Anal. Chem. **2001,** *73,* 740−745

Solubility of Triazine Pesticides in Pure and Modified Subcritical Water

Meredith S. S. Curren*,† and Jerry W. King

Food Quality and Safety Research, National Center for Agricultural Utilization Research, ARS/USDA, 1815 North University Street, Peoria, Illinois 61604

Solubility measurements in pure and modified water serve as a basis for optimizing the subcritical water extraction of target analytes such as food contaminants. The solvent strength of the water is affected by both the system's temperature and the amount and type of cosolvent modifier that is added to the water, which causes a reduction in the dielectric constant of water. In the present work, the solubilities of the triazine pesticides atrazine, cyanazine, and simazine were measured in pure and modified water at temperatures ranging from 50 to 125 °C and at a pressure of 50 atm. The solubility data were obtained using a static solubility apparatus with on-line liquid chromatographic (LC) detection. By increasing the temperature of the water, the solubilities of the triazine pesticides increased approximately 3-fold in pure water for each 25 °C temperature increment. Cyanazine was 5 times more soluble than atrazine and an order of magnitude more soluble than simazine at 100 °C. The solubility of atrazine was also measured in ambient and hot water modified with ethanol and urea. At 100 °C, the solubility of atrazine is doubled when the water is modified with urea, and is increased over an order of magnitude when ethanol is used as modifier. The data, therefore, indicate that adding a cosolvent to water in addition to increasing the system temperature increases the solubilities of triazine pesticides in subcritical water. It was further determined that the solutes do not thermally degrade or hydrolyze at the temperatures reported in this study.

The reduction or total elimination of toxic organic solvents used in analytical extraction procedures is highly desirable from environmental and health perspectives. Toward that end, subcritical or "hot" water has been investigated as an alternative extraction agent over the past several years.[1−10] The advantages of using subcritical water are its nontoxic nature, low cost, and the fact that it can be readily obtained and disposed of. In addition, its solubility characteristics can be varied as a function of temperature if the water is compressed to maintain the liquid state. Water is also a convenient solvent with respect to the sample matrix in that the sample does not have to be dried prior to extraction.

The dielectric constant (ϵ) of ambient water is very high (ϵ = 78.5), thereby limiting the extraction of many target analytes. However, the polarity of water is lowered by increasing the temperature, which disrupts the interactions between water molecules. Supercritical water (T_c = 374 °C; P_c = 221 bar) has a low dielectric constant ($\epsilon \approx 5-15$) and good solvating properties for relatively nonpolar organics, but its use is limited by its high temperature and pressure requirements and by its potential reactivity and corrosivity. Fortunately, water exhibits modest polarities and attractive solvent properties at subcritical temperatures, that is, at temperatures between 50 and 250 °C. Increasing the temperature of compressed water has permitted the extraction of moderately polar and nonpolar organics from a wide variety of matrixes. For example, subcritical water has been used for the removal of pesticides and hydrocarbons from environmental solids.[1−8] Subcritical water extraction has also been used for the extraction of flavor and fragrance compounds from plant material and for the removal of fungicides from food samples.[9,10] Other novel applications of subcritical water have been for the remediation of hydrocarbons and pesticides in soils, and for the elution of organics from sorbents.[11−13]

Moderate pressures (>40 bar) are required to maintain the liquid state of water at subcritical temperatures. However, the narrow range of pressures required for subcritical extractions has only a small effect on the dielectric constant of water. Anderson et al. determined that the dielectric constant of water increases by only 0.6% over the pressure range of 0.101 to 11.4 bar.[14] The

* Corresponding author. Tel: (309) 681-6236. Fax: (309) 681-6524. E-mail: currenms@mail.ncaur.usda.gov.

† Although the use of brand names is necessary for the factual reporting of available data, the USDA neither guarantees nor warrants the standards of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

