Solubilities of *N*-[(4-Bromo-3,5-difluorine)phenyl]acrylamide in Benzene, Methanol, Pyridine, Ethanol, Acetonitrile, and Toluene at Temperatures between (284.65 and 348.95) K

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The solubility of *N*-[(4-bromo-3,5-difluorine)phenyl]acrylamide (BDPA) in pure benzene, methanol, pyridine, ethanol, acetonitrile, and toluene was measured at temperatures ranging from (284.65 to 348.95) K under atmospheric pressure. 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

Fluorine-containing polymers are particularly attractive and useful compounds because of their unique properties including high thermal, chemical, aging, and weather resistance, low dielectric constants, refractive index, surface energy, and flammability.[1,2] There are various approaches for preparing fluorine-containing acrylate emulsion, such as synthesizing core−shell fluorine-containing polyacrylate emulsion with fluorine-free acrylate and fluorine-containing acrylate monomers.[3−5]

N-[(4-Bromo-3,5-difluorine)phenyl]acrylamide (BDPA, Figure 1) is a new fluorine-containing acrylate monomer for polyreaction. BDPA was synthesized by the interaction of 4-bromo-3,5-difluoroaniline with acryloyl chloride in the presence of triethylamine. Crude BDPA was gained after concentrating and filtrating. For an extensive fluorine-containing polymer investigation, crude BDPA has to be purified by crystallization. To improve the purity and yield of BDPA, the solubility data of BDPA in different solvents are required.

In this article, solubility measurement of BDPA in pure benzene, methanol, pyridine, ethanol, acetonitrile, and toluene in the temperatures ranging from (284.65 to 348.95) K were performed at atmospheric pressure by a laser monitoring observation technique. Experimental data were correlated by the modified Apelblat equation.[6,7]

Experimental Section

Materials. The BDPA was produced in our laboratory. Portions of 200 mL of ethyl acetate, 32.1 g of 4-bromo-3,5-difluoroaniline, 25 g of sodium bicarbonate, and 0.5 g of ethyl hydroxylamine were put into a 500 mL four-mouth flask, respectively, and then 22 mL of acryloyl chloride was dropwise added. The mixture was maintained for 10 h at the temperature of 293.15 K, followed by 15 h of reflux. Ethyl acetate was removed by distillation and then cooled to room temperature. BDPA [12 g, mp (454.9 to 455.5) K, ^{1}H NMR ($CDCl_3$, 400 MHz) δ: (5.83 to 5.86) (m, 2H, CH_2), (6.19 to 6.26) (m, 1H, CH), (7.26 to 7.34) (m, 2H, ArH), (7.43 to 7.44) (m, 1H, NH), high-resolution molecular masses (calcd for $C_9H_6ONF_2Br$ 261.9679, found 261.9676)] were obtained by filtering, washing, and drying.

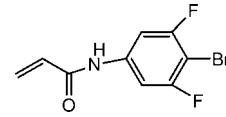

Figure 1. Structure of BDPA.

Its mass fraction purity was more than 99.2 %, determined by high-performance liquid chromatography (HPLC). The melting point is (455.0 ± 0.3) K (measured by DSC). All of the solvents, benzene, methanol, pyridine, ethanol, acetonitrile, and toluene (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 solubility of BDPA in six pure solvents was measured by the method that was described in the literature.[8−10] 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. A laser monitoring system, which 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 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 vessel. The contents of the vessel were 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 a 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 BDPA can be determined from eq 1

