0.0015	26.48	−0.020	313.16	0.0026	30.294	−0.007
		298.17	0.0017	27.16	−0.006	318.17	0.0030	31.328	−0.007
		303.18	0.0020	28.065	−0.002	323.16	0.0035	31.631	0.016
	water[24]	307.45	0.0099	6.633	0.036	342.45	0.1166	1.668	−0.063
		317.46	0.0206	4.456	−0.022	346.58	0.1662	1.311	0.024
		327.57	0.0424	2.975	−0.051	352.8	0.2474	1.040	0.029
		338.15	0.0966	1.784	0.036	357.11	0.3120	0.922	−0.002
	butanone	288.15	0.0013	24.377	−0.010	313.16	0.0024	32.981	0.001
		293.16	0.0015	25.629	0.007	318.17	0.0027	35.123	−0.006
		298.17	0.0017	27.746	−0.005	323.16	0.0029	37.487	−0.015
		303.18	0.0019	29.186	0.000	328.17	0.0033	38.738	0.000
		308.14	0.0022	30.667	0.007	333.16	0.0037	40.772	0.000

Table 4. Continued

solute	solvent	T/K	x	γ	$(x - x^{calcd})/x$	T/K	x	γ	$(x - x^{calcd})/x$
	cyclohexane	288.15	0.0010	30.710	−0.002	313.16	0.0015	54.294	−0.001
		293.16	0.0011	34.568	0.002	318.17	0.0016	60.142	0.001
		298.17	0.0012	38.928	0.001	323.16	0.0017	66.631	−0.002
		303.18	0.0013	43.710	−0.001	328.17	0.0018	73.331	0.000
		308.14	0.0014	48.654	0.002	333.16	0.0019	80.559	0.000
	toluene	288.15	0.0010	33.075	0.004	313.16	0.0020	39.821	0.000
		293.16	0.0011	34.577	−0.001	318.17	0.0023	41.566	−0.010
		298.17	0.0013	36.306	−0.013	323.16	0.0026	42.331	0.004
		303.18	0.0015	37.001	0.005	328.17	0.0029	43.832	0.000
		308.14	0.0018	38.108	0.010	333.16	0.0033	45.161	0.000
	benzene	293.16	0.0009	43.955	0.007	318.17	0.0022	41.861	−0.007
		298.17	0.0011	43.344	0.007	323.16	0.0027	41.475	−0.009
		303.18	0.0013	43.599	−0.011	328.16	0.0032	40.501	0.004
		308.14	0.0016	42.349	0.005	333.15	0.0037	39.797	0.011
		313.16	0.0019	42.434	−0.009				
	dichloromethane	293.16	0.00061	63.882	0.007	303.14	0.00143	39.412	0.006
		296.17	0.00079	55.719	−0.006	305.15	0.00169	35.968	0.004
		301.13	0.00119	44.142	−0.012				
	diethyl ether	293.16	0.00113	34.589	−0.005	303.14	0.00212	26.634	0.001
		296.17	0.00138	31.679	0.004	305.15	0.00238	25.464	−0.004
		301.13	0.00188	27.911	0.004				
	2-ethoxyethanol	293.16	0.04614	0.848	−0.120	318.17	0.07773	1.209	−0.119
		298.17	0.05117	0.922	−0.128	323.16	0.08489	1.297	−0.126
		303.18	0.05708	0.991	−0.127	328.16	0.09373	1.370	−0.118
		308.14	0.06380	1.054	−0.118	333.15	0.10152	1.468	−0.128
		313.16	0.07086	1.125	−0.113				
CEPPA	acetone	293.16	0.00074	15.942	0.009	313.16	0.00197	14.436	0.002
		298.17	0.00093	15.963	−0.021	318.17	0.00248	14.001	0.008
		303.18	0.00124	14.941	0.019	323.16	0.00305	13.857	−0.005
		308.14	0.00153	15.011	−0.012				