(1) Yang, Y.; Hawthorne, S. B.; Miller, D. J. *Environ. Sci. Technol.* **1997**, *31*, 430−437.
(2) Yang, Y.; Bøwadt, S.; Hawthorne, S. B.; Miller, D. J. *Anal. Chem.* **1995**, *67*, 4571−4576.
(3) Hartonen, K.; Inkala, K.; Kangas, M.; Riekkola, M.-L. *J. Chromatogr. A* **1997**, *785*, 219−226.
(4) Hawthorne, S. B.; Grabanski, C. B.; Hageman, K. J.; Miller, D. J. *J. Chromatogr. A* **1998**, *814*, 151−160.
(5) Field, J. A.; Monohan, K.; Reed, R. L. *Anal. Chem.* **1998**, *70*, 1956−1962.
(6) Hyötyläinen, T.; Andersson, T.; Hartonen, K.; Kuosmanen, K.; Riekkola, M.-L. *Anal. Chem.* **2000**, *72*, 3070−3076.
(7) Lou, X.; Miller, D. J.; Hawthorne, S. B. *Anal. Chem.* **2000**, *72*, 481−488.
(8) Hawthorne, S. B.; Trembley, S.; Moniot, C. L.; Grabanski, C. B.; Miller, D. J. *J. Chromatogr. A* **2000**, *886*, 237−244.
(9) Basile, A.; Jiménez-Carmona, M. M.; Clifford, A. A. *J. Agric. Food Chem.* **1998**, *46*, 5205−5209.
(10) Pawlowski, T. N.; Poole, C. F. *J. Agric. Food Chem.* **1998**, *46*, 3124−3132.
(11) Lagadec, A. J. M.; Miller, D. J.; Lilke, A. V.; Hawthorne, S. B. *Environ. Sci. Tech.* **2000**, *34*, 1542−1548.
(12) Yang, Y.; Belghazi, M.; Lagaduc, A.; Miller, D. J.; Hawthorne, S. B. *J. Chromatogr. A* **1998**, *810*, 149−159.
(13) Yang, Y.; Jones, A. D.; Eaton, C. D. *Anal. Chem.* **1999**, *71*, 3808−3813.

10.1021/ac000906n Not subject to U.S. Copyright. Publ. 2001 Am. Chem. Soc.
Published on Web 01/23/2001

measurements by Rössling and Franck indicate that the solubility of anthracene in water decreases by an order of magnitude over the pressure range of 60−2850 bar at 150 °C; however, there was negligible change in analyte solubility at the pressures normally applied for subcritical water extractions.[15] Miller and Hawthorne made the same observation for the solubility of naphthalene in water at 25 °C and over the pressure range of 1−65 bar.[16]

Extractions can be performed at lower temperatures if cosolvents are used in conjunction with adjustment of temperature to reduce the hydrogen bond density of water. This approach is preferred for solutes that are thermally unstable. Ethanol and urea are suitable salting-in agents for the solubilization of nonpolar organics into aqueous solution.[17] Both of these cosolvents are nontoxic and can be safely disposed with the rest of the aqueous media. Lawrence and co-workers demonstrated the effectiveness of ethanol as a cosolvent during subcritical water extraction of fumonisins from contaminated corn products.[18] Field and Reed also utilized ethanol as cosolvent in the removal of surfactants from sludge samples.[19]

Solubility data in pure and modified subcritical water provide essential information on the solvent strength of water than is required for the extraction of a target analyte. Although there is an abundance of solubility data in ambient water, only a few studies have investigated solute solubilities in subcritical water. Further, there is even less information on cosolvent-modified water under subcritical conditions. Several studies have shown that temperature has a positive effect on the solubilization of organic analytes in subcritical water. For example, Hawthorne and co-workers have measured the solubilities of a variety of compounds such as pesticides and flavor and fragrance compounds in pure subcritical water.[16,20−22] Ro et al. have determined the solubility of 2,4,6-trinitrotoluene over the small temperature range of 6−42 °C.[23] The solubilities of anthracene and *p*-xylene in hot water have also been measured.[15,24] In each of the cited cases, there were significant increases in solute solubilities as the temperature was increased. For example, the solubility of the pesticide propazine was enhanced 4300-fold as the temperature of water was raised from 25 to 200 °C.[16] The cosolvent ternary system cyanazine plus ethanol plus water has also been examined over the narrow temperature range 10−30 °C by Hurley et al.[25] In this study, both temperature and added cosolvent had the effect of increasing the solubility of cyanazine in the three-component system.

To support the development of a novel extraction method for triazine pesticides that employs hot water as an environmentally benign solvent, the solubilities of atrazine, cyanazine, and simazine have been measured in pure subcritical water. Atrazine solubility has also been measured in hot water modified with both urea and ethanol to further investigate the dual effect of added cosolvent and adjustment of temperature on the extraction of triazine pesticides. All measurements were made using a static equilibration cell and on-line liquid chromatographic detection for quantitation of the dissolved solutes.

EXPERIMENTAL SECTION

Materials and Instrumentation. Static solubility measurements were performed with the apparatus shown in Figure 1. The solubility apparatus is similar to one used for solubility measurements in supercritical carbon dioxide.[26,27] The apparatus is enclosed in a modified Spe-ed unit oven (Applied Separations, Inc.; Allentown, PA) for constant temperature control. The solubility cell is constructed of a section of 0.5-in.-o.d. stainless steel tubing (0.0625-in. wall thickness) with appropriate Swagelok fittings. All other tubing used in the solubility apparatus was 0.0625-in.-o.d. stainless steel. Pure or modified water was delivered to the solubility cell using an ISCO 100DX syringe pump that was set to maintain a constant pressure. As shown in Figure 1, the water first passed through a preheating coil in the oven. In addition, a cooling coil was placed in-line after the pump to prevent solute migration back to the pump. The cell contents were mixed with a magnetic stir bar (10 × 3 mm) that was driven by a remote stirrer (Variomag-U.S.A.; Daytona Beach, FL).

