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Solubilities of Triadimefon in Acetone + Water from (278.15 to 333.15) K

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The solubilities of triadimefon in acetone + water were measured at temperatures from (278.15 to 333.15) K by a synthetic method at atmospheric pressure. The experimental data were well correlated with the modified Apelblat equation.

Introduction

Triadimefon (1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)butanone, CAS Registry No. 43121-43-3) is a systemic, broad spectrum, eradicant, and protectant fungicide against plant pathogens, especially powdery mildew, loose smut, and rust of cereals and other crops.[1−3] The molecular structure of triadimefon is illustrated in Figure 1. Pure triadimefon is obtained by crystallization, but there are few solubility data for triadimefon reported.[4] In this study, the solubilities of triadimefon in acetone + water have been measured from (278.15 to 333.15) K at atmospheric pressure. The experimental data were correlated with the modified Apelblat equation.[5−7]

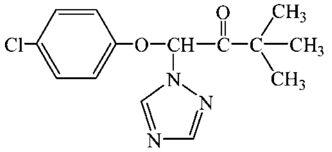

Figure 1. Molecular structure of triadimefon.

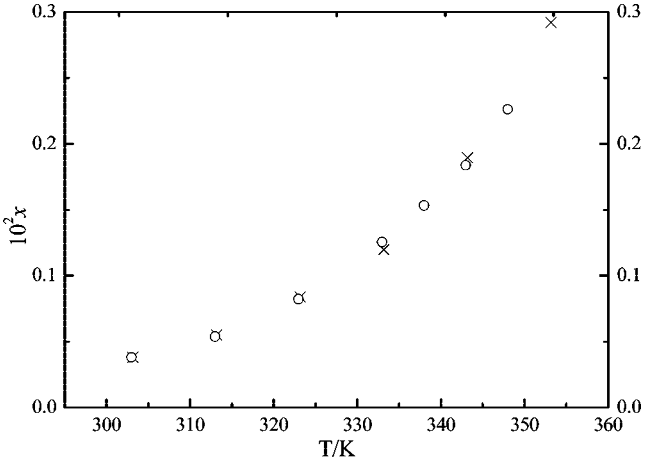

Figure 2. Solubility of 2-hydroxybenzoic acid in water: ×, this work; ○, literature.[9]

Experimental Section

Materials. High-grade acetone from Tianjin Kemel Chemical Reagent Co., Ltd. was used directly without further purification, and its mass fraction purity was greater than 99 %. Triadimefon crystals (mass fraction purity > 95 %) from Jiangsu Jiannong Agrochemical Co., Ltd. were recrystallized with ethanol at least three times to obtain the purity of 99.5 % determined by liquid chromatography (type Waters 600E, Waters Co.) and was stored under nitrogen. Analysis for water contamination using the Karl Fischer technique (method TitroLine KF) for triadimefon showed that the mass fraction was less than 0.001 %. The melting point temperature (T_m) is (355.15 to 355.85) K measured by a digital melting point apparatus (type RY-51, Shanghai Precision & Scientific Instrument Co., Ltd.), which compares well with the literature value.[4] The water used in the experiments was double distilled water.

Apparatus and Procedure. The solubilities were measured by a dynamic method at atmospheric pressure.[6,8] The experiments were carried out in a magnetically stirred, jacketed glass vessel (80 cm^3). A constant temperature (± 0.05 K) was maintained by circulating water through the outer jacket from a super thermostatic water-circulator bath (type HWC-52, Shanghai Cany Precision Instrument Co., Ltd.) at the required temperature. A condenser was connected with the vessel to prevent the solvent from evaporating. A mercury-in-glass thermometer was inserted into the inner chamber of the vessels for the measurement of the temperature. The laser monitoring system consists of a laser generator, a photoelectric transformer, and a light intensity display. A laser beam was used to observe the dissolution of the solid−liquid mixture. The light signal transmitted through the vessel was collected by a detector (type FGF-III), which decided the rate of temperature rise and estimated the equilibrium point of acetone + water on the basis of the signal change. In the early stage of the experiment, the laser beam was blocked by the unsolved particles of triadimefon in the solution, so the intensity of the laser beam penetrating the vessel was lower. The intensity increased gradually along with the increase of the amount of triadimefon dissolved. When the last portion of triadimefon just disappeared, the intensity of the laser beam penetrating the vessel reached the maximum, and the temperature was recorded.