	butanone	293.16	0.00061	19.238	0.012	318.17	0.00206	16.895	0.004
		298.17	0.00077	19.264	−0.019	323.16	0.00253	16.722	−0.011
		303.18	0.00103	18.030	0.019	328.16	0.00316	16.186	−0.002
		308.14	0.00127	18.114	−0.013	333.15	0.00395	15.597	0.011
		313.16	0.00163	17.420	−0.001				
	water[25]	298.25	0.00178	8.356	0.061	337.55	0.02492	2.891	−0.034
		308.66	0.00366	6.427	−0.010	342.75	0.03388	2.550	−0.042
		318.07	0.00671	5.163	−0.079	345.06	0.04121	2.269	0.018
		327.17	0.01332	3.701	−0.002	349.47	0.05682	1.907	0.079
	benzene	293.16	0.00081	14.487	−0.010	318.17	0.00126	27.632	0.007
		298.17	0.00091	16.375	0.009	323.16	0.00134	31.539	−0.005
		303.18	0.00099	18.828	0.007	328.16	0.00145	35.214	0.001
		308.14	0.00107	21.578	0.002	333.15	0.00156	39.444	0.001
		313.16	0.00114	24.909	−0.013				
	toluene	293.16	0.00051	23.119	0.008	318.17	0.00105	33.201	−0.003
		298.17	0.00059	25.202	−0.003	323.16	0.00119	35.434	−0.004
		303.18	0.00068	27.195	−0.007	328.16	0.00138	37.100	0.017
		308.14	0.00079	28.928	0.001	333.15	0.00154	39.984	−0.003
		313.16	0.00092	31.003	−0.000				
	ethyl acetate	293.16	0.00128	9.205	−0.002	318.17	0.00226	15.371	−0.008
		298.17	0.00148	10.027	0.021	323.16	0.00254	16.647	0.005
		303.18	0.00162	11.442	−0.006	328.16	0.00281	18.193	0.005
		308.14	0.00182	12.645	−0.006	333.15	0.00311	19.818	0.006
		313.16	0.00202	14.065	−0.014				
	cyclohexane	293.16	0.00088	13.371	0.006	318.17	0.00222	15.664	−0.007
		298.17	0.00108	13.782	0.007	323.16	0.00263	16.112	−0.009
		303.18	0.00128	14.469	−0.011	328.16	0.00314	16.317	0.004
		308.14	0.00157	14.643	0.005	333.15	0.00371	16.608	0.011
		313.16	0.00186	15.273	−0.009				
	2-ethoxyethanol	293.16	0.0461	0.255	0.002	318.17	0.0777	0.447	0.002
		298.17	0.0512	0.290	−0.006	323.16	0.0849	0.498	−0.004
		303.18	0.0571	0.325	−0.004	328.16	0.0937	0.546	0.004
		308.14	0.0638	0.360	0.004	333.15	0.1015	0.606	−0.005
		313.16	0.0709	0.400	0.008				
	acetic acid	293.16	0.01047	1.124	0.014	318.17	0.01825	1.905	−0.004
		298.17	0.01160	1.279	−0.006	323.16	0.02047	2.066	0.007
		303.18	0.01304	1.424	−0.008	328.16	0.02247	2.277	−0.001
		308.14	0.01468	1.567	−0.003	333.15	0.02487	2.473	0.003
		313.16	0.01641	1.729	−0.003				
	acetonitrile	293.16	0.00006	192.940	−0.004	318.17	0.00053	65.209	0.024
		298.17	0.00010	152.020	0.008	323.16	0.00078	54.037	0.020
		303.18	0.00015	122.740	0.004	328.16	0.00109	47.113	−0.029
		308.14	0.00023	102.270	−0.023	333.15	0.00161	38.141	0.003
		313.16	0.00035	81.848	−0.005				