A six-port valve (Valco Instruments Co., Inc.; Houston, TX) designed to withstand pressures and temperatures up to 3000 psi and 175 °C was used for sampling the water. An in-line Valco filter with a 0.5-μm frit prevented solid solute from entering the 2-μL sample loop. The solutes were separated on a VYDAC reverse-phase C_{18} column (25 cm × 4.6 mm i.d.; 5 μm). The LC mobile phase was delivered using a Beckman 114M solvent delivery pump. Detection was by a Thermo Separation Products SP8490 UV detector. As required, sample aliquots were further analyzed by GC/MS using a Varian Saturn 4D ion trap in tandem with a Varian 3600 gas chromatograph equipped with a DB-5 column (30m × 0.25 mm i.d.; 0.10 μm). In these cases, a 100 μm poly(dimethylsiloxane) solid-phase microextraction (SPME) fiber (Supelco; Bellefonte, PA) was used to sample the water samples.

The solutes cyanazine and simazine (Crescent Chemical Co., Inc.; Hauppauge, NY) had purities of 98.5 and 98.0%, respectively. Atrazine (Chem Service, Inc.; West Chester, PA) had a purity of 99.0%, and naphthalene (Aldrich; Milwaukee, WI) was scintillation grade (i.e., 99+%). The urea (J. T. Baker, Inc.; Phillipsburg, NJ) was Baker-analyzed according to A. C. S. specifications. Acetonitrile (Fisher Scientific; Pittsburgh, PA) was HPLC grade. The ethanol (Aaper Alcohol and Chemical Co.; Shelbyville, KY) was absolute 200 proof. Distilled water was passed through a MilliQ water system for deionization prior to use.

Solubility Measurements. For solubility measurements, 10−30 mg of solute was placed in the solubility cell. The cell was then charged with water from the syringe pump. Modified water

(14) Anderson, G. S.; Miller, R. C.; Goodwin, A. R. H. *J. Chem. Eng. Data* **2000**, *45*, 549−554.
(15) Röβling, G. L.; Franck, E. U. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 882−890.
(16) Miller, D. J.; Hawthorne, S. B. *Anal. Chem.* **1998**, *70*, 1618−1621.
(17) Yalkowsky, S. H. *Solubility and Solubilization in Aqueous Media*; Oxford University Press: 1999; Chapter 6.
(18) Lawrence, J. F.; Niedzwiadek, B.; Scott, P. M. *J. AOAC Int.* **2000**, *83*, 604−611.
(19) Field, J. A.; Reed, R. L. *Environ. Sci. Tech.* **1999**, *33*, 2782−2787.
(20) Miller, D. J.; Hawthorne, S. B. *J. Chem. Eng. Data* **2000**, *45*, 78−81.
(21) Miller, D. J.; Hawthorne, S. B.; Gizir, A. M.; Clifford, A. A. *J. Chem. Eng. Data* **1998**, *43*, 1043−1047.
(22) Miller, D. J.; Hawthorne, S. B. *J. Chem. Eng. Data* **2000**, *45*, 315−318.
(23) Ro, K. S.; Venugopal, A.; Adrian. D. D.; Constant, D.; Qaisi, K.; Valsaraj, K. T.; Thibodeaux, L. J.; Roy, D. *J. Chem. Eng. Data* **1996**, *41*, 758−761.
(24) Knauss, K. G.; Copenhaver, S. A. *Geochim. Cosmochim. Acta* **1995**, *59*, 2443−2448.
(25) Hurley, L. A.; Jones, A. G.; Drummond, J. N. *J. Chem. Eng. Data* **1995**, *40*, 277−279.
(26) Curren, M. S.; Burk, R. C. *J. Chem. Eng. Data* **1997**, *42*, 727−730.
(27) Curren, M. S. S.; Burk, R. C. *J. Chem. Eng. Data*, **2000**, *45*, 746−750.

