Solubilities of *N*-[(4-Bromo-3,5-difluorine)-phenyl]maleimide in Different Organic Solvents

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N-[(4-Bromo-3,5-difluorine)phenyl]maleimide (BDPM) is a new monomer for polyreaction. Its corresponding solid−liquid equilibrium data provide essential support for industrial design and further theoretical studies. Using a laser detecting system, solubility data were measured for the title compound dissolved in different organic solvents including *N*,*N*-dimethylformamide, dimethyl sulfoxide, 2-butanone, cyclohexanone, 1,4-dioxane, and toluene at temperatures between (285.15 and 356.25) K. The solubility data were correlated with the Apelblat equation and Buchowski−Ksiazczak λh equation. Both the Apelblat equation and the Buchowski−Ksiazczak λh equation can regress the solubility data well.

Introduction

N-Substituted maleimide monomers, such as *N*-phenylmaleimide (PM), *N*-hydroxyphenylmaleimide (HPM), and halogen-substituted *N*-phenylmaleimide (XPM), are usually designed to modify the thermal stability and fire resistance of organic matrix materials.[1−3] The polymers of PM and their derivatives have been known to exhibit high T_g values due to the rigid imide rings in the backbones.[4,5] Halogen-substituted PM polymers possess the thermal stability from an imide ring and flame retardancy from halides.[6,7] The incorporation of fluorine atoms (or groups containing fluorine atoms) into polymer chains increases the solubility, glass transition temperature (T_g), and thermal stability of polymers in addition to decreasing moisture absorption and dielectric constant.[8]

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 the extensive XPM polymer investigation, crude BDPM has to be purified by crystallization. To select the suitable solvent used for polymerization, the solubility data of BDPM in different solvents are required.

In this article, solubility measurements of BDPM in pure *N*,*N*-dimethylformamide, dimethyl sulfoxide, 2-butanone, cyclohexanone, 1,4-dioxane, and toluene at temperatures between (285.15 and 356.25) K were performed at atmospheric pressure by a laser monitoring observation technique. Experimental data were correlated by the modified Apelblat equation and the Buchowski−Ksiazczak λh equation.[9,10]

Experimental Section

Materials. The *N*-[(4-bromo-3,5-difluorine)-phenyl]maleimide was produced by ourselves. Portions of 80 mL of toluene, 15 mL of dimethylformamide (DMF), and 4.54 g of maleic anhydride were put into a 250 mL four-mouth flask, respectively, and then 8.00 g of 4-bromo-3,5-difluoroaniline was added to three flasks in batches; 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 *p*-dihydroxybenzene as an inhibitor were added to the reaction flask; the mixture was maintained for hours at the temperature of 383.15 K until no water drops appear in the water separator. Toluene was removed by vacuum distillation and then cooled to room temperature. BDPM [11.12 g, mp (470.45 to 470.85) K (measured by differential scanning calorimetry), ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.13−7.18 (m, 2H, CH), 7.35−7.42 (m, 2H, ArH)] was obtained by filtering, washing, and drying.

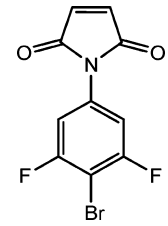

Figure 1. Structure of BDPM.

Its mass fraction purity was more than 0.993, as determined by high-performance liquid chromatography (HPLC). All of the solvents (purchased from the Tianjin Kewei of China) used for experiments were analytical reagent grade, and their mass fraction purities were higher than 0.998. Distilled deionized water of HPLC grade was used throughout.

Apparatus and Procedure. The solubility of BDPM in six pure solvents was measured by the method that was described in the literature.[11−13] 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, a condenser vessel was introduced. The dissolution of the solute was examined by the intensity of the laser beam that penetrated through the suspension. The laser monitoring system (purchased from Physics Department of Peking University) consisted of a laser generator (type JD-3, China), a photoelectric switch (type model 271, China), and a light intensity display. An electronic balance (Shimadzu AX200) with an 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

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

T/K	$x_i \cdot 10^2$	T/K	$x_i \cdot 10^2$	T/K	$x_i \cdot 10^2$
N,*N*-Dimethylformamide		Dimethyl Sulfoxide		1,4-Dioxane	
289.45	2.08	289.35	1.16	287.65	1.22
293.65	2.28	293.65	1.31	290.65	1.33
300.83	2.69	297.05	1.43	293.85	1.46
305.65	3.01	301.45	1.61	297.15	1.60
308.85	3.24	305.95	1.84	302.05	1.83
317.55	3.98	309.45	2.02	306.25	2.06
320.45	4.26	314.05	2.31	310.05	2.30
322.95	4.52	318.15	2.60	317.15	2.81
325.25	4.77	324.55	3.14	321.65	3.18
333.55	5.82	328.05	3.48	324.45	3.42
337.65	6.43	333.65	4.06	330.85	4.08
342.65	7.22	338.85	4.73	335.35	4.64
346.65	7.94	342.55	5.27	339.15	5.13
350.75	8.76	346.05	5.80	342.25	5.58
353.35	9.32	349.35	6.37	347.25	6.39
356.25	10.00	355.95	7.68	353.65	7.59
2-Butanone		Cyclohexanone		Toluene	
289.75	0.86	285.15	1.29	291.05	0.31
299.25	1.12	291.25	1.51	296.35	0.37
303.5	1.28	295.15	1.67	299.15	0.41
308.75	1.49	300.15	1.91	302.95	0.47
313	1.70	305.65	2.21	306.05	0.53
316.25	1.87	311.65	2.59	310.15	0.61
318.6	2.02	316.55	2.95	315.95	0.75
321.75	2.20	321.85	3.42	321.05	0.89
324.25	2.37	324.95	3.70	325.15	1.03
327.05	2.57	328.75	4.11	330.65	1.24
331.95	2.96	333.25	4.62	334.45	1.40
335.25	3.26	337.35	5.15	340.75	1.75
338.85	3.60	341.35	5.72	343.55	1.92
341.55	3.90	348.35	6.90	348.45	2.26
343.5	4.11	351.65	7.51	350.65	2.44
345.25	4.32	355.05	8.23	354.45	2.76