Table 4. Continued

solute	solvent	T/K	x	γ	$(x - x^{calcd})/x$	T/K	x	γ	$(x - x^{calcd})/x$
	dichloromethane	288.15	0.00029	31.563	0.301	303.18	0.00080	23.135	0.273
		293.16	0.00042	28.309	0.293	308.14	0.00111	20.801	0.272
		298.17	0.00059	25.219	0.292	313.16	0.00149	18.949	0.262
	chloroform	288.15	0.00021	44.206	−0.001	313.16	0.00063	45.293	−0.004
		293.16	0.00026	44.557	−0.004	318.17	0.00079	44.308	0.022
		298.17	0.00033	44.402	0.003	323.16	0.00093	45.359	0.002
		303.18	0.00041	45.192	−0.010	328.16	0.00112	45.841	−0.005
		308.14	0.00052	44.686	0.005	333.15	0.00133	46.201	−0.009
TMOPPO	butanone	293.16	0.00621	4.902	−0.002	318.17	0.00962	7.945	0.001
		298.17	0.00684	5.418	0.002	323.16	0.01033	8.732	−0.006
		303.18	0.00749	5.981	0.003	328.17	0.01126	9.423	0.004
		308.14	0.00815	6.602	0.001	333.16	0.01208	10.275	0.000
		313.16	0.00884	7.270	−0.002				
	2-ethoxyethanol	293.16	0.00522	5.832	−0.015	323.16	0.02094	4.309	0.006
		298.17	0.00693	5.347	0.021	328.17	0.02547	4.167	−0.003
		303.18	0.00862	5.198	−0.000	333.16	0.0311	3.994	−0.001
		308.14	0.01082	4.971	−0.003	338.17	0.0377	3.828	0.002
		313.16	0.01357	4.738	−0.001	343.15	0.04537	3.691	0.000.
		318.17	0.01679	4.548	−0.005				
	methanol	293.16	0.00022	141.390	−0.026	308.14	0.00051	104.160	0.029
		298.17	0.00029	128.120	−0.021	313.16	0.00066	98.851	−0.013
		303.18	0.00040	111.410	0.039	318.17	0.00083	92.999	−0.031
	ethanol	323.16	0.00107	85.547	−0.026	308.14	0.00142	37.232	37.232
		293.16	0.00084	36.606	36.606	313.16	0.00173	37.554	37.554
		298.17	0.00102	36.802	36.802	318.17	0.00202	38.185	38.185
		303.18	0.00121	36.792	36.792	323.16	0.00241	37.952	37.952
	diethyl ether	293.16	0.00587	5.189	−0.001	301.16	0.01008	4.121	0.001
		296.17	0.00721	4.762	−0.003	303.15	0.01142	3.920	−0.004
		299.18	0.00889	4.333	0.0061				
	benzene	293.16	0.00029	104.010	−0.001	313.16	0.00068	94.963	0.011
		298.17	0.00037	99.661	0.021	318.17	0.00082	93.703	0.006
		303.18	0.00045	100.370	−0.006	323.16	0.00099	90.816	0.020
		308.14	0.00054	99.390	−0.016				
	toluene	293.16	0.00035	88.052	0.005	318.17	0.00089	85.468	0.015
		298.17	0.00042	87.530	0.006	323.16	0.00105	85.638	0.009
		303.18	0.00051	88.050	−0.004	328.17	0.00123	85.992	0.002
		308.14	0.00061	88.342	−0.011	333.15	0.00145	85.790	0.001
		313.16	0.00075	86.082	0.0113				
	cyclohexane[24]	299.15	0.00054	71.416	0.022	323.65	0.00326	28.128	0.007
		304.05	0.00082	56.197	0.059	328.45	0.00436	24.556	−0.026
		308.85	0.00107	51.571	−0.046	332.85	0.00596	20.623	−0.002
		313.95	0.00151	43.769	−0.081	337.65	0.00848	16.781	0.043
		318.45	0.00231	33.388	0.024				
TMOPP	toluene	293.16	0.00036	156.070	0.001	318.17	0.00099	128.270	0.004
		298.17	0.00045	147.990	0.013	323.16	0.00121	122.220	0.017
		303.18	0.00055	143.860	0.001	328.17	0.00143	120.240	−0.000
		308.14	0.00066	141.250	−0.019	333.15	0.00169	116.230	0.001
		313.16	0.00083	131.070	0.018				
	butanone	288.15	0.00567	8.199	0.001	313.16	0.01016	10.755	0.000
		293.16	0.00642	8.690	0.001	318.17	0.01125	11.351	−0.005
		298.17	0.00725	9.183	0.002	323.16	0.01251	11.857	−0.001
		303.18	0.00814	9.704	0.002	328.17	0.01391	12.342	0.005
		308.14	0.00907	10.261	−0.003	333.16	0.01531	12.907	0.005
	benzene	293.16	0.00031	184.980	−0.013	313.16	0.00076	144.820	0.008
		298.17	0.00039	172.300	−0.003	318.17	0.00094	137.520	0.008
		303.18	0.00048	162.710	0.003	323.16	0.00112	134.840	−0.023
		308.14	0.00061	152.040	0.020				
	diethyl ether	293.16	0.00607	9.198	0.000	301.16	0.01057	6.977	0.009
		296.17	0.00739	8.392	−0.010	303.15	0.01181	6.687	−0.012
		299.18	0.00929	7.419	0.013				
	ethanol[24]	298.25	0.00037	178.550	0.044	317.75	0.00128	98.477	0.004
		303.75	0.00049	164.040	−0.060	322.35	0.00168	86.191	−0.001
		308.05	0.00067	139.170	−0.036	328.15	0.00236	72.674	−0.000
		313.35	0.00102	107.820	0.049				
	methanol[24]	293.35	0.00019	295.650	0.052	313.15	0.00056	194.110	0.000
		298.25	0.00024	278.240	−0.009	318.15	0.00071	179.720	−0.034
		303.15	0.00031	257.140	−0.050	322.65	0.00098	148.620	0.058
		308.05	0.00042	222.600	−0.021				
	2-ethoxyethanol	293.16	0.00573	9.746	0.016	323.16	0.02226	6.664	0.007
		298.17	0.00716	9.295	−0.007	328.17	0.02759	6.218	0.018
		303.18	0.00919	8.600	0.003	333.17	0.03301	5.987	0.000
		308.14	0.01142	8.153	−0.009	338.25	0.04013	5.660	0.001
		313.16	0.01431	7.641	−0.008	343.17	0.04816	5.376	0.000
		318.17	0.01754	7.279	−0.022				
	cyclohexane	298.15	0.00053	75.801	0.020	323.65	0.00322	25.575	−0.014
		304.05	0.00082	59.106	−0.007	328.45	0.00455	20.472	0.017
		308.32	0.00113	48.378	0.000	332.85	0.00589	17.615	−0.004
		313.95	0.00166	38.458	−0.017	337.65	0.00806	14.460	0.012
		318.45	0.00229	31.497	−0.008				