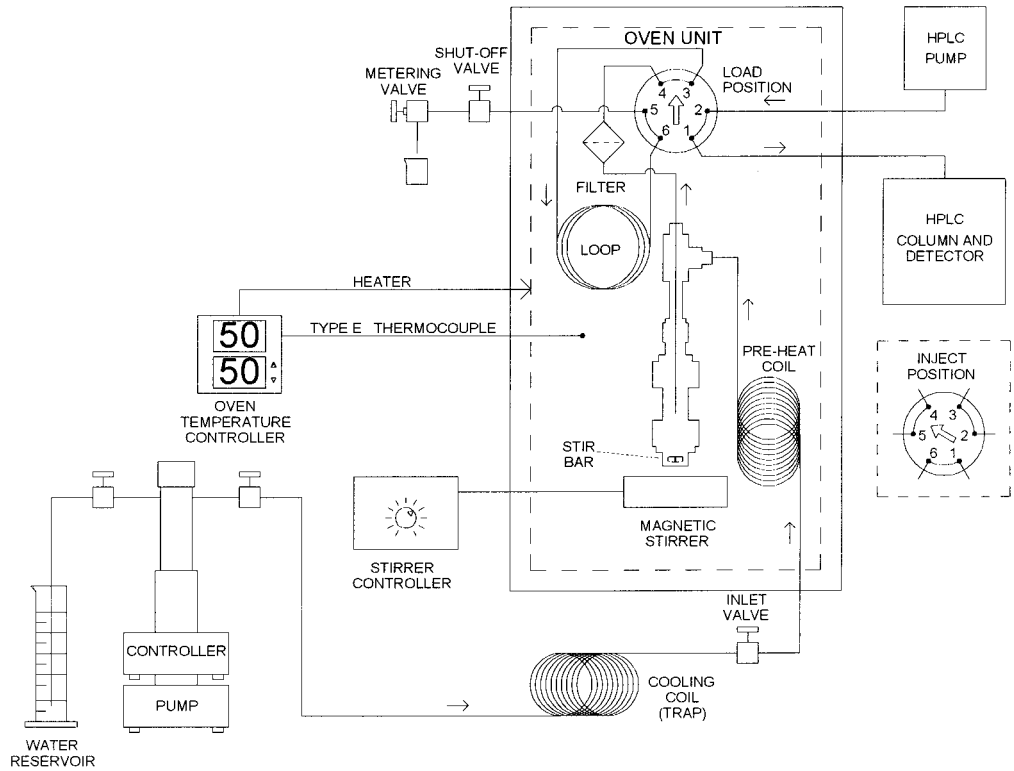

Figure 1. Static solubility apparatus with on-line LC analysis.

solutions were prepared by dissolving known weights of either ethanol or urea in the water (the unit wt % was chosen because cosolvent concentration does not change when the temperature is increased). Once the cell contents reached the desired temperature, they were stirred until equilibrium was achieved. Solubility equilibria were verified by varying the stirring times from 2 to 16 h until there were no further increases in the measured solute solubilities at each temperature. Four or more measurements were performed at each temperature. The solute-saturated water was sampled by opening the shut-off valve with the six-port valve in the "load" position. A metering valve regulated the flow of effluent through the sample loop. The six-port valve was then turned to the "inject" position, and the mobile phase delivered the sample to the LC system.

The solubilities of atrazine in pure or modified ambient water were determined by adding excess solute to the solutions and stirring them until equilibrium was achieved. Each solution was introduced to the LC system by manual injection with a syringe.

Sample Analysis. The LC mobile phase was composed of 75% methanol/25% water by volume for the separation of each of the pesticides. The mobile phase used for the analysis of naphthalene was 70% acetonitrile/30% water by volume. Solute detection was accomplished at a wavelength of 254 nm for all analytes, except for high concentrations of atrazine. In these cases, a wavelength of 280 nm was used. Calibration curves were constructed using pesticide standards of appropriate concentrations prepared in both methanol and water to ensure that there was no solvent effect on chromatography. Naphthalene standards were prepared in acetonitrile or water. Each curve had a minimum of four calibration points and an r^2 value of at least 0.99.

The SPME method employed a 40-min sorption time (with stirring) and 3-min desorption in the GC injector that was heated to 250 °C. It was determined that there were no solute residues on the fibers during subsequent injections. Water samples from the solubility experiments were collected in 1.6-mL autosampler vials for qualitative analysis of any degradation products.

Table 1. Solubility of Naphthalene (μg/mL) in Subcritical Water at Different Temperatures and Pressures

temp °C	pressure bar	solubility μg/mL ± SD[a]	solubility [from ref 16] μg/mL ± SD[a]
25	1	36 ± 2	36 ± 1
25	40	39 ± 2	34 ± 1
35	40	65 ± 2	49 ± 3
50	70	120 ± 3	101 ± 5
65	30	210 ± 25	216 ± 8

[a] Errors are expressed as the standard deviation of ≥4 measurements.

