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Solubility of Liquid Organic Flavor and Fragrance Compounds in Subcritical (Hot/Liquid) Water from 298 K to 473 K

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The solubilities of *d*-limonene, carvone, eugenol, 1,8-cineole, and nerol were determined in water at temperatures ranging from 298 K to 473 K. In general, increasing the temperature up to 473 K increased solubilities by a factor of ∼25 to 60. For example, increasing the temperature from 298 K to 473 K increased the mole fraction solubility of carvone from $(9.7 \pm 0.8) \times 10^{-5}$ to $(250 \pm 8) \times 10^{-5}$. 1,8-Cineole exhibited an initial decrease in solubility with increasing temperature before following the trend of increasing solubility with increasing temperature. Analyses were performed to determine whether the compounds degraded at experimental conditions. Unlike α-pinene, these compounds showed no degradation, with the exception of nerol at 473 K.

Introduction

Recent reports have demonstrated the ability of "subcritical" water (water heated to any temperature up to its critical temperature with enough pressure to maintain its liquid state) to quantitatively remove a variety of polar and nonpolar organics from many matrixes (Hawthorne et al., 1994; Yang et al., 1995; Hartonen et al., 1997; Yang et al., 1997; Basile et al., 1998; Yang et al., 1998). The ability of water to solvate hydrophobic organic compounds is due to the effect of temperature on the polarity of water (measured by its dielectric constant, ϵ). Increasing the temperature of water at constant pressure decreases the dielectric constant from ∼80 at 298 K to ∼35 at 473 K (Haar et al., 1984), which is approximately equal to that of ethanol ($\epsilon = 33$).

Recently, subcritical water has been used to extract flavor and fragrance components from various plant matricies (Basile et al., 1998; Hawthorne et al., 1999). Basile et al. (1998) compared the recoveries of oxygenated compounds obtained from subcritical water extraction from rosemary (Rosmarinus officinalis) to those of steam distillation. They report more rapid extraction and higher yields with only very small amounts of sesquiterpenes, waxes, and lipids extracted with subcritical water. As previously reported, raising the temperature of the water (with enough pressure to maintain liquid water) has a marked effect on the extraction of organic compounds. However, extraction behavior is hard to understand, since little solubility data have been reported for organic compounds at elevated temperatures, and most of the solutes studied are solids at ambient conditions. The data which do exist show dramatic increases in solubilities with water temperature. For example, the solubilities of several polycyclic aromatic hydrocarbons (PAHs) and several pesticides (all of which are solids at ambient conditions) are reported to increase ∼5 orders of magnitude with increases in temperature from 298 K to 498 K (Rössling and Franck, 1983; Miller and Hawthorne, 1998; Miller et al., 1998).

While there is a wealth of ambient-temperature solubility data in the literature for organic compounds that are normally liquids, the vast majority of these compounds are of environmental interest and very few data are available for the solubility of flavor and fragrance compounds in water. For the compounds reported here, a literature value for ambient water solubility is available only for *d*-limonene. The present work reports on the application of a method for determining the solubility of liquid (at room temperature) hydrophobic organic compounds in water at temperatures from 298 K to 473 K (Miller and Hawthorne, 2000) to flavor and fragrance compounds. A dynamic method for solids reported by Miller and Hawthorne (1998) was modified to allow solubilities of liquid solutes to be rapidly determined over a wide range of temperatures and pressures.

Experimental Section

All solubility determinations were performed using a dynamic method previously used for solid organics which was modified in the present study for liquid organics. A detailed description of the method and a schematic of the apparatus for solids has been previously reported (Miller and Hawthorne, 1998). Briefly, a high-pressure saturation cell is filled with the test solute and placed in the oven of a HP 5890 gas chromatograph (Hewlett-Packard, Wilmington, DE) to provide precise temperature control (±0.1 °C according to manufacturer's specifications). An Isco model 100D syringe pump (Isco, Lincoln, NE) was used in the constant flow mode to supply water (purged with N_2 to remove dissolved oxygen) at 0.1 mL/min (±0.3% according to manufacturer's specifications) via a 3-m preheating coil (placed in the GC oven) to the saturation cell. A mixing "tee" was installed in the GC oven between the outlet of the saturation cell and an external cooling coil to allow introduction of methylene chloride as a collection solvent. A second Isco model 100D syringe pump operating in the constant flow mode was used to deliver methylene chloride at 0.4 mL/min to one leg of the mixing tee. This arrangement allowed the solutes saturated in the hot water to partition into the methylene chloride as the water cooled, preventing deposition in the transfer line upon cooling the

