Solubilities of *N*-[(4-Bromo-3,5-difluorine)-phenyl]maleimide in Pyridine, Acetone, Tetrahydrofuran, Ethanol, Trichloromethane, and Acetonitrile at Temperature between (285.00 and 350.15) K

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The solubility of *N*-[(4-bromo-3,5-difluorine)-phenyl]maleimide in pure pyridine, acetone, tetrahydrofuran, ethanol, trichloromethane, and acetonitrile at temperature between (285.00 and 350.15) K under atmospheric pressure was investigated. A laser monitoring observation technique was used to determine the dissolution of the solid phase in solid + liquid mixture. The experimental solubility data were correlated with the modified Apelblat equation.

Introduction

Halogen-substituted *N*-phenylmaleimide (XPM) monomers due to the rigid imide rings in the backbones are usually designed to modify thermal stability and fire resistance of organic matrix materials.[1−5] *N*-[(4-Bromo-3,5-difluorine)phenyl]maleimide (BDPM, Figure 1) is a new XPM monomer with fluorine and bromine atoms for polyreaction. BDPM was synthesized by the interaction of 4-Bromo-3,5-difluoroaniline with maleic anhydride. Crude BDPM was gained after concentrating and filtrating. For extensive halogen-substituted *N*-phenylmaleimide polymers investigation, crude BDPM has to be purified by crystallization. To improve the purity and yield of BDPM, we require the solubility data of BDPM in different solvents.

In this article, solubility measurement of BDPM in pure pyridine, acetone, tetrahydrofuran, ethanol, trichloromethane, and acetonitrile at temperature between (285.00 and 350.15) K was performed at atmospheric pressure by a laser monitoring observation technique. Experimental data were correlated by the modified Apelblat equation.[6]

Experimental Section

Materials. The *N*-[(4-bromo-3,5-difluorine)-phenyl]maleimide was produced by ourselves. Its mass fraction purity was > 99.3 %, determined by HPLC [column: ZORBAX SA C18 (5 μm, 200 nm × 4.6 mm) using the methanol as the mobile phase]. The melting point is (470.6 ± 0.3) K (measured by DSC). All of the solvents, pyridine, acetone, tetrahydrofuran, ethanol, trichloromethane, and acetonitrile (purchased from the Tianjin Kewei of China) used for experiments were analytical reagent grade, and their mass fraction purities were higher than 99.8 %. Distilled deionized water of HPLC grade was used throughout.

Apparatus and Procedure. The BDPM was produced by the following method: 80 mL of toluene, 15 mL of DMF, and 4.54 g maleic anhydride were put in a 250 mL four-mouth flask, respectively; then, 8.00 g 4-bromo-3,5-difluoroaniline was added to three flasks in batches, and the mixture was maintained for 1.5 h at the temperature of 293.15 K. Then, 0.88 g of toluene-*p*-sulfonic acid and an appropriate amount of inhibitor were added to the reaction flask, and the mixture was maintained for hours at the temperature of 383.15 K until no water drops appeared in the water separator. Toluene was removed by distillation and then cooled to room temperature, and BDPM [11.12 g, mp (470.45 to 470.85) K, ^{1}HNMR ($CDCl_3$, 400 MHz, δ): 7.13−7.18 (m, 2H, CH), 7.35−7.42 (m, 2H, ArH)] was obtained by filtering, washing, and drying.

The solubility of BDPM in six pure solvents was measured by the similar method that was described in the literature.[7−9] The experiments were carried out in a 50 mL jacketed glass vessel with a magnetic stirrer. The temperature, with an uncertainty of ± 0.05 K, was controlled by circulating water through the outer jacket. To prevent the evaporation of the solvent, we introduced a condenser vessel. A laser monitoring system that consisted of a laser generator, a photoelectric transformer, and a light intensity display was used to determine the disappearance of the last crystal in the mixtures. An electronic balance (Shimadzu AX200) with uncertainty of ± 0.0001 g was used for the mass measurements.