RESULTS AND DISCUSSION

Solubility Apparatus. The solubility of naphthalene in pure subcritical water was first measured at several temperatures and pressures to ensure that the static solubility apparatus was functioning correctly. These results are listed in Table 1. Note that the results are within close proximity to data published in the literature.[16] By using a static solubility apparatus with on-line LC detection, we were able to avoid solute losses associated with sample collection. Solubility equilibria could also be verified with this apparatus by varying the stirring times until there was no further increase in the measured solute solubility at each temperature. During the course of these experiments, the stainless steel cell was carefully monitored for corrosion, and no adverse effects were noted.

Table 2. Solubility of Atrazine (μg/mL) in Subcritical Water at Different Temperatures and Pressures

temp, °C	P, bar	ϵ^a	solubility, μg/mL ± SD[b]
50	50	70	70 ± 1
75	50	62	210 ± 2
100	50	55	500 ± 30
125	50	49	1780 ± 70
125	40	49	1770 ± 210

[a] Dielectric constant data were adapted from ref 28. [b] Errors are expressed as the standard deviation of ≥4 measurements.

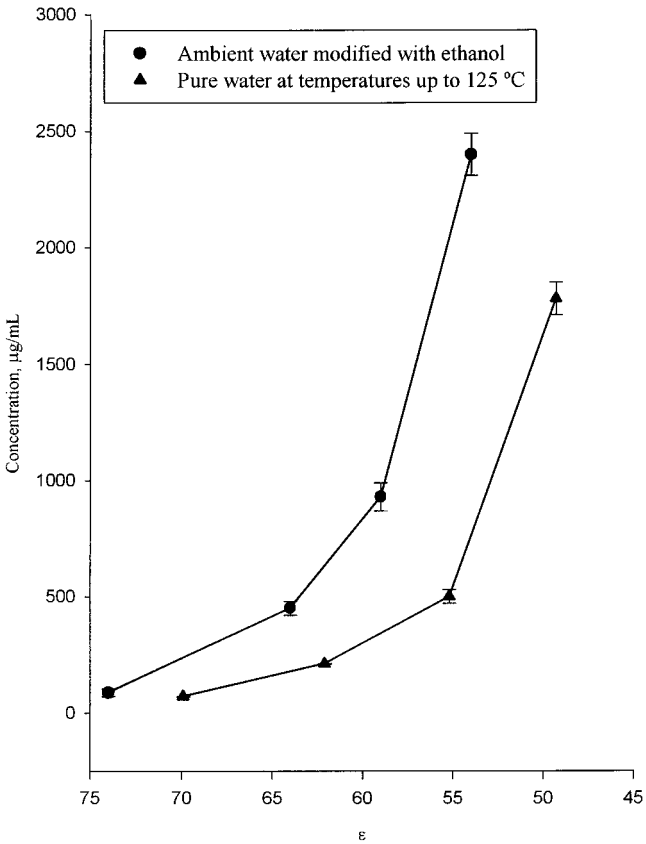

Figure 2. Solubility of atrazine (μg/mL) in pure water and water modified with ethanol as a function of dielectric constant.

The stability of the solutes in water was verified by GC/MS analysis of the saturated aqueous solutions after completion of the solubility experiments at the highest temperatures investigated. Additional verification of analyte stability was provided by the observation that there were no extraneous peaks on the LC chromatograms during solubility measurements of each analyte.

Effects of Temperature and Added Cosolvent on Atrazine Solubility. The solubility of atrazine in pure subcritical water is summarized in Table 2. Atrazine solubility increases 25-fold as the temperature is raised from 50 to 125 °C. The increase in atrazine solubility is mainly due to the decrease in the dielectric constant of water to about 50 at 125 °C.[28] This conclusion is supported by the plots in Figure 2, which compare the solubility of atrazine in pure, heated water to its solubility in ambient water that is modified with the cosolvent ethanol (shown in Table 3). The addition of ethanol to ambient water creates a solvent mixture

(28) Åkerlöf, G. *J. Am. Chem. Soc.* **1932**, *54*, 4125−4139.

Table 3. Solubility of Atrazine (μg/mL) in Water Modified with Ethanol at 25 °C and at 1 Bar

wt % ethanol	ϵ^a	solubility, μg/mL ± SD[b]
8	74	87 ± 16
25	64	450 ± 30
33	59	930 ± 60
42	54	2400 ± 90

[a] Dielectric constant data were adapted from ref 28. [b] Errors are expressed as the standard deviation of ≥4 measurements.