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Table 1. Mole Fraction Solubility of *d*-Limonene in Water

T/K	P/bar	$10^6(x_2 \pm \mathrm{SD}^a)$
	Literature	
298	1	1.8^b
	This Work	
298	70	1.0 ± 0.1
323	71	1.3 ± 0.1
373	72	4.3 ± 0.1
423	70	21 ± 1
473	69	57 ± 2

[a] Standard deviations (SDs) are based on 10 fractions collected at each condition. [b] Massaldi and King, 1973.

Table 2. Mole Fraction Solubility of Carvone in Water

T/K	P/bar	$10^5(x_2 \pm \mathrm{SD}^a)$
298	64	9.7 ± 0.8
323	65	10 ± 1
373	61	31 ± 1
423	64	80 ± 2
473	64	250 ± 8

[a] Standard deviations (SDs) are based on 10 fractions collected at each condition.

Table 3. Mole Fraction Solubility of Eugenol in Water

T/K	P/bar	$10^4(x_2 \pm \mathrm{SD}^a)$
298	65	1.9 ± 0.1
323	68	2.5 ± 0.1
373	64	5.8 ± 0.2
423	69	15.8 ± 0.4
473	69	49 ± 1

[a] Standard deviations (SDs) are based on 10 fractions collected at each condition.

Table 4. Mole Fraction Solubility of 1,8-Cineole in Water

T/K	P/bar	$10^4(x_2 \pm \mathrm{SD}^a)$
298	66	3.3 ± 0.1
323	64	1.93 ± 0.02
373	67	1.65 ± 0.04
423	68	2.8 ± 0.1
473	64	5.3 ± 0.4

[a] Standard deviations (SDs) are based on 10 fractions collected at each condition.

Table 5. Mole Fraction Solubility of Nerol in Water

T/K	P/bar	$10^5(x_2 \pm \mathrm{SD}^a)$
298	68	6.2 ± 0.5
323	68	7.3 ± 0.4
373	68	17 ± 1
423	69	51 ± 3
473	70	ND^b

[a] Standard deviations (SDs) are based on 10 fractions collected at each condition. [b] Not determined because of substantial degradation of the nerol at 473 K.

water to room temperature. In the present study, the original apparatus was modified to replace the outlet control valve with a miniature back-pressure regulator (Upchurch Scientific, Oak Harbor, WA) factory adjusted to operate at ~69 bar (measured at the pump, ±2% according to manufacturers specifications) to maintain sufficient pressure to ensure that water in the liquid state was present throughout the entire temperature range.

The original method was further modified to allow solubility determinations of liquid organic solutes. Rather than mixing the organic solute with sea sand (as reported by the original method for solids), the saturation cell (10.4 mL, 150-mm × 9.4-mm i.d. "SFE" cell, Keystone Scientific, Bellefonte, PA) was filled with 3-mm diameter solid glass beads (Fisher Scientific, Pittsburgh, PA). The beads provide a torturous path for the water as it passes through the saturation cell. The direction of the water flow was also changed depending on the density of the organic solute. Flow was from top to bottom when the density of the organic solute is less than that of water and from bottom to top when the density of the organic solute is greater than the density of water. The filling procedure differs, again depending on the density of the organic solute. If the solute is less dense than water, ~0.5 mL of water is pipetted in the bottom of the saturation cell containing the glass beads and the organic solute is then added, filling the remainder of the cell. If the solute is more dense than water, the organic solute is added to the saturation cell first to within ~1 cm of the top of the cell. The remaining void volume is then filled with 0.5 mL water.