vessel. The contents of the vessel were stirred continuously for 30 min at a fixed temperature. Then, an additional solvent of known mass was introduced to the cell. The dissolution of the solute was monitored by a laser beam. When the solute dissolved completely, the solution was clear, and the laser intensity that penetrated through the solution attained its maximum. Otherwise, the solute was believed not to be dissolved completely. When the last solute just disappeared, the laser intensity penetrating through the vessel reached a maximum, and the solvent mass consumed 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 of the 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 %.

Results and Discussion

The solubility data of BDPM in pure *N*,*N*-dimethylformamide, dimethyl sulfoxide, 2-butanone, cyclohexanone, 1,4-dioxane, and toluene are listed in Table 1. From Table 1, it can be seen that at temperatures ranging from (285.15 and 356.25) K, the solubility of BDPM increases with temperature in all six pure solvents, and the BDPM is slightly soluble in toluene, while

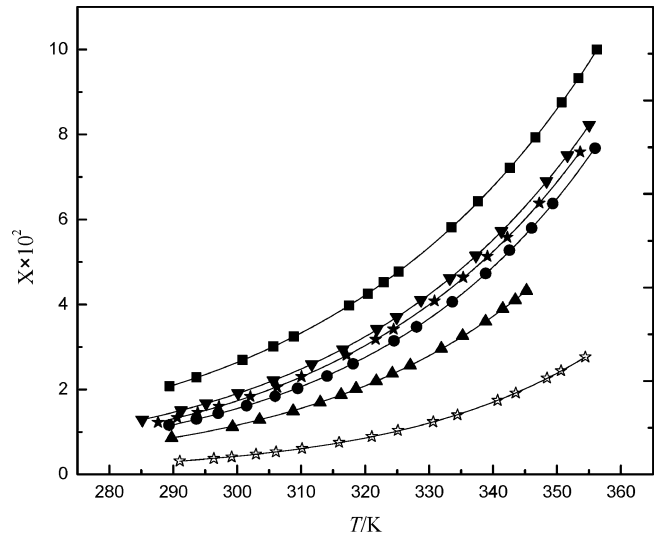

Figure 2. Solubilities of BDPM in different solvents: ■, *N*,*N*-dimethylformamide; ●, dimethyl sulfoxide; ▲, 2-butanone; ▼, cyclohexanone; ★, 1,4-dioxane; ☆, toluene. The line is well-fit of the experimental data calculated with the modified Apelblat equation.

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

solvent	A	B	C	10^5 rmsd
N,*N*-dimethylformamide	−109.81	2980.7	16.87	5.64
dimethyl sulfoxide	−118.21	2917.7	18.29	9.43
2-butanone	−107.84	2369.4	16.74	8.98
cyclohexanone	−109.85	2704.0	16.98	6.28
1,4-dioxane	−96.05	2181.1	15.66	6.72
toluene	−122.46	2546.2	19.02	3.78

the solubility of BDPM in pure *N*,*N*-dimethylformamide is higher than that in the solvents of dimethyl sulfoxide, 2-butanone, cyclohexanone, and 1,4-dioxane.

To describe the solid−liquid equilibrium, the relationship between solubility and temperature can be described as the modified Apelblat equation

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

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 results are shown in Figure 2.

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

$$\mathrm{rmsd} = \left\{\frac{1}{N}\sum_{i=1}^{N}(x_i^{\mathrm{calc}} - x_i)^2\right\}^{1/2} \tag{3}$$

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

The another way to describe the solution behavior is the Buchowski−Ksiazczak λh equation

$$\ln\left[1 + \frac{\lambda(1-x)}{x}\right] = \lambda h\left(\frac{1}{T} - \frac{1}{T_{\mathrm{m}}}\right) \tag{4}$$

Table 3. Regression Result of the Buchowski−Ksiazczak λh Equation for BDPM in Different Pure Solvents

solvent	λ	h	10^4 rmsd
N,*N*-dimethylformamide	0.46	5266.4	10.42
dimethyl sulfoxide	0.56	5387.8	8.08
2-butanone	0.40	7473.1	2.65
cyclohexanone	0.51	5455.5	8.78
1,4-dioxane	0.51	5567.9	6.80
toluene	0.33	11086.2	2.20

where λ and h are the empirical parameters, T is the absolute temperature, x is the mole fraction solubility of BDPM, and T_m is the melting temperature of BDPM, $T_m = 470.65$ K. The experimental data of mole fraction solubility in Table 1 were correlated with eq 4, and the values of the two parameters λ and h together with the rmsd's are listed in Table 3; the correlation is also satisfactory.

Conclusions

Using the laser monitoring observation technique, the solubility of BDPM in pure *N*,*N*-dimethylformamide, dimethyl sulfoxide, 2-butanone, cyclohexanone, 1,4-dioxane, and toluene as a function of temperature was determined in this study. Depending on Tables 1 to 3 and Figure 2, some conclusions can be obtained: (1) The solubilities of BDPM in all selected solvents increase with increasing temperature. (2) The solubility of BDPM increases with the solvents in the order: toluene, 2-butanone, dimethyl sulfoxide, 1,4-dioxane, cyclohexanone, and *N*,*N*-dimethylformamide. (3) Both the Apelblat equation and the λh equation can regress the solubility data well. (4) The solubility measured in this study can be used as the solvent for the polymerization of BDPM.

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