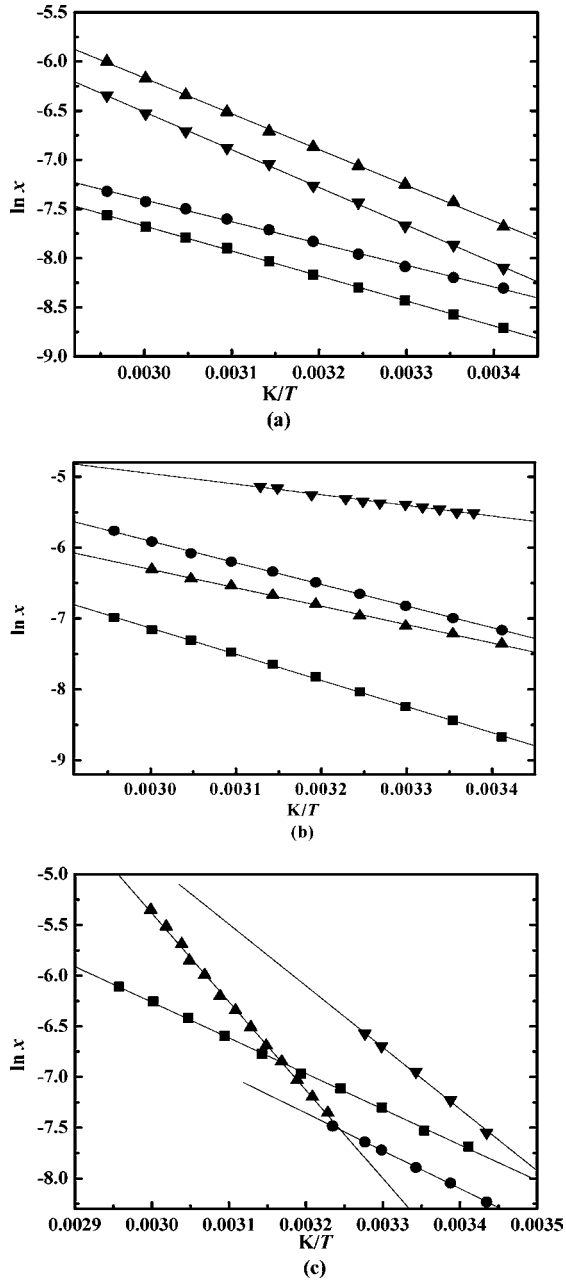

Figure 4. Mole fraction solubilities of dihydroxy-TDUD in selected solvents: (a) experimental data: ■, cyclohexane; ▼, benzene; ●, 1,4-dioxane; ▲, toluene; (b) experimental data: ■, acetic acid; ▲ butanone; ●, ethyl acetate; ▼, acetone, data from ref 9; (c) experimental data: ●, dichloromethane; ▲, acetonitrile, data from ref 9; ■, chloroform; ▼, diethylether; —, solubility curve calculated from eq 3.

diphenoxy-TDUD. A higher thermal stability is required for the FRs because of the conditions of polymer processing. From Table 3 it can be seen that the thermal stabilities of CEPPA and HMPPA were not satisfactory. The initial decomposition temperature of HMPPA was around 488.15 K, and the initial decomposition temperature of CEPPA was around 463.15 K. As a monomer for polycondensation of PET, the decomposition temperatures of CEPPA and HMPPA are much lower than the temperature range of esterification and polycondensation of PET. The weight loss of CEPPA and HMPPA at a relatively low temperatures results from dehydrolysis between the molecules. Therefore, CEPPA or HMPPA should be incorporated into PET by a pre-esterification of the CEPPA or HMPPA with the ethylene glycol procedure.