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

T/K	100 x_1	100($x_1 - x_1^{calc}$)/x_1	T/K	100 x_1	100($x_1 - x_1^{calc}$)/x_1
Benzene			Methanol		
296.35	0.07	−3.45	294.25	1.42	−0.23
302.95	0.11	3.99	298.65	1.63	−0.07
308.75	0.14	−0.12	303.16	1.89	0.40
310.75	0.15	1.35	308.45	2.21	0.02
317.65	0.22	2.33	312.35	2.49	−0.04
324.25	0.30	−0.06	318.15	2.98	0.16
332.05	0.44	−0.84	321.05	3.25	0.14
335.95	0.54	1.02	324.65	3.60	−0.12
340.85	0.67	−2.63	327.45	3.91	−0.24
347.05	0.94	1.05	328.95	4.10	0.09
Pyridine			Ethanol		
288.95	13.93	−0.07	295.25	2.509	0.34
292.45	14.53	0.03	297.65	2.643	−0.21
298.95	15.67	−0.002	301.55	2.919	0.33
303.85	16.59	0.04	309.25	3.508	0.02
310.25	17.84	−0.04	312.95	3.840	0.02
317.05	19.28	0.03	318.55	4.403	−0.04
322.55	20.50	0.01	326.45	5.341	−0.22
328.45	21.88	−0.01	331.35	6.039	−0.07
333.15	23.04	−0.01	334.85	6.586	−0.08
338.25	24.35	−0.03	339.55	7.401	−0.10
344.95	26.18	0.007	344.45	8.375	0.07
348.85	27.29	0.002	347.55	9.050	0.11
Acetonitrile			Toluene		
284.65	0.60	2.81	286.65	0.06	6.92
291.45	0.79	0.54	291.95	0.08	5.48
294.75	0.90	0.13	292.05	0.08	5.89
298.25	1.04	0.09	295.95	0.09	4.17
301.85	1.21	0.05	301.75	0.11	−1.35
305.35	1.39	0.14	301.85	0.12	0.83
308.45	1.58	0.26	307.95	0.15	−1.22
312.75	1.86	−0.41	312.05	0.19	1.34
316.65	2.17	−0.27	312.35	0.19	−0.03
320.05	2.48	0.07	316.05	0.22	1.65
323.85	2.88	0.21	319.25	0.26	0.15
327.65	3.32	0.25	319.35	0.26	0.09
331.75	3.86	−0.33	323.75	0.30	−2.77
334.15	4.23	0.04	327.95	0.35	−6.22
337.75	4.82	−0.22	331.15	0.43	−0.77
340.45	5.33	−0.12	334.65	0.51	2.34
343.55	5.96	−0.17	337.65	0.59	2.88
346.35	6.62	0.21	342.35	0.69	−1.24
348.95	7.25	0.10			

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

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 the experimental results. Considering other factors, the relative uncertainty in the measurement of the mole fraction of BDPA was within 0.5 %.

Results and Discussion

The solubility data of BDPA in pure benzene, methanol, pyridine, ethanol, acetonitrile, and toluene are listed in Table 1 and shown in Figure 2. In Table 1, x_1 expresses the experimental solubility value. x_1^{calc} expresses the calculated solubility value. From Table 1 and Figure 2, it can be seen that at temperatures ranging from (284.65 to 348.95) K, the solubility of BDPA increases with temperature in all six pure solvents, and the BDPA is slightly soluble in toluene and benzene, while the solubility of BDPA in pure pyridine is obviously higher than in other solvents. The temperature T dependence of BDPA solubility in pure solvents can be computed by the modified Apelblat equation

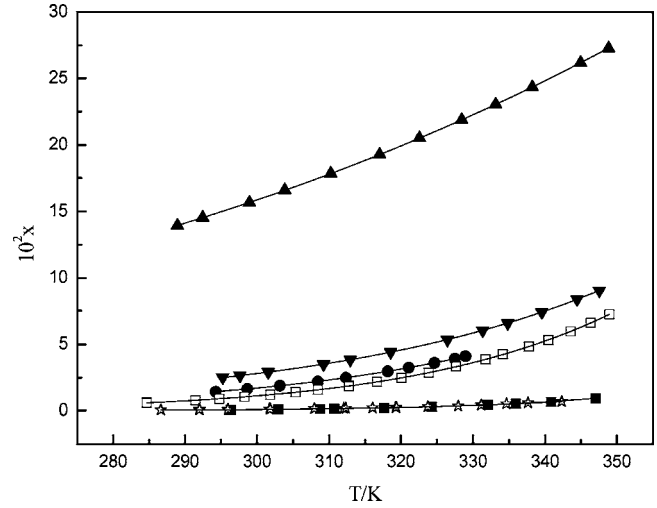

Figure 2. Solubilities of BDPA in different solvents: ■, benzene; ●, methanol; ▲, pyridine; ▼, ethanol; □, acetonitrile; ☆, toluene. The value of calculated solubility is shown as a solid line.

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

solvent	A	B	C	10^5 rmsd
benzene	−155.50	2640.1	24.48	7.09
methanol	−88.57	1404.4	13.99	4.84
pyridine	−32.30	474.4	5.06	5.22
ethanol	−114.76	3130.3	17.66	6.84
acetonitrile	−81.81	323.2	13.37	7.89
toluene	−99.22	488.6	15.90	8.03

$$\ln x_1^{calc} = A + \frac{B}{T/\mathrm{K}} + C \ln T/\mathrm{K} \quad (2)$$

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's), are listed in Table 2. The rmsd is defined as

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

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.

Conclusions

From Tables 1 and 2 and Figure 2, we can draw the following conclusions: (1) The solubilities of BDPA in pure benzene, methanol, pyridine, ethanol, acetonitrile, and toluene are a function of temperature. (2) The solubility of BDPA increases with the solvents in the following order: toluene, benzene, acetonitrile, methanol, ethanol, and pyridine. (3) The calculated solubility of BDPA sets a good coherence with the experimental values. The experimental solubility and correlation equation in this work can be used as essential data and models in the purification process of BDPA.

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