Solubility of Triadimefon in Organic Solvents at Temperatures between (288.15 and 333.15) K

Xu-Zhao Yang* and Jun Wang

Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou University of Light Industry, Henan 450002, People's Republic of China

Using a laser monitoring technique, the solubility of triadimefon in acetonitrile, hexane, heptane, cyclohexane, methylbenzene, and 1,4-dimethylbenzene was measured at temperatures from (288.15 to 333.15) K at a pressure of 0.1 MPa. The experimental data were well-correlated with the modified Apelblat equation and the λh model.

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.[1–4] Pure triadimefon is obtained by crystallization, and solvent selection is important for the optimization of the crystallization process, so it is necessary to get the solubility data of triadimefon in different solvents. In a previous study, the solubilities of triadimefon in (acetone + water) were measured at temperatures from (278.15 to 333.15) K at $p = 0.1$ MPa.[5] This paper is a continuation of our systematic study of triadimefon solubility measurements. In this work, the solubilities of triadimefon in acetonitrile, hexane, heptane, cyclohexane, methylbenzene, and 1,4-dimethylbenzene have been measured at temperatures between (288.15 and 333.15) K at $p = 0.1$ MPa. The experimental data were correlated with the modified Apelblat equation and the λh model.

Experimental Section

Materials. Triadimefon crystals (mass fraction purity > 0.95) from Jiangsu Jiannong Agrochemical Co., Ltd. were recrystallized from aqueous acetone solution at least three times to obtain the purity of 0.995 determined by liquid chromatography (type Waters 600E, Waters Co.) and was stored under nitrogen. The analysis for water content with Karl Fischer titration (method TitroLine KF) for triadimefon showed that the water mass fraction was less than 0.0001. The melting point temperature was between (355.15 and 355.85) K as measured by a digital melting point apparatus (type RY-51, Shanghai Precision & Scientific Instrument Co., Ltd.), which compares well with the literature value.[4] High-grade acetonitrile, hexane, heptane, cyclohexane, methylbenzene, and 1,4-dimethylbenzene from Tianjin Kemel Chemical Reagent Co., Ltd. was used directly without further purification, and its mass fraction purity was greater than 0.99.

Apparatus and Procedure. The solubilities were measured by a dynamic method at atmospheric pressure. The experiments were carried out in a magnetically stirred, jacketed glass vessel (15 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. At the beginning of the experiment, solvents for the solubility measurement were prepared by mass using an analytical balance (type FA2004A, Shanghai Jingtian Electronic Instrument Co., Ltd.). The balance has a range of measurement up to 200 g, with an uncertainty of ± 0.0001 g. Before the solubility measurement, through the condenser, high-purity nitrogen (0.999995 by mass, 10 $cm^3 \cdot min^{-1}$) 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 heated very slowly at rates less than 1 $K \cdot h^{-1}$ with continuous stirring to approach the solid−liquid equilibrium point.

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 the triadimefon + organic solvent 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. 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 temperatures was 0.1 K. 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.

Results and Discussion

The measured mole fraction solubilities (x) of triadimefon in acetonitrile, hexane, heptane, cyclohexane, methylbenzene, and 1,4-dimethylbenzene are listed in Table 1 and shown in

* Corresponding author. E-mail: xuzhao5378@sina.com.

10.1021/je901024t
Published on Web 03/17/2010

Table 1. Mole Fraction Solubility of Triadimefon in Organic Solvents

T	$10^2\,x$					
K	acetonitrile	hexane	heptane	cyclohexane	methylbenzene	1,4-dimethylbenzene
288.15	1.1015	0.0262	0.1287	0.0445	9.1554	6.3077
293.15	1.3167	0.0539	0.2043	0.1425	11.8879	8.4624
298.15	1.6218	0.1037	0.3207	0.3818	15.3630	11.2477
303.15	1.9623	0.1971	0.4835	0.8731	19.1764	14.6843
308.15	2.3803	0.3505	0.7369	1.7798	23.4827	18.8092
313.15	2.8519	0.5917	1.1109	3.1521	28.2491	23.8838
318.15	3.4015	0.9839	1.6367	4.8935	33.3137	29.9020
323.15	4.0722	1.5569	2.3838	6.9153	38.0972	37.1877
328.15	4.7921	2.3304	3.4031	8.6871	43.1157	45.5620
333.15	5.6985	3.5427	4.9107	9.8619	47.4974	55.3111

Table 2. Parameters of Equations 1 and 2 for Triadimefon in Organic Solvents

	λh equation			Apelblat equation			
solvent	Λ	h	10^3 (rmsd)	A	B	C	10^3 (rmsd)
acetonitrile	0.0173	73815	1.68	−40.81	−1295	7.20	0.12
hexane	0.1425	58655	0.47	631.32	−38166	−89.54	0.17
heptane	0.1324	50641	0.42	18.85	−7692	0.21	0.11
cyclohexane	0.2380	23853	0.78	2828.11	−139954	−414.96	0.17
methylbenzene	0.7889	3851	4.54	407.69	−21816	−59.04	1.28
1,4-dimethylbenzene	2.0821	2557	2.94	143.15	−10595	−19.27	0.36