At the beginning of the experiment, solvents for the solubility measurement were prepared by mass using an analytical balance (type XS104, Mettler-Toledo Co.). The balance has a range of measurement up to 120 g, with an uncertainty of ± 0.0001 g. Before the solubility measurement, through the condenser, high-purity nitrogen (99.9995 % by mass, 10 mL·min^{-1}) was fed into the solvent for 2 h to remove the dissolved oxygen. Predetermined amounts of triadimefon were weighed and transferred into the vessel. The contents of the vessel were

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Table 1. Mole Fraction Solubilities (x) of Triadimefon in (w) Water + (1 − w) Acetone, Where w is the Mass Fraction

T/K	10^2x	$10^2\Delta x^a$	T/K	10^2x	$10^2\Delta x^a$
		$w = 0.10$			
278.15	10.5988	0.06	308.15	26.5799	0.02
283.15	12.3423	0.05	313.15	31.0321	0.04
288.15	14.3648	0.01	318.15	36.2446	0.04
293.15	16.7415	0.02	323.15	42.3454	0.02
298.15	19.5241	0.03	328.15	49.4832	0.00
303.15	22.7780	0.02	333.15	57.8315	0.04
		$w = 0.20$			
278.15	6.6177	0.11	308.15	9.9311	0.18
283.15	7.1003	0.00	313.15	10.5880	0.09
288.15	7.6094	0.17	318.15	11.2780	0.03
293.15	8.1460	0.03	323.15	12.0020	0.07
298.15	8.7111	0.08	328.15	12.7600	0.19
303.15	9.3058	0.04	333.15	13.5551	0.11
		$w = 0.30$			
278.15	3.2397	0.02	308.15	4.4131	0.05
283.15	3.4906	0.02	313.15	4.5144	0.11
288.15	3.7233	0.00	318.15	4.6005	0.14
293.15	3.9309	0.10	323.15	4.6428	0.05
298.15	4.1207	0.03	328.15	4.6585	0.01
303.15	4.2875	0.11	333.15	4.6490	0.05
		$w = 0.40$			
278.15	0.9900	1.93	308.15	1.8602	1.24
283.15	1.1767	1.32	313.15	1.9644	1.50
288.15	1.3080	0.46	318.15	2.0509	0.85
293.15	1.4944	2.04	323.15	2.1183	0.92
298.15	1.6366	1.80	328.15	2.1660	1.17
303.15	1.7348	0.31	333.15	2.1939	0.81
		$w = 0.50$			
278.15	0.2693	2.00	308.15	0.5755	1.14
283.15	0.3253	0.38	313.15	0.6006	3.55
288.15	0.3816	0.37	318.15	0.6332	3.48
293.15	0.4496	3.44	323.15	0.6719	1.37
298.15	0.4893	0.52	328.15	0.7075	1.16
303.15	0.5566	3.60	333.15	0.7277	2.51
		$w = 0.60$			
278.15	0.0532	1.25	308.15	0.1590	2.62
283.15	0.0653	2.95	313.15	0.1719	0.63
288.15	0.0853	2.02	318.15	0.1830	0.96
293.15	0.1006	0.53	323.15	0.1925	1.90
298.15	0.1182	0.94	328.15	0.2036	0.52
303.15	0.1372	0.18	333.15	0.2128	1.30
		$w = 0.70$			
278.15	0.0072	0.05	308.15	0.0400	4.03
283.15	0.0103	0.49	313.15	0.0454	0.68
288.15	0.0148	3.03	318.15	0.0517	2.67
293.15	0.0182	5.64	323.15	0.0588	2.36
298.15	0.0247	0.97	328.15	0.0662	0.82
303.15	0.0326	3.73	333.15	0.0742	2.33
		$w = 0.80$			
278.15	0.0007	6.87	308.15	0.0057	2.02
283.15	0.0011	3.57	313.15	0.0074	3.58
288.15	0.0016	6.56	318.15	0.0105	0.31
293.15	0.0021	0.22	323.15	0.0136	4.63
298.15	0.0029	0.71	328.15	0.0189	1.87
303.15	0.004	1.23	333.15	0.0274	5.34
		$w = 0.90$			
278.15	0.00003	3.33	308.15	0.0007	7.44
283.15	0.00006	1.67	313.15	0.0012	4.51
288.15	0.0001	7.39	318.15	0.0017	0.33
293.15	0.0002	8.88	323.15	0.0023	7.96
298.15	0.0003	0.12	328.15	0.0036	1.67
303.15	0.0005	3.69	333.15	0.0051	3.00