Table 4. Solubility of Atrazine (μg/mL) in Subcritical Water Modified with Ethanol at 100 °C and at 50 Bar

wt % ethanol	ϵ^a	solubility, μg/mL ± SD[b]
0	55	500 ± 30
8	51	1900 ± 20
12	49	3560 ± 170
16	48	4810 ± 120
20	46	6240 ± 130

[a] Dielectric constant data were adapted from ref 28. [b] Errors are expressed as the standard deviation of ≥4 measurements.

that has the same dielectric constant as pure water heated to the appropriate temperature. The data in Figure 2 are, therefore, plotted as a function of solvent polarity. The ethanol/water curve in Figure 2 resembles a typical cosolvent solubilization curve; that is, there is an exponential increase in atrazine solubility as the amount of ethanol in the water is increased. The slope of this curve is similar to that of the temperature/water curve, which indicates that raising the temperature of pure water has a similar effect on atrazine solubility as adding the cosolvent ethanol to ambient water. However, the slope of the ethanol/water curve increases more rapidly than that of the temperature/water curve. In addition, atrazine solubility is higher in ambient water that is modified with ethanol than it is in subcritical water at the same values of ϵ. Both of these observations are the result of additional analyte−cosolvent interactions that are occurring in the presence of ethanol. The plots in Figure 2, therefore, suggest that utilizing the cosolvent ethanol in conjunction with temperature to reduce the polarity of water should result in a significant increase in atrazine's solubility as compared to experiments in pure, heated water.

The solubility of atrazine was, therefore, measured in water modified with ethanol at 100 °C. The data in Table 4 indicate there is a significant increase in solute solubility when ethanol is used as a modifier at elevated temperatures. The solubility of atrazine increases over an order of magnitude in an aqueous solution composed of 20 wt % ethanol when compared to its solubility in pure water at 100 °C. It is clear that both temperature and cosolvent contribute to an overall increase in atrazine solubility.

The solubility of atrazine was also measured in water modified with urea at several temperatures, as summarized in Table 5. Atrazine solubility in 28 wt % urea is about twice its value in pure, subcritical water at each temperature investigated, again because both temperature and the addition of cosolvent are each enhancing analyte solubility. The increase in the solubility of atrazine in the presence of urea suggests that either the hydrogen bond density of water is being disrupted by the addition of this cosolvent, or

Table 5. Solubility of Atrazine (μg/mL) in 28 wt % Urea at Different Temperatures and at 50 Bar

temp, °C	solubility, μg/mL ± SD[a]
50	120 ± 20
75	360 ± 20
100	970 ± 10

[a] Errors are expressed as the standard deviation of ≥4 measurements.

Table 6. Solubilities of Cyanazine and Simazine (μg/mL) in Subcritical Water at Different Temperatures and at 50 Bar

temp °C	solubility cyanazine μg/mL ± SD[a]	solubility simazine μg/mL ± SD[a]
50	290 ± 30[b]	17 ± 1
75	950 ± 50[c]	52 ± 2
100	2740 ± 80[d]	240 ± 7

[a] Errors are expressed as the standard deviation of ≥4 measurements.

that there are significant interactions between the analyte and the cosolvent, or both. The action of urea on the structure of an aqueous solution is somewhat controversial. The increase in the dielectric constant of water that is produced by urea suggests that it actually strengthens the hydrogen bonding capacity of water.[29] However, this is in contrast to the results reported in this study and the results and explanations offered by other investigators in the literature.[30,31] Unfortunately, it was impractical to investigate this point further by utilizing a higher concentration of urea for solubility experiments because the urea is prone to precipitation out of solution, thereby creating a residue problem in the analytical equipment. The fact that the solubility of atrazine in water modified with 20 wt % ethanol is 6 times higher than in water modified with 28 wt % urea at 100 °C suggests that the reduction in the dielectric constant of subcritical water is important, despite any cosolvent interactions that might be occurring. It is for these reasons that solubility experiments in solutions containing higher concentrations of urea were not performed.

Other Solutes. The solubilities of two other triazine pesticides, cyanazine and simazine, were measured in pure subcritical water. The solubilities of both pesticides are given in Table 6. Cyanazine exhibits higher solubilities in water than either atrazine or simazine. The supporting data in Table 6 indicate that its solubility increases 10-fold to a value of 2740 μg mL^{-1} as the temperature is raised from 50 to 100 °C. At 100 °C, cyanazine is 5 times more soluble than atrazine in pure water and its solubility is a full order of magnitude higher than that of simazine. The higher solubility of cyanazine is probably due to its more polar character. Although atrazine, simazine, and cyanazine have the same basic structure, the cyanazine molecule also contains a cyano functional group, as shown in Figure 3. The solubilities of all three triazine pesticides are also plotted as a function of solvent polarity in Figure 4 to show that all of the plots have positive slopes that increase exponentially with increased temperature. This causes them to

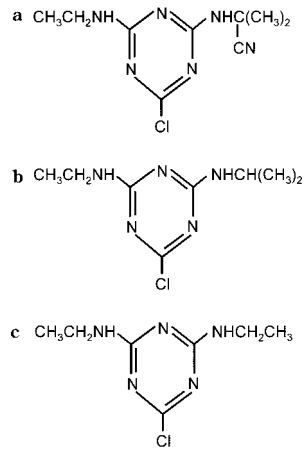

Figure 3. Chemical structures of the triazine pesticides (a) cyanazine, (b) atrazine, and (c) simazine.