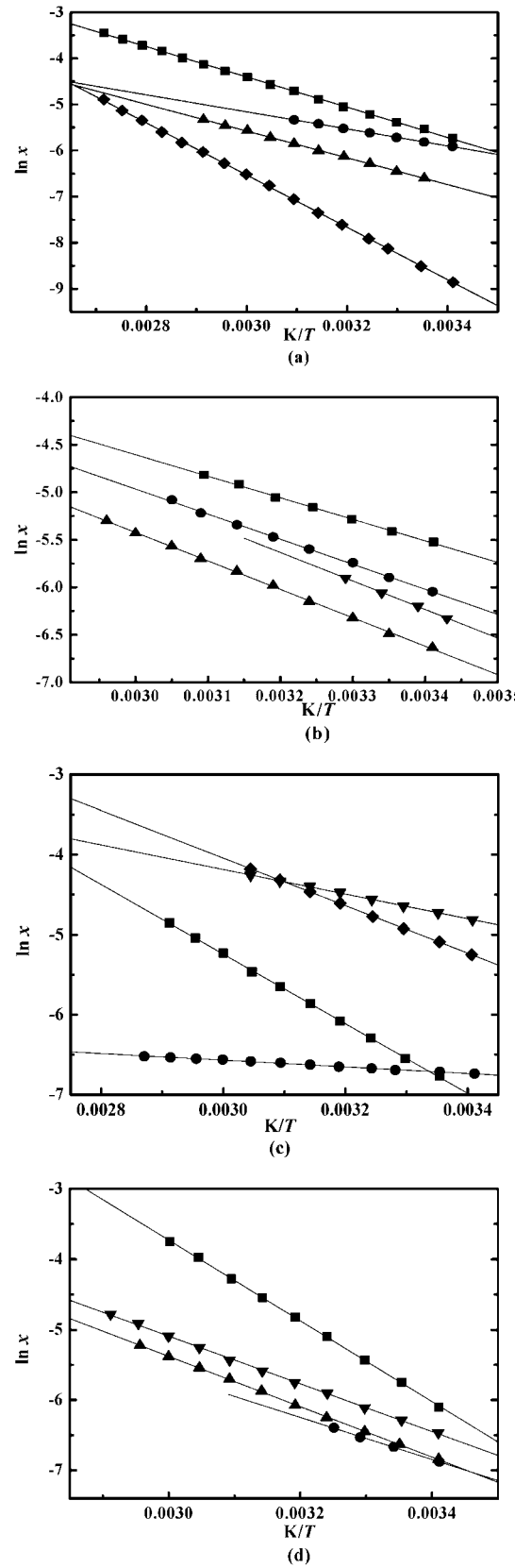

Figure 5. Mole fraction solubilities of diphenyl-TDUD in selected solvents: (a) experimental data: ♦, water; ▲, ethanol; ●, methanol; ■, 2-ethoxyethanol; (b) experimental data: ■, butanone; ▼, diethylether; ●, acetone; ▲, 1,4-dioxane; (c) experimental data: ●, benzene; ■, toluene; ♦, tetrahydrofuran; ▼, pyridine; (d) experimental data: ●, dichloromethane; ▲, ethyl acetate; ▼, chloroform; ■, acetonitrile; —, solubility curve calculated from eq 3.

Solubility. The mole fraction solubilities x of solute in selected solvents measured in this work are summarized in Table 4 and

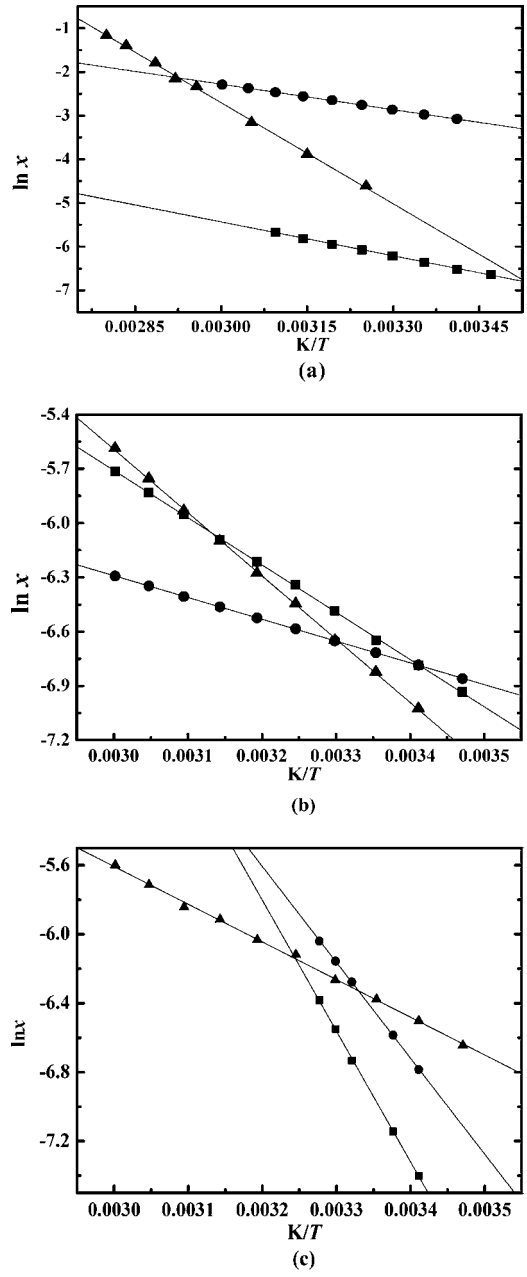

Figure 6. Mole fraction solubilities of HMPPA in selected solvents: (a) experimental data: ●, 2-ethoxyethanol; ▲, water; data from ref 24; ■, acetone; (b) experimental data: ●, cyclohexane; ▲, benzene; ■, toluene; (c) experimental data: ●, diethylether; ▲, butanone; ■, dichloromethane; —, solubility curve calculated from eq 3.

plotted as ln x versus T in Figures 4 to 9. The solubilities were correlated as a function of temperature by

$$\ln x = A + B/(T/\mathrm{K}) \tag{2}$$

Parameters A and B for each solvent are listed in Table 5. The relative standard deviations (RSDs), defined by eq 3, are also presented in Table 5. The smoothed data calculated from eq 2 are compared with the data listed in Table 4.

$$\mathrm{RSD} = \left[\frac{1}{N}\sum_{1}^{n}\left(\frac{x_i - x_i^{\mathrm{calcd}}}{x_i}\right)^2\right]^{1/2} \tag{3}$$