[a] $\Delta x = (x - x_c)/x$, where x_c is the solubility value calculated from eq 1.

heated very slowly at rates less than 1 K·h^{-1} with continuous stirring to approach the solid−liquid equilibrium point. In the processes of solubility measurement, some of the solubility experiments were conducted at least three times to check the reproducibility, and the mean values were considered as the measured results. The reproducibility of the measurements was 0.1 K, which corresponds to a relative error in composition smaller than ± 1 %. Moreover, to testify the uncertainty of the measurement, a comparison with the literature values[9] for the solubility of 2-hydroxybenzoic acid in water was made, and the results are shown in Figure 2. In Figure 2, T is the absolute temperature and x is the experimental solubility in mole fraction. It is clear from Figure 2 that our experimental results show good agreement with the literature data. The deviations of the solubility are less than 2 %. In this work, the uncertainty for solubility measurement is estimated on the basis of the principle of the error propagation to be 2.0 % at the 95 % confidence level.

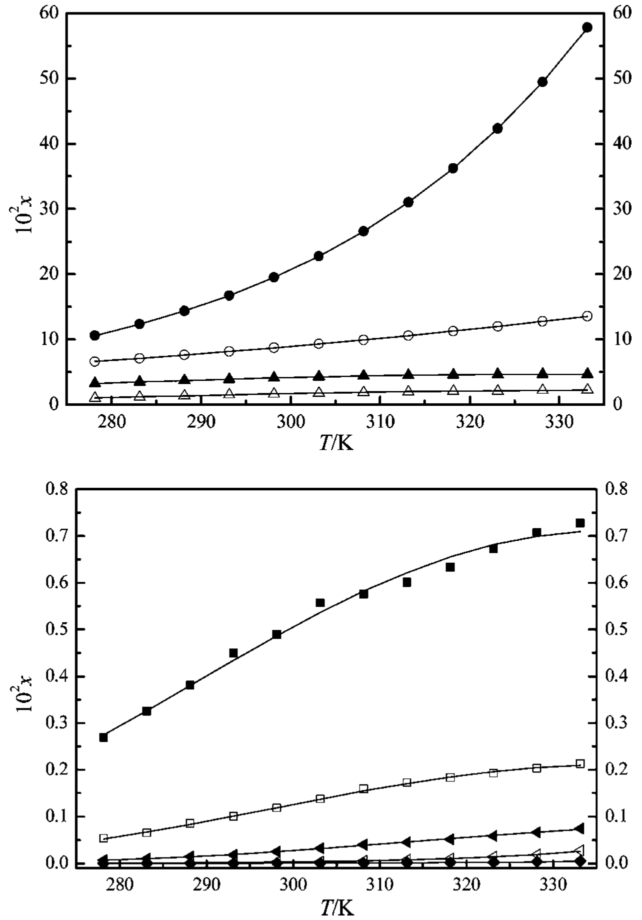

Figure 3. Solubilities of triadimefon in (w) water + (1 − w) acetone, where w is the mass fraction. ●, w = 0.10; ○, w = 0.20; ▲, w = 0.30; △, w = 0.40; ■, w = 0.50; □, w = 0.60; solid triangle pointing left, w = 0.70; open triangle pointing left, w = 0.80; ♦, w = 0.90; —, calculated from eq 1.

Results and Discussion

The measured mole fraction solubilities (x) of triadimefon in acetone + water at different temperatures (T) are presented in Table 1. The mass fraction (w) of water in the solvents was 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, and 0.90. The experimental values and calculated values are shown in Figure 3. The relationship between the mole fraction solubility and temperature is described by the modified Apelblat equation.[10]

$$\ln x = A + \frac{B}{T/\mathrm{K}} + C \ln(T/\mathrm{K}) \qquad (1)$$

Table 2. Parameters of Equation 1 for the Triadimefon + Water + Acetone System at Various Contents of Water (*w*) in the Mixed Solvent

