Solubility and Density for Cyanazine + Ethanol + Water

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The solubility of cyanazine in water (1) and ethanol (2) has been determined over the temperature range 10–30 °C and the whole range of solvent water mass fractions $W_1 = 0.0–1.0$, and the densities of the resulting saturated solutions have also been measured. At each temperature, the solubility of cyanazine increases with increasing mole fraction x_2 of ethanol up to a local maximum at $x_2 \simeq 0.9$. The density of saturated aqueous ethanol solutions of cyanazine decreases with increasing ethanol content over the whole range. The solubility of cyanazine in aqueous ethanol at each temperature is correlated by polynomial ($W_1 = 0.3–1.0$) and exponential ($W_1 = 0.0–0.4$) expressions while the density results are fitted to an exponential expression.

Introduction

The majority of crop protection agents are currently formulated as emulsifiable concentrates. These are solutions, usually based on aromatic hydrocarbons, which form emulsions when diluted with water. Use of these solvents, however, is subject to increasing concern by international regulatory bodies. A potential alternative is a dispersible concentrate. These are solutions based on water soluble solvents which precipitate the active ingredient when diluted with water. The key to developing commercially acceptable dispersion concentrates is the control of this crystal precipitation process. The aim of the present work is to determine solubility and density data for solutions of cyanazine (systematic IUPAC name 2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropionitrile) in aqueous ethanol mixtures. Such solubility data can be used to determine the supersaturation of the system from which induction periods can be measured (the time from the creation of the supersaturation state to the detection of the first crystal). These times may then be used to identify the crystallization kinetics and mechanism using the theories developed for inorganic substances (*1*).

Experimental Section

For the solubility and density measurements, 100 cm^3 centrifuge tubes stoppered to prevent liquid evaporation were used to prepare saturated solutions. Each tube was immersed in its respective water bath controlled to ±0.1 °C and continuously shaken for 24 h to ensure equilibrium saturation. At the end of this period, the solutions were allowed to stand for at least 2 h at constant temperature until clear. The solutions were then filtered, and liquor samples diluted with absolute alcohol were analyzed. The solvents used were distilled water and analytical-grade ethanol with a minimum assay of 99 mass % (BDH Chemicals Ltd.). The cyanazine used was 97.6 mass % pure (Bladex; Shell Chemicals Ltd.).

HPLC calibration curves of peak area versus cyanazine concentration for undersaturated cyanazine solutions were first obtained at all three temperatures having correlation coefficients ≥0.9999. The concentrations of the saturated cyanazine solutions were then determined over the whole mole fraction range for ethanol + water. The densities of

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Table 1. Measured Solubility s and Solution Density ϱ of Cyanazine in Water (1) + Ethanol (2) at 10, 20, and 30 °C

W_1	x_2	$s \times 10^{-2}$/(g/100 g of solvent)	ϱ/(g cm^3) solution	ϱ/(g cm^3) solvent
		$T = 10$ °C		
1.00	0.000	1.14	0.9997	0.9997
0.90	0.042	2.59	0.9841	0.9840
0.80	0.089	6.03	0.9728	0.9726
0.70	0.144	19.90	0.9603	0.9599
0.60	0.207	68.60	0.9437	0.9425
0.55	0.243	113.60		
0.50	0.281	129.10	0.9246	0.9217
0.45	0.324	178.40		
0.40	0.370	192.20	0.9048	0.8994
0.35	0.421	231.50		
0.30	0.477	239.60	0.8849	0.8761
0.25	0.540	321.40		
0.20	0.610	328.90	0.8637	0.8521
0.15	0.689	324.50		
0.10	0.779	313.80	0.8389	0.8266
0.05	0.881	365.10		
0.00	1.000	305.60	0.8090	0.7980
		$T = 20$ °C		
1.00	0.000	1.43	0.9983	0.9983
0.90	0.042	3.45	0.9820	0.9820
0.80	0.089	8.86	0.9689	0.9688
0.70	0.144	28.10	0.9546	0.9536
0.60	0.207	94.20	0.9371	0.9354
0.55	0.243	113.60		
0.50	0.281	129.10	0.9181	0.9140
0.45	0.324	224.10		
0.40	0.370		0.8985	0.8913
0.35	0.421	264.70		
0.30	0.477	304.80	0.8788	0.8677
0.25	0.540	287.80		
0.20	0.610	334.50	0.8580	0.8435
0.15	0.689	338.20		
0.10	0.779	339.20	0.8334	0.8180
0.05	0.881	309.60		
0.00	1.000	325.20	0.8027	0.7895
		$T = 30$ °C		
1.00	0.000	1.89	0.9949	0.9957
0.90	0.042	4.94	0.9789	0.9788
0.80	0.089	16.30	0.9643	0.9640
0.70	0.144	50.20	0.9489	0.9476
0.60	0.207		0.9309	0.9287
0.55	0.243	170.80		
0.50	0.281	212.30	0.9120	0.9059
0.45	0.324	302.30		
0.40	0.370	268.70	0.8935	0.8829
0.35	0.421	363.80		
0.30	0.477	341.10	0.8749	0.8592
0.20	0.610	471.40	0.8551	0.8350
0.10	0.779	508.20	0.8308	0.8093
0.05	0.881	521.70		
0.00	1.000	438.00	0.7989	0.7809