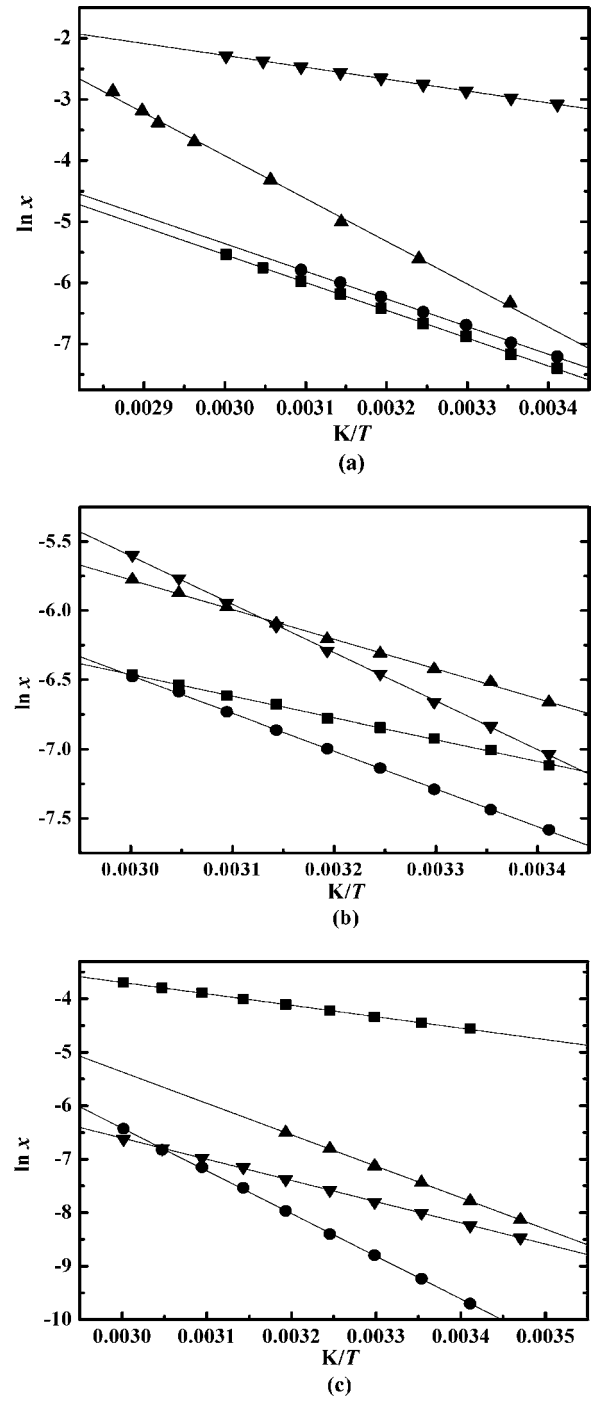

Figure 7. Mole fraction solubilities of CEPPA in selected solvents: (a) experimental data: ▼, 2-ethoxyethanol; ▲, water, data from ref 25; ●, acetone; ■, butanone; (b) experimental data: ▼, cyclohexane; ▲, ethyl acetate; ●, toluene; ■, benzene; (c) experimental data: ●, acetonitrile; ▲, dichloromethane; ■, acetic acid; ▼, chloroform; —, solubility curve calculated from eq 3.

where calcd stands for the calculated values and N is the number of experimental points. The results show that eq 2 can be used to correlate the solubility data. The accuracy of the experimental data used in the correlations is satisfactory. The obtained RSD values for different systems are all less than 0.05. Most of them are less than 0.02. Within the temperature range of the measurements, the solubilities of the solute in all of the investigated solvents increased with an increase in temperature.

The solubility of dihydroxy-TDUD in acetone shows the highest value from (295.75 to 319.15) K and in cyclohexane

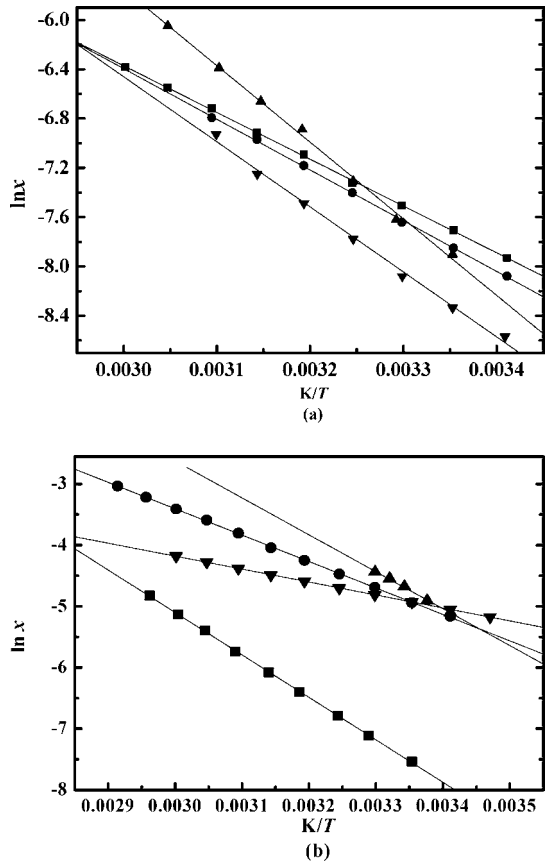

Figure 8. Mole fraction solubilities of TMOPP in selected solvents: (a) experimental data: ■, toluene; ●, benzene; ▲, ethanol, data from ref 24; ▼, methanol, data from ref 24; (b) experimental data: ■, cyclohexane; ●, 2-ethoxyethanol; ▼, butanone; ▲, diethylether; —, solubility curve calculated from eq 3.