During the measurement, predetermined excess amounts of solute and solvent of known masses were added to the jacket vessel. The contents of the vessel was stirred continuously for 30 min at a fixed temperature. Then, additional solvent of known mass was introduced to the cell. When the last solute just disappeared, the laser intensity penetrating through the vessel reached maximum, and the solvent mass consumed in the measure was recorded. Together with the mass of solute, the solubility would be obtained. The saturated mole fraction solubility of BDPM can be determined from eq 1

$$x_i = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \tag{1}$$

where m_1 and m_2 represent the masses of the solute and solvent and M_1 and M_2 are the molecular weights of the solute and the solvent, respectively. All experiments were repeated three times, and the solubility data were the average of experimental results. Considering other factors, the relative uncertainty in the measurement of the concentration of BDPM was within 0.5 %.

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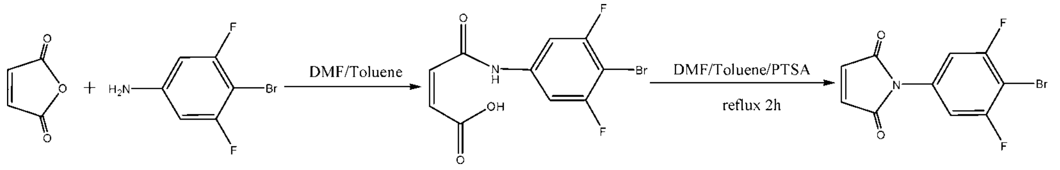

Figure 1. Synthesis of BDPM.

Table 1. Mole Fraction Solubility of BDPM in Different Solvents at Different Temperatures

T/K	$100x_1$	$100(x_1 - x_1^{\text{calcd}})/x_1$	T/K	$100x_1$	$100(x_1 - x_1^{\text{calcd}})/x_1$
pyridine			tetrahydrofuran		
285.55	1.16	−0.54	285	1.48	−0.71
289.66	1.29	0.02	288.45	1.62	0.37
293.95	1.44	0.88	291.55	1.76	1.21
297.15	1.54	−0.31	294.25	1.85	−0.26
300.85	1.69	0.04	297.55	2.00	−0.41
304.65	1.86	−0.13	302.8	2.28	0.01
310.05	2.14	0.46	306.65	2.49	−0.27
315.65	2.46	0.29	310.8	2.75	−0.09
318.65	2.65	0.31	315	3.03	−0.40
322.55	2.91	−0.03	318.45	3.29	−0.12
328.45	3.41	0.76	321.45	3.55	0.42
334.15	3.94	0.79	324.65	3.83	0.50
337.95	4.32	0.38	327.65	4.09	0.12
340.65	4.62	0.06	330.35	4.37	0.30
344.85	5.14	0.13	333.65	4.70	0.11
346.35	5.33	−0.13	336.25	4.97	−0.43
acetone			ethanol		
287.65	0.71	−0.36	288.65	0.03	4.45
291.85	0.81	−0.62	293.59	0.03	6.33
295.55	0.92	0.79	299.85	0.04	−0.85
298.35	1.00	0.48	305.72	0.06	0.39
301.25	1.09	0.43	311.15	0.08	3.51
304.55	1.20	0.04	318.15	0.11	2.15
307.6	1.31	−0.51	324.35	0.14	−0.97
309.45	1.39	−0.78	327.85	0.16	−0.38
311.95	1.52	0.67	332.95	0.20	−1.23
313.95	1.59	−0.62	336.05	0.23	−0.39
316.55	1.74	0.39	339.65	0.27	−1.61
319.55	1.90	−0.25	341.85	0.30	0.54
321.45	2.02	0.47	344.15	0.33	−0.16
323.35	2.14	0.15	346.15	0.36	−0.03
325.15	2.25	−0.27	347.75	0.39	0.89
trichloromethane			acetonitrile		
289.25	0.55	−0.42	291.95	0.28	1.41
294.85	0.66	0.09	296.65	0.33	−0.78
296.65	0.69	−0.38	299.25	0.37	−0.61
300.85	0.78	0.17	302.45	0.40	−3.01
302.75	0.82	−0.88	304.85	0.44	−2.02
305.65	0.92	1.35	307.15	0.49	−1.08
307.45	0.96	1.04	311.55	0.57	−0.99
309.55	1.01	−0.69	316.95	0.70	0.29
311.65	1.08	0.21	320.15	0.78	−0.34
315.35	1.20	0.11	325.45	0.95	1.34
318.65	1.32	−0.28	328.55	1.07	2.20
322.15	1.46	−0.42	332.05	1.19	0.24
324.65	1.57	−0.63	338.65	1.46	−1.27
326.45	1.66	0.15	341.65	1.65	0.72
328.35	1.76	0.25	347.25	1.98	0.02
330.65	1.88	0.20	350.15	2.17	−0.34