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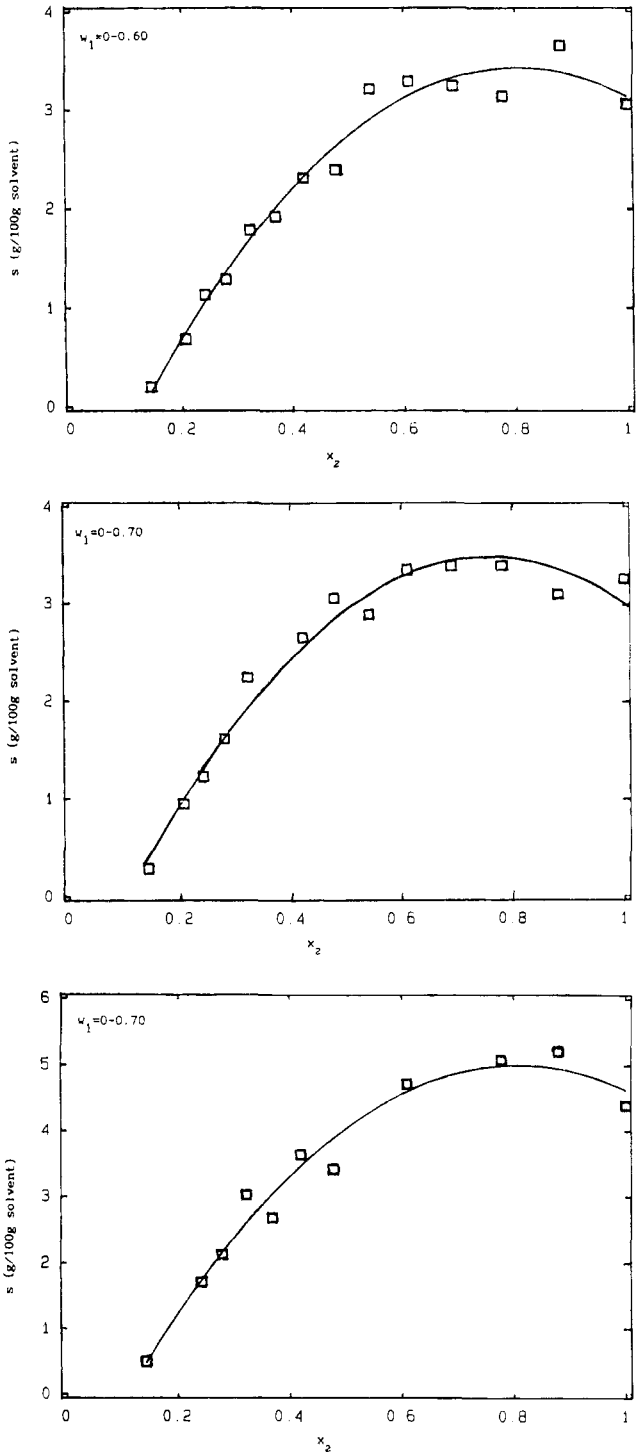

Figure 1. (a, top) Solubility s of cyanazine in water (1) + ethanol (2) at 10 °C. (b, middle) Solubility s of cyanazine in water (1) + ethanol (2) at 20 °C. (c, bottom) Solubility s of cyanazine in water (1) + ethanol (2) at 30 °C.