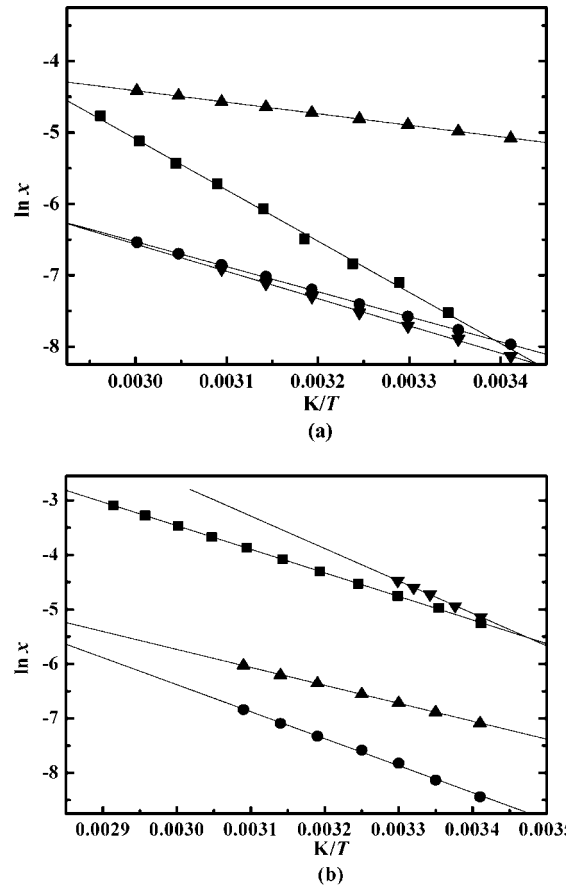

Figure 9. Mole fraction solubilities of TMOPPO in selected solvents: (a) experimental data: ■, cyclohexane, data from ref 24; ●, toluene; ▼, butanone; ▲, benzene; (b) experimental data: ■, 2-ethoxyethanol; ●, methanol; ▲, ethanol; ▼, diethylether; —, solubility curve calculated from eq 3.

shows the lowest value, which was probably related to the theory of similarity and compatibility and the certain polarity of dihydroxy-TDUD. Thus, acetone is recommended as the best solvent for the purification of dihydroxy-TDUD.

The solubility of diphenoxy-TDUD in 2-ethoxyethanol shows the highest value from (358.15 to 368.15) K and in water shows the lowest value from (298.15 to 328.45) K. However, because of its higher boiling temperature and good dissolubility with diphenoxy-TDUD, 2-ethoxyethanol is recommended as the best solvent for the recrystallization of diphenoxy-TDUD, as the second stage of purification. For the final stage of purification, water is recommended as the solvent to remove the 2-ethoxyethanol from the slurry by quickly filtrating and drying.

The solubility of HMPPA in water shows the highest value from (343.15 to 363.15) K and in dichloromethane shows the lowest value from (293.15 to 303.15) K. Because of its higher boiling temperature and good dissolubility with HMPPA, water is recommended as the best solvent for purification and recrystallization of HMPPA.

The solubility of CEPPA in 2-ethoxyethanol shows the highest value from (293.15 to 363.15) K and in acetonitrile shows the lowest value from (293.15 to 313.15 K). Compared to 2-ethoxyethanol, water is not only environmentally friendly as solvent, but also the solubility of CEPPA in water increases more greatly than that in 2-ethoxyethanol as the temperature increases. Therefore, water is undoubtedly recommended as the best solvent for the recrystallization of CEPPA in this work.

The solubility of TMOPP in 2-ethoxyethanol shows the highest value from (203.15 K to 343.15) K and in methanol shows the lowest value from (293.15 to 313.15 K). Thus, 2-ethoxyethanol is recommended as the best solvent for the purification of TMOPP.

The solubility of TMOPPO in 2-ethoxyethanol shows the highest value from (298.15 to 358.15) K and in methanol shows the lowest value from (298.15 to 323.15) K. Because of its higher boiling temperature and good dissolubility with TMOPPO, 2-ethoxyethanol is recommended as the best solvent for the recrystallization of TMOPPO, as the second stage of purification. For the final stage of purification, methanol is recommended as the solvent to remove the 2-ethoxyethanol from the slurry by quickly filtrating and drying.