Results and Discussion

The solubility data of BDPM in pure pyridine, acetone, tetrahydrofuran, ethanol, trichloromethane, and acetonitrile are listed in Table 1 and shown in Figure 2. In Table 1, x_1 expresses the experimental solubility value. x_1^{calcd} expresses the calculated solubility value. From Table 1 and Figure 2, it can be seen that at temperature ranging from (285.00 to 350.15) K, the solubility of BDPM increases with temperature in all six pure solvents, and the BDPM is slightly soluble in ethanol, whereas the solubility of BDPM in pure pyridine and tetrahydrofuran is slightly higher than that in the solvents of ethanol, acetonitrile, trichloromethane, and acetone. The temperature T dependence of BDPM solubility in pure solvents can be computed by the modified Apelblat equation

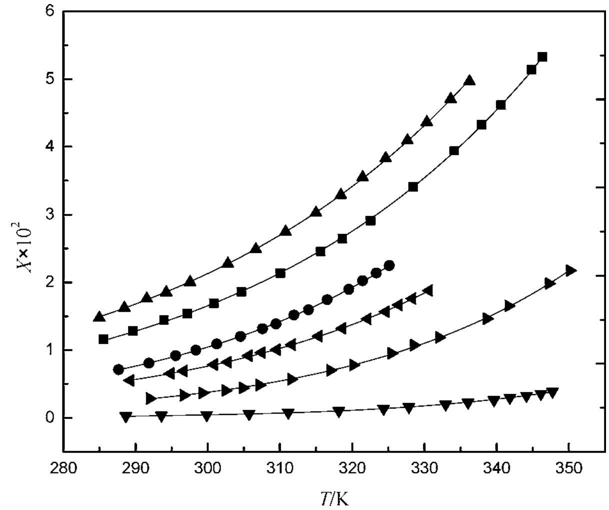

Figure 2. Solubilities of BDPM in different solvents: ■, pyridine; ●, acetone; ▲, tetrahydrofuran; ▼, ethanol; left tilted triangle, trichloromethane; right tilted triangle, acetonitrile. The line is well fit to the experimental data calculated with the modified Apelblat equation.

Table 2. Parameters of the Modified Apelblat Equation for BDPM in Different Pure Solvents

solvent	A	B	C	10^4 rmsd
pyridine	−118.07	3210.6	18.11	1.24
tetrahydrofuran	−82.66	1702.2	12.82	1.17
acetone	−104.35	2098.9	16.27	0.68
ethanol	−117.39	1238.0	18.50	0.20
trichloromethane	−100.46	1997.2	15.59	0.59
acetonitrile	−95.91	1223.0	15.12	1.00

$$\ln x_1^{\text{calcd}} = A + \frac{B}{T/\text{K}} + C \ln T/\text{K} \qquad (2)$$

where A, B, and C are the empirical parameters. The experimental data of mole fraction solubility in Table 1 were correlated with eq 2.

The values of the three parameters, A, B, and C together with the root-mean-square deviations (rmsd), are listed in Table 2. The rmsd is defined as

$$\text{rmsf} = \left\{\frac{1}{N}\sum_{i=1}^{N}(x_i^{\text{calcd}} - x_i)^2\right\}^{1/2} \qquad (3)$$

where N is the number of experimental points; x_i^{calcd} represents the solubility calculated; and x_1 represents the experimental solubility values. As can be seen from Figure 2 and Table 2, the correlation is satisfactory.

From Tables 1 and 2 and Figure 2, we can find that the solubility of BDPM increases with the solvents in the order: ethanol, acetonitrile, trichloromethane, acetone, pyridine, and tetrahydrofuran. The experimental solubility and correlation equation in this work can be used as essential data and models in the purification process of BDPM.

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