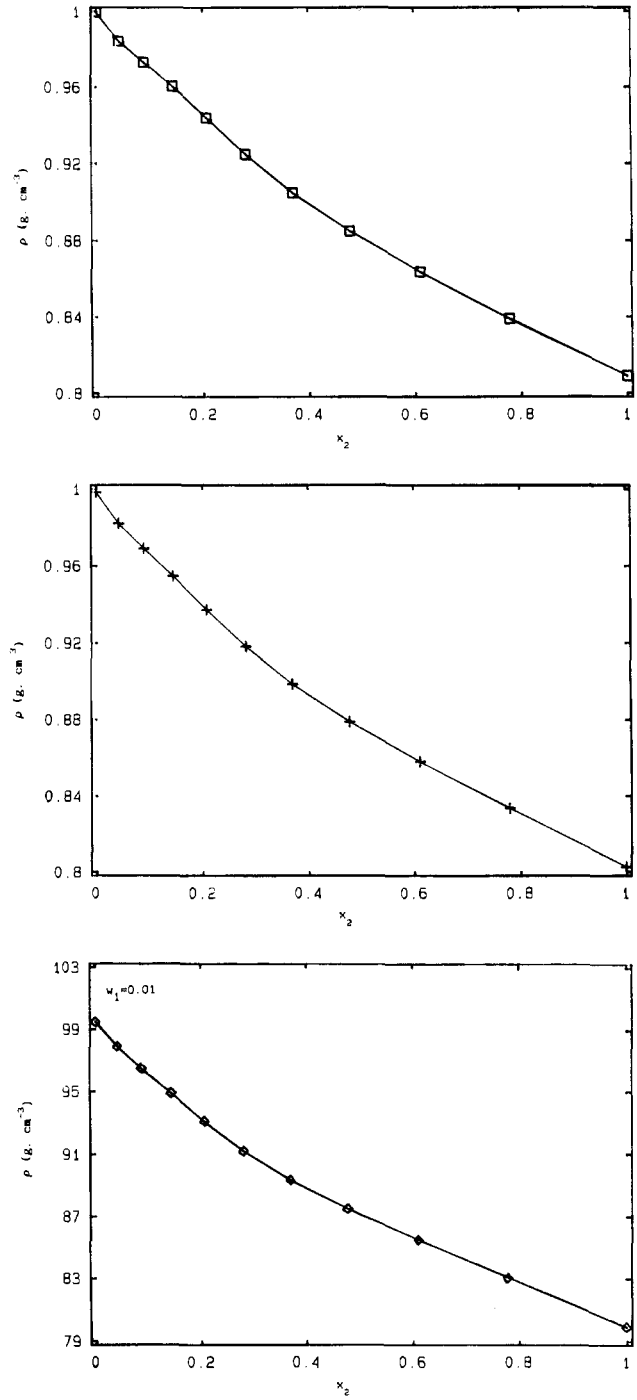

Figure 2. (a, top) Density ϱ of saturated solutions of cyanazine in water (1) + ethanol (2) at 10 °C. (b, middle) Density ϱ of saturated solutions of cyanazine in water (1) + ethanol (2) at 20 °C. (c, bottom) Density ϱ of saturated solutions of cyanazine in water (1) + ethanol (2) at 30 °C.