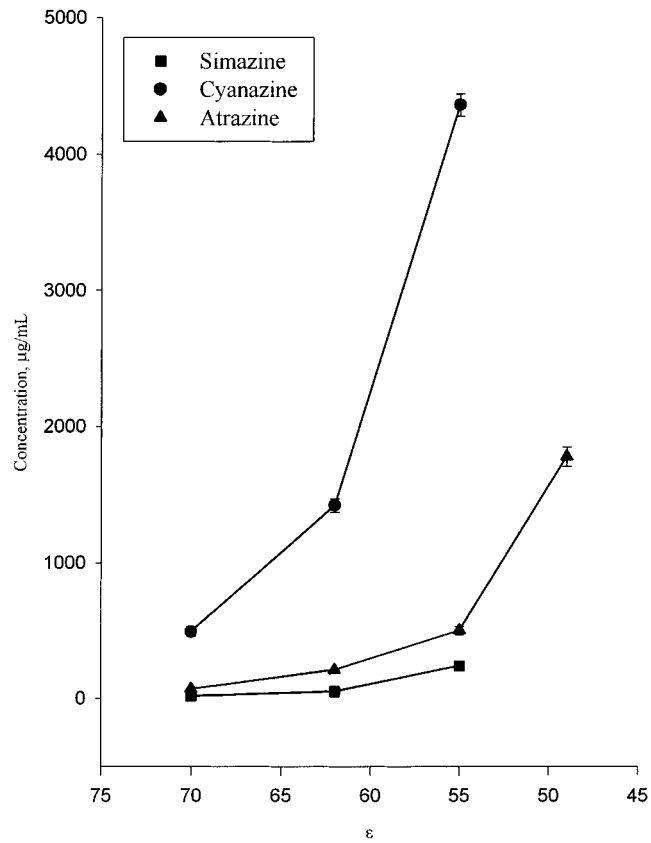

Figure 4. Solubilities of triazine pesticides (μg/mL) in subcritical water as a function of dielectric constant at temperatures up to 125 °C.

resemble cosolvent solubilization curves even though temperature, not the use of a cosolvent modifier, facilitated the change in the dielectric constant of water.

The solubility data in Figure 4 suggest the possibility of a semilogarithmic correlation with temperature, similar to a Van't Hoff correlation in which the natural logarithm of the mole fraction solubility, x_1, is plotted versus the reciprocal of absolute temperature. For an ideal solution, the mole fraction solubility can be used in place of the equilibrium constant, K, if it is assumed to be equal to the activity of the analyte. This gives an equation for the enthalpy of solution, ΔH_s

(29) Abu-Hamdiyyah, M. *J. Phys. Chem.* **1965**, *69*, 2720−2725.
(30) Wetlaufer, D. B.; Malik. S. K.; Stoller, L.; Coffin, R. L. *J. Am. Chem. Soc.* **1964**, *86*, 508−514.
(31) Frank, H. S.; Franks, F. *J. Chem. Phys.* **1968**, *48*, 4746−4757.

$$\frac{d \ln x_1}{d(1/T)} = \frac{-\Delta H_s}{R} \quad (1)$$

When the data in Tables 2 and 6 are plotted in this fashion, linear correlations result for the three triazine pesticides, as shown in Figure 5. The values for ΔH_s are, therefore, approximately constant over the temperature range being considered and are also endothermic. However, the solution enthalpies that were calculated from the slopes are approximately the same for each of the triazine pesticides, as shown in Figure 5. These results suggest that the dissolution of triazine pesticides is an entropy-driven process, despite the fact that the polarity of cyanazine is noticeably different from that of the other analytes and that the entropy term in the Gibb's free energy equation is expected to be small as compared to the change in enthalpy upon dissolution of each solute. The enthalpy of solution for each of the triazine pesticides should be approximately equal to the Gibb's function of solution during solubility experiments; that is,

$$\Delta G_s \approx \Delta H_s \quad (2)$$

Equation 2 is true if it is assumed that the change in entropy upon dissolution of each of the analytes in a real solution is of the same order of magnitude as in an ideal solution. In this case, the entropy of solution is defined as

$$\Delta S_s = -R(x_1 \ln x_1 + x_2 \ln x_2) \quad (3)$$

The solvent term $x_2 \ln x_2$ can be omitted from eq 3, because it is small when compared to $x_1 \ln x_1$; hence, the entropy of solution is rewritten as

$$\Delta S_s \approx -Rx_1 \ln x_1 \quad (4)$$

The entropy term in the Gibb's free energy equation is, therefore, $RTx_1 \ln x_1$, which is a factor x_1 smaller than ΔG_s, which validates eq 2.