Solubility determinations are begun by starting the flow of both pumps and allowing the system to equilibrate. After a 60-min equilibration period at the initial (ambient) temperature, 10 fractions were collected for 3 min (0.3 mL of water per fraction) each in autosampler vials, the appropriate internal standard was added, and the vials were capped for analysis. The temperature was then raised to the next temperature and the cycle repeated.

The solutes tested in this work were α-pinene, *d*-limonene ((*R*)-(+)-*p*-mentha-1,8-diene), carvone (*p*-mentha-6,8-dien-2-one), eugenol (4-allyl-2-methoxyphenol), 1,8-cineole (1,8-epoxy-*p*-menthane or "eucalyptol"), and nerol (*cis*-3,7-dimethyl-2,6-octadien-1-ol) (Sigma-Aldrich, Milwaukee, WI). All solutes were of the highest purity available (≥97% for all compounds and confirmed by GC analysis). Solubility determinations were performed between 298 K and 473 K and at ~65 bar.

Analyses of the methylene chloride fractions were performed using a HP model 5890 GC with flame ionization detection (FID). Chromatographic separations were accomplished with a 30-m HP-5 (0.25-mm i.d., 0.25-μm film thickness, Hewlett-Packard) fused silica capillary column. Three-point calibration curves were generated for each solute to determine the response with respect to the internal standard. Internal standards were chosen which eluted near and were similar to the solute of interest. Solubilities were calculated on the basis of the quantity of test solute in the methylene chloride collection solvent versus the quantity of water used to obtain each fraction (0.3 mL). Representative samples from each temperature range were analyzed by gas chromatography/mass spectrometry (GC/MS, HP 5973) and compared to spectra obtained from standards for each solute to either confirm that no degradation of the organic solute occurred or identify major degradation products.

Results and Discussion

Effect of Temperature on Solubilities. The mole fraction solubilities of *d*-limonene, carvone, eugenol, 1,8-cineole, and nerol are shown in Tables 1−5. A literature value for ambient-temperature solubility was available only for *d*-limonene. The value obtained using our method is in fair agreement with that reported in the literature $(1.0 \pm 0.1) \times 10^{-6}$ compared to 1.8×10^{-6} (Massaldi and King, 1973). Although no ambient solubility data are available in the literature for the other test compounds, previous data for the ambient-temperature water solubility of eight compounds including benzene, toluene, *m*-xylene, *p*-cymene, octane, 2,2,4-trimethylpentane, tetrachloroethyl-