To obtain the activity coefficients of solute in the solvents from the experimental data, the following equilibrium equation for solute 1 was derived as a fair approximation[35]

$$\ln \frac{1}{x_1 \gamma_1} = \frac{\Delta_{fus} H}{R T_m}\left(\frac{T_m}{T} - 1\right) \qquad (4)$$

where $\Delta_{fus}H$ refers to the enthalpy of fusion; T_m is the melting temperature; R is the gas constant; and x_1 and γ_1 refer to the mole fraction and activity coefficient of solute in the solution, respectively. With the experimental x_1, T, $\Delta_{fus}H$, and T_m values known, the activity coefficients of solute in different solvents were obtained. The results are listed in Table 4. From Table 4, it can be seen that the activity coefficients of solute in these selected solvents are all more than unity. Generally, a relatively

Table 5. Parameters of Equation 2 and Relative Standard Deviations (RSDs) of the Measured Solubility of Solute in Selected Solvents from the Calculated Results

solute	solvent	*A*	*B*	RSD
dihydroxy-TDUD	acetone[9]	−0.3730	−1523.6	0.001
	butanone	1.4829	−2596.5	0.016
	dichloromethane	4.5628	−3724.5	0.006
	chloroform	4.2862	−3516.0	0.017
	benzene	5.0048	−3839.1	0.014
	toluene	4.7613	−3642.6	0.014
	acetonitrile[9]	19.4760	−8311.1	0.023
	diethyl ether	13.3376	−6074.5	0.018
	1,4-dioxane	−0.7670	−2213.6	0.013
	ethyl acetate	3.2622	−3056.8	0.012
	acetic acid	3.9362	−3690.5	0.016
	cyclohexane	−0.0485	−2541.5	0.006
diphenoxy-TDUD	water	10.4950	−5675.5	0.016
	methanol	0.3926	−1850.8	0.006
	ethanol	3.1345	−2903.8	0.010
	benzene	−5.3253	−414.7	0.005
	acetone	2.9177	−2627.5	0.005
	butanone	2.1939	−2266.2	0.010
	dichloromethane	3.3502	−3000.1	0.009
	toluene	7.7952	−4346.4	0.011
	acetonitrile	5.0878	−3392.8	0.016
	ethyl acetate	5.3630	−3580.6	0.008
	chloroform	13.6150	−5776.9	0.011
	diethyl ether	3.9792	−3003.7	0.006
	1,4-dioxane	3.5153	−2980.3	0.013
	pyridine	0.4220	−1535.9	0.005
	tetrahydrofuran	4.8670	−2970.2	0.004
	2-ethoxyethanol	5.4692	−3290.6	0.014
HMPPA	acetone	2.3411	−2591.2	0.015
	butanone	0.8342	−2147.4	0.007
	water	20.4410	−7714.9	0.014
	cyclohexane	−2.6769	−1204.5	0.002
	toluene	2.1239	−2611.2	0.008
	diethyl ether	12.1490	−5549.3	0.005
	benzene	4.8994	−3497.4	0.009
	dichloromethane	18.4270	−7573.2	0.010
	diethyl ether	12.1490	−5549.4	0.005
	2-ethoxyethanol	3.6676	−1943.9	0.005
CEPPA	acetone	8.2144	−4524.7	0.015
	butanone	8.1217	−4553.6	0.014
	water[25]	17.0910	−7004.1	0.016
	benzene	−1.7597	−1567.3	0.008
	toluene	1.7163	−2728.4	0.007
	ethyl acetate	0.6635	−2146.9	0.011
	cyclohexane	4.8883	−3497.4	0.009
	2-ethoxyethanol	3.5526	−1943.8	0.005
	acetic acid	2.7209	−2138.3	0.007
	acetonitrile	17.5220	−7980.7	0.019
	dichloromethane	12.5920	−6075.2	0.005
	chloroform	5.2807	−3962.1	0.010
TMOPPO	butanone	0.4378	−1617.3	0.003
	2-ethoxyethanol	9.4988	−4320.8	0.011
	methanol	8.6347	−4999. 6	0.019
	ethanol	4.1489	−3294.3	0.006
	diethyl ether	15.1620	−5950. 8	0.005
	benzene	4.8033	−3793.1	0.005
	toluene	3.9739	−3502.7	0.005
	cyclohexane	16.4310	−7173.4	0.047
TMOPP	butanone	2.1565	−2112.5	0.003
	2-ethoxyethanol	9.5459	−4316.9	0.015
	methanol	9.4070	−5288.9	0.017
	ethanol	4.1703	−2697.4	0.013
	diethyl ether	15.4820	−6035.4	0.013
	benzene	5.9108	−4105.8	0.016
	toluene	5.0493	−3807.1	0.006
	cyclohexane	15.7260	−6941.8	0.015

small solubility and a large activity coefficient result from the deviation from ideal behavior ($\gamma_{1=1}$), which illustrated that the interaction between the solutes and the solvents is weak and the polar or specific chemical force between the molecules of the solid is strong.

Supporting Information Available:

The ^{1}H NMR and ^{31}P NMR spectra and the DSC graphs of dihydroxy-TDUD, diphenoxy-TDUD, HMPPA, CEPPA, TMOPP, and TMOPPO information. This material is available free of charge via the Internet at http://pubs.acs.org.

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