We conclude, therefore, that it is necessary to account for the change in the dielectric constant of water if the Van't Hoff relationship is to be used to correlate analyte solubilities with system temperature. This conclusion is supported by the findings of Clifford and Basile, who developed a predictive method to estimate analyte solubilities in water at high temperatures.[32] They used the above thermodynamic relationships in addition to solubility data to develop an equation which accounts for the effect of the change in the dielectric constant of water with temperature, given as

$$\ln[x_1(T)] \approx \left(\frac{T_0}{T}\right) \ln[x_1(T_0)] + 15\left[\left(\frac{T}{293}\right) - 1\right]^3 \quad (5)$$

T_0 is a temperature near ambient at which the solubility of the solute in water is known.

We have calculated the solubilities of atrazine, simazine, and cyanazine at 50, 75, and 100 °C using eq 5 and have obtained a relatively good correlation with our experimental solubility results in Table 7.

As shown by Clifford and Basile, the correlation offered by eq 5 is independent of the molecular type of the analyte. This is consistent with our findings in Figure 5, which indicate that the increase in the solubility of each of the triazine pesticides with increasing temperature is approximately the same.

(32) Clifford, A. A.; Basile, A. *Proceedings of the 5th Meeting on Supercritical Fluids: Materials and Natural Products Processing*; March, 1998; Nice, France; pp 723−728.

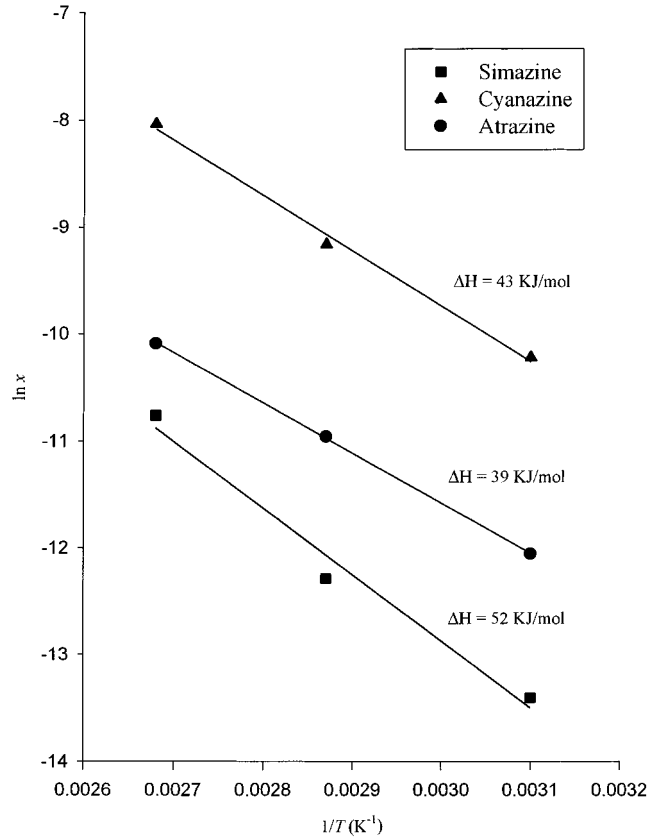

Figure 5. Mole fraction solubility of triazine pesticides, expressed as ln *x*, as a function of 1/T.

Table 7. Experimental and Calculated Mole Fraction Solubilities for Triazine Pesticides in Subcritical Water

	10^6x					
	323 K		348 K		373 K	
compound	exptl	calcd	exptl	calcd	exptl	calcd
simazine	1.5	1.2	4.6	3.7	21	10
atrazine	5.8	6.9	17	17	41	46
cyanazine	36	27	110	65	320	150

ACKNOWLEDGMENT

The authors thank Marvin Hopper of FDA's Total Diet and Pesticide Research Center in Lenexa, KS, for helpful information about the stability of the standard solutes in heated water and Jeffrey Teel of our laboratory for technical assistance in the construction of the solubility apparatus.

Received for review August 3, 2000. Accepted November 27, 2000.

AC000906N