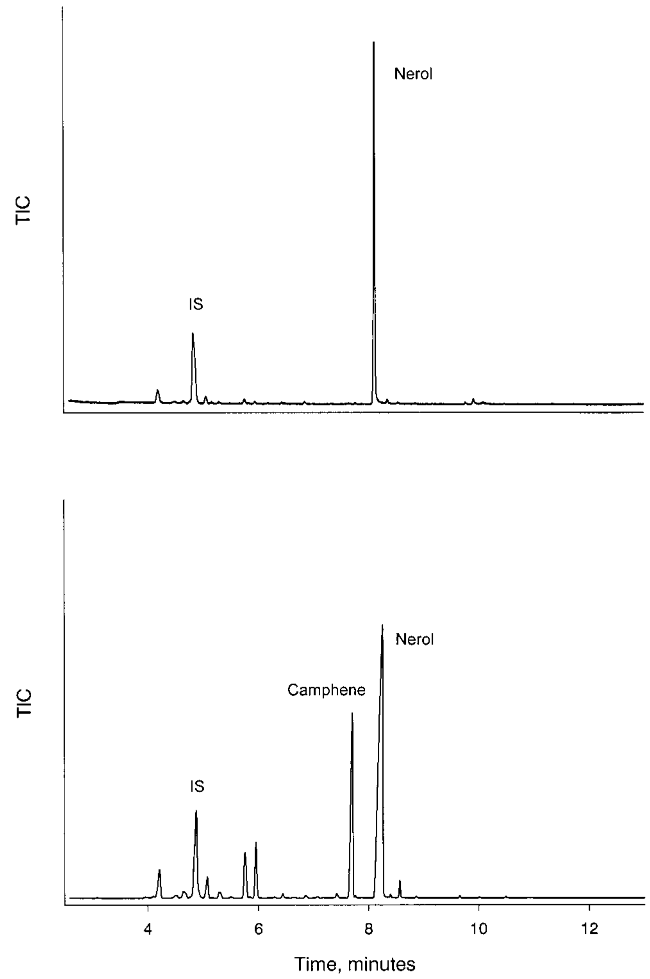

Figure 1. GC/MS (total ion current) chromatogram of fractions collected from a nerol/water solubility determination at 298 K (top) and 473 K (bottom). The internal standard (IS) used for nerol quantitation was *d*-limonene.

ene, and 1,2-dichlorobenzene (Miller and Hawthorne, 2000) were in good agreement with literature values. Ambient solubilities followed expected trends; more polar solutes (e.g., eugenol) were substantially more soluble than less polar solutes (e.g., *d*-limonene).

As expected, increasing temperature increases the mole fraction solubility of *d*-limonene in water (Table 1). For example, increasing the temperature from 298 K to 473 K increases the mole fraction solubility of *d*-limonene nearly 60-fold to (57 ± 2) × 10^{-6}.

Tables 2 and 3 show the mole fraction solubilities obtained for carvone and eugenol, respectively. Even though there is no literature value available for either carvone or eugenol solubility at ambient temperature, the values obtained by our method appear reasonable and follow the same trend of increasing solubility with increasing temperature. For example, raising the temperature of eugenol from 298 K to 474 K results in a 25-fold enhancement in mole fraction solubility from (1.9 ± 0.1) × 10^{-4} to (49 ± 1) × 10^{-4} (Table 3).

Table 4 shows the mole fraction solubility obtained for 1,8-cineole at temperatures from 298 K to 473 K. Inspection of the values in Table 4 indicates something different has occurred as the temperature of the solubility determination is raised from 298 K to 473 K. At ambient conditions, the mole fraction solubility of 1,8-cineole is (3.3 ± 0.1) × 10^{-4}. Raising the temperature to 323 K does not result in a corresponding increase in the mole fraction solubility. Rather, the rise in temperature results in an ~40% reduction in mole fraction solubility to (1.9 ± 0.02) × 10^{-4}. This drop in solubility with increasing temperature continues as the temperature is raised to 373 K. Only after the temperature is raised to 423 K does the mole fraction solubility start to rise ((2.8 ± 0.1) × 10^{-4}), but it is still 15% less that the ambient-temperature solubility. Finally, at 473 K a significant increase in solubility is observed [(5.3 ± 0.4) × 10^{-4}]. This effect has been noted at lower temperatures for benzene, toluene, and *m*-xylene and is related to a negative enthalpy of solution (Bohon and Claussen, 1951). As the temperature is increased (e.g., to 291 K for benzene), the enthalpy of solution approaches zero and is positive at higher temperatures. Higgins et al. (1959) reported a similar decrease in solubility of tributyl phosphate in water at temperatures between 278 K and 323 K.