w	*A*	*B*	*C*	10^4 (rmsd)
0.10	−128.93	3337	20.38	1.01
0.20	−26.96	84	4.25	1.14
0.30	161.69	−7979	−24.24	0.32
0.40	259.76	−13052	−38.63	2.14
0.50	323.28	−16227	−48.12	1.34
0.60	446.54	−22493	−66.31	0.21
0.70	532.13	−27758	−78.51	0.10
0.80	−126.83	199	20.31	0.05
0.90	287.08	−20688	−40.44	0.01

where x is the mole fraction solubility of triadimefon, and A, B, and C are empirical constants. The values of A, B, and C obtained from the experimental solubility data in the systems together with the root-mean-square deviations (rmsd's) are listed in Table 2, respectively. The rmsd is defined as

$$\mathrm{rmsd} = \left[\sum_{i=1}^{N} \frac{(x_{\mathrm{ci}} - x_{\mathrm{i}})^2}{N}\right]^{1/2} \quad (2)$$

where N is the number of experimental points; x_{ci} is the solubility calculated by eq 1; and x_{i} represents the experimental solubility value.

From Table 1 and Table 2, the calculated solubilities are in good agreement with the experimental data, which indicate that the modified Apelblat equation can be used to correlate the solubility data of triadimefon in actone + water. The overall rmsd of 108 data points for the acetone + water system at various contents of water in the mixed solvent is 0.0079 %. The experimental solubility and correlation equation in this work can be used as essential data and models to serve the purification process of triadimefon.

From the data shown in Table 1, the T, x curves for the triadimefon + acetone + water system are shown in Figure 3. It described the temperature dependence of the solubility at various compositions of the mixed solvent. From the results shown in Table 1 and Figure 3, it can be seen that the solubility of triadimefon increases at constant temperature with the increase of the amount of acetone in the mixed solvent, which may be explained by the "like dissolves like" principle. When the water mass fractions are equal to 0.1 and 0.2, the solubilities of triadimefon in the mixed solvent are small at low temperatures but quickly increase at high temperatures, which could be used for the recrystallization process of triadimefon.

Literature Cited

(1) Singh, N. Factors Affecting Triadimefon Degradation in Soils. *J. Agric. Food Chem.* **2005**, *53*, 70–75.

(2) Silva, J. P. D.; Silva, A. M. D. Vapor Pressure of Triadimefon by the Gas Saturation Method. *J. Chem. Eng. Data* **1997**, *42*, 538–540.

(3) Gagnaire, F.; Micillino, J. C. Effects of Triadimefon on Extracellular Dopamine, DOPAC, HVA and 5-HIAA in Adult Rat Striatum. *Toxicology* **2006**, *217*, 91–104.

(4) Kidd, H.; James, D. R. *The Agrochemicals Handbook*, 3rd ed.; Thomas Graham House: Cambridge, 1991.

(5) Wang, F. A.; Wang, L. C.; Song, J. C.; Wang, L.; Chen, H. S. Solubilities of Bis(2,2,6,6-tetramethyl-4-piperidinyl)Maleate in Hexane, Heptane, Octane, m-Xylene, and Tetrahydrofuran from (253.15 to 310.15) K. *J. Chem. Eng. Data* **2004**, *49*, 1539–1541.

(6) Robert, K. L.; Rousseau, R. W.; Teja, A. S. Solubility of Long Chain n-Alkanes in Heptane Between 280 and 350. *J. Chem. Eng. Data* **1994**, *39*, 793–795.

(7) Kong, M Z.; Shi, X. H.; Cao, Y. C.; Zhou, C. R. Solubility of Imidacloprid in Different Solvents. *J. Chem. Eng. Data* **2008**, *53*, 615–618.

(8) Buchowski, H.; Ksiazczak, A.; Pietrzyk, S. Solvent Activity along a Saturation Line and Solubility of Hydrogen Bonding Solid. *J. Phys. Chem.* **1980**, *84*, 975–979.

(9) Shalmashi, A.; Eliassi, A. Solubility of Salicylic Acid in Water, Ethanol, Carbon Tetrachloride, Ethyl Acetate, and Xylene. *J. Chem. Eng. Data* **2008**, *53*, 199–200.

(10) Apelblat, A.; Manzurola, E. Solubilities of o-Acetylsalicylic, 4-Aminosalicylic, 3,5-Dinitrosalicylic, and p-Toluic Acid, and Magnesium-DL-Aspartate in Water from T=(278 to 348) K. *J. Chem. Thermodyn.* **1999**, *31*, 85–91.

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