the saturated solutions were determined using a digital densitometer (PAAR DMA60) and measuring cell (PAAR DMA 602W) with a claimed accuracy to 0.000 01 g/cm^3 (*3*). The solubility and density data are listed in Table 1. For convenience during mass balance calculations during subsequent crystallization kinetics experiments, solvent concentrations are expressed on a mass fraction basis while for solubility and density correlation solution concentrations are best expressed on a mole fraction basis. The resulting solubility results for cyanazine in water (1) + ethanol (2) are best correlated over two ranges using polynomial and exponential expressions, respectively. The following expressions have been fitted to the data over the ranges of concentration and temperature indicated:

$$0.3 < W_1 < 1.0 \quad t = 10, 20, 30\ ^\circ\mathrm{C} \quad s = A + Bx_2 + Cx_2^2 \tag{1}$$

$$0.0 < W_1 < 0.4 \quad t = 20, 30\ ^\circ\mathrm{C} \quad \ln(s) = A + Bx_2 + Cx_2^2 \tag{2}$$

$$0.0 < 0.4 \quad t = 10\ ^\circ\mathrm{C} \quad \ln(s) = A + Bx_2 \tag{3}$$

where W_1 is the mass fraction of water in the solvent, s is the equilibrium concentration of cyanazine (g of cyanazine/

Table 2. Coefficients of Model Eqs 1–3, Standard Deviation σ, and Correlation Coefficient R^2 for the Solubility of Cyanazine in Water (1) + Ethanol (2)

(a) Coefficients of Model Eqs 1–3

T/K	W_1	A	B	C
283	1.0–0.60	−4.497 68	19.921 23	
283	0.7–0.00	−1.434 67	12.117 54	−7.550 19
293	1.0–0.60	−4.376 50	23.349 71	−12.012 18
293	0.7–0.00	−1.216 90	12.403 48	−8.183 53
303	1.0–0.60	−4.281 80	32.481 74	−42.028 16
303	0.7–0.00	−1.694 37	16.597 93	−10.292 87

(b) Standard Deviation σ and Correlation Coefficient R^2

T/K	W_1	$\sigma \times 10^5$/(g/100 g of solvent)	R^2
283	1.0–0.60	1.33	0.9999
283	0.7–0.00	3380.00	0.9761
293	1.0–0.60	0.78	0.9999
293	0.7–0.00	3570.00	0.9733
303	1.0–0.55	1.60	0.9999
303	0.7–0.00	8850.00	0.9683

100 g of aqueous ethanol), x_2 is the molar fraction of ethanol, and A, B, and C are coefficients for each of the eqs 1–3. Values obtained for A, B, and C are listed in Table 2. The standard deviations σ for solubility and the density curves at 10, 20, and 30 °C are obtained from the following expression:

$$\sigma^2 = \frac{\sum(x - \bar{x})^2}{N - 1} \tag{4}$$

where x is the experimental value, $\bar{x}$ is the calculated value, and N is the number of data points.

Densities at 10, 20, and 30 °C were also closely fitted using eq 2. Solubility curves over the range $x_2 = 0–1.0$ are illustrated in Figure 1, and those for density in Figure 2. The standard deviation and the correlation coefficient for each set of solubility and density measurements are reported in Table 3.

Table 3. Coefficients of Model Eqs 1–3, Standard Deviation σ, and Correlation Coefficient R^2 for the Density of Cyanazine + Water (1) + Ethanol (2) Solutions

(a) Coefficients of Model Eqs 1–3

T/K	W_1	A	B	C
283	0–0.60	−0.005 66	−0.275 95	0.070 83
293	0–0.60	−0.013 71	−0.271 00	0.066 29
303	0–0.60	−0.024 40	−0.251 27	0.052 82

(b) Standard Deviation σ and Correlation Coefficient R^2

T/K	W_1	$\sigma \times 10^6$/(g/cm^3)	R^2
283	0.6–0.00	3.80	0.9991
293	0.6–0.00	4.60	0.9989
303	0.6–0.00	6.20	0.9983

Conclusion

The solubility measurements are well-correlated by the exponential function (eq 2) in the range $W_1 = 0.0–0.40$ while those in the range $W_1 = 0.3–1.0$ fitted using eq 3 are somewhat less precise, but are, nevertheless, still accurate enough for the intended purpose, *i.e.*, estimation of the level of supersaturation in studies of nucleation and crystal growth.

Similarly the correlation coefficients obtained for density measurements indicate that the experimental data are well-correlated by the polynomial expression (eq 1) at 10, 20, and 30 °C.

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Received for review July 7, 1994. Accepted September 28, 1994.[⊗]

JE940130L

[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1994.