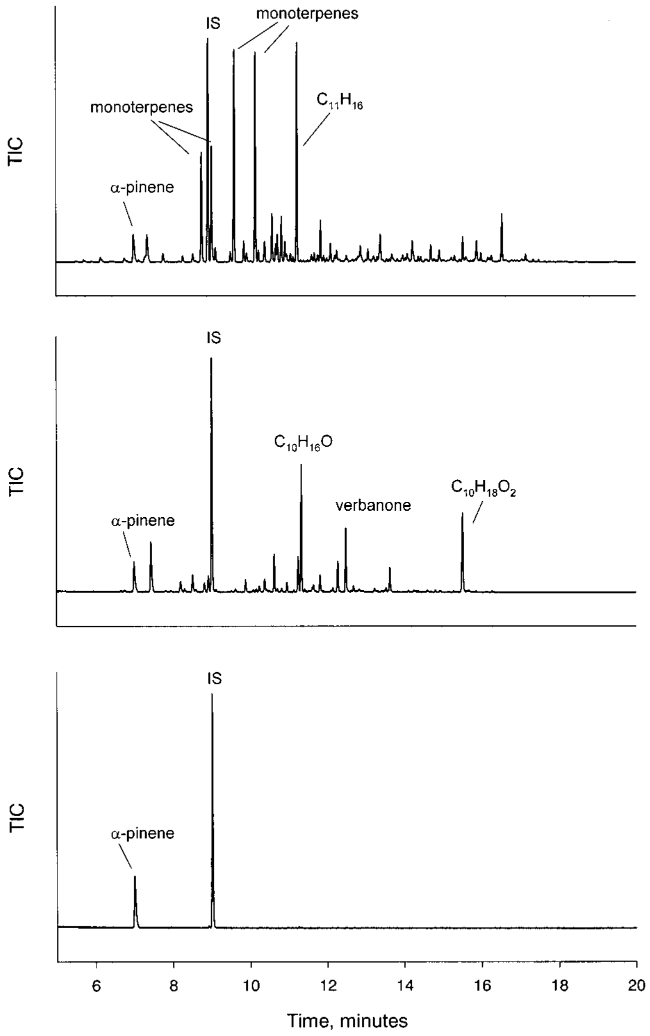

Figure 2. GC/MS (total ion current) chromatogram of an α-pinene standard in CH_2Cl_2 (bottom) and fractions collected from an α-pinene/water solubility determination at 323 K (middle) and 473 K (top).

Table 5 shows the results obtained for the solubility of nerol in water. No degradation products were detected at temperatures up to and including 423 K. However, no value is reported for nerol at 473 K because significant degradation of nerol occurred at that temperature. Figure 1 shows a GC/MS total ion chromatogram (TIC) of a 298 K determination (top) and 473 K (bottom) of nerol. The major degradation product is the result of the loss of water from nerol and cyclization to camphene.

Reactivity

On the basis of the results shown above for nerol, representative fractions at each temperature condition for each compound reported here were analyzed to determine whether any degradation of analyte occurred for compounds other than nerol. No degradation of *d*-limonene, carvone, eugenol, or 1,8-cineole was observed at any temperatures. Basile et al. (1998), in their report on the extraction of rosemary by superheated water, found that the slow initial extraction of α-pinene may be due to the fact that it is oxidized by residual oxygen in the system to verbenone. To determine whether this occurs during subcritical water solubility determinations, experiments were performed with α-pinene at temperatures from 298 K to 473 K and a pressure of 65 bar. Even though the water used in these determinations was thoroughly deoxygenated by a nitrogen purge prior to use, considerable degradation occurred at each temperature and increasing amounts of verbenone and other compounds were present in the collected water, as shown for 323 K and 473 K in Figure 2. Although verbanone was a major product, several monoterpenes and other unidentified products were formed. At higher temperatures (≥473 K) nearly all of the α-pinene was degraded.

Conclusions

Slight modifications of a previously reported method for determining solid organic/water solubilities (Miller and Hawthorne, 1998) allow rapid determination of the water solubilities of *d*-limonene, carvone, eugenol, 1,8-cineole, and nerol over a wide range of temperatures. Raising the temperature of water from 298 K to 473 K (with enough pressure to maintain the liquid state) typically increased the solubilities of liquid organics by ~2 orders of magnitude, compared to 4 or 5 orders of magnitude for organics such as PAHs and pesticides, which are solids at ambient conditions (Miller and Hawthorne, 1998; Miller et al., 1998). Previously reported solubilities determined by this method showed no degradation over a comparable temperature range (Miller and Hawthorne, 2000). While no degradation of *d*-limonene, carvone, eugenol, or 1,8-cineole was observed (confirmed by GC/MS), nerol showed significant degradation at 473 K and α-pinene showed degradation at all temperatures studied.

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