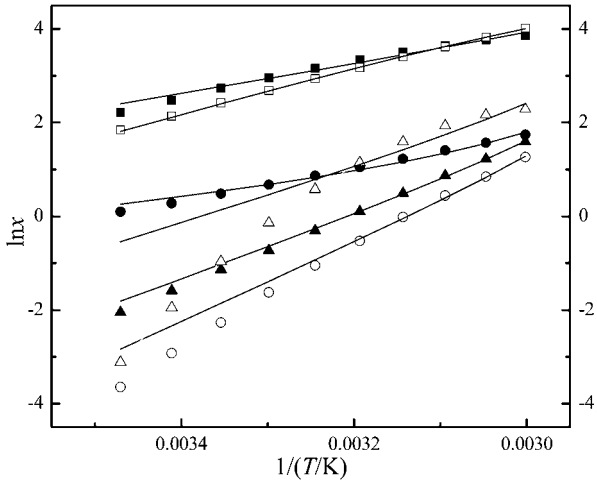

Figure 1. Mole fraction solubilities of triadimefon in pure solvents. ●, acetonitrile; ○, hexane; ▲, heptane; △, cyclohexane; ■, methylbenzene; □, 1,4-dimethylbenzene; —, calculated from the λh model.

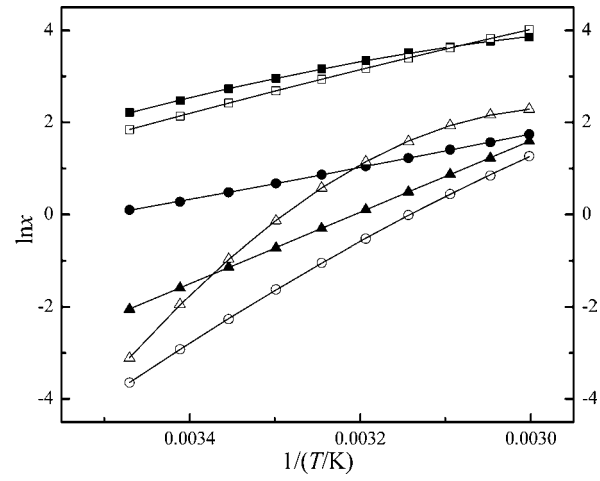

Figure 2. Mole fraction solubilities of triadimefon in pure solvents. ●, acetonitrile; ○, hexane; ▲, heptane; △, cyclohexane; ■, methylbenzene; □, 1,4-dimethylbenzene; —, calculated from the modified Apelblat equation.

Figures 1 and 2. The relationship between mole fraction of the solubility and temperature is described by the λh model and the modified Apelblat equation.[6–9] The λh model which is a semiempirical equation is shown as follows

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

where λ and h are the model parameters determined by the experimental data and are listed in Table 2, x is the mole fraction of the solubility of triadimefon at the system temperature T, and T_m is the normal melting temperature of triadimefon.

The modified Apelblat equation is shown as follows

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

where x is the mole fraction solubility of triadimefon, T is the absolute temperature, and A, B, and C are empirical constants. The values of A, B, and C obtained from the experimental solubility data in the systems are listed in Table 2.

The root-mean-square deviations (rmsd's) for the λh model and the modified Apelblat equation are listed in Table 2, respectively. The rmsd is defined as

$$\mathrm{rmsd} = \left[\sum_{i=1}^{N}\frac{(x_{ci} - x_i)^2}{N}\right]^{1/2} \qquad (3)$$

where N is the number of experimental points, x_{ci} is the calculated solubility, and x_i represents the experimental solubility value.

From Tables 1 and 2 and Figures 1 and 2, we can draw the following conclusions: (a) The solubility of triadimefon in acetonitrile, hexane, heptane, cyclohexane, methylbenzene, and 1,4-dimethylbenzene is a function of temperature and increases with increasing temperature. (b) The calculated solubilities of triadimefon 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. (c) The Apelblat equation was more accurate than the λh equation for this system. The experimental solubilities and correlation equation in this

work can be used as fundamental data and models in the purification process of crystallization 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) Yang, X. Z.; Wang, J.; Li, G. S. Solubilities of Triadimefon in Acetone + Water from (278.15 to 333.15) K. *J. Chem. Eng. Data* **2009**, *54*, 1409–1411.
(6) 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*-1,4-dimethylbenzene, and Tetrahydrofuran from (253.15 to 310.15) K. *J. Chem. Eng. Data* **2004**, *49*, 1539–1541.
(7) Robert, K. L.; Rousseau, R. W.; Teja, A. S. Solubility of Long Chain n-Alkanes in Heptane Between 280 and 350 K. *J. Chem. Eng. Data* **1994**, *39*, 793–795.
(8) 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.
(9) 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.

Received for review December 3, 2009. Accepted March 6, 2010.

JE901024T