

Gas Scavenging of Soluble and Insoluble Organic Vapors by Levitated Water Drops

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ABSTRACT

Three-millimeter-diameter drops of water were levitated with a standing acoustic wave centered in the jet of a small wind tunnel and the volume changes as the drop evaporates in the presence of 1-propanol vapor were measured. The results are compared with a steady-state continuum evaporation model based on nonideal solution theory. Because the thermodynamic parameters for the 1-propanol-water system are well known, this system provides a test for our model. Good overall agreement between model and experimental results means that small discrepancies can be used to establish limits for dynamic effects. An immiscible liquids version of this model, which accounts for gas scavenging of methyl salicylate, is used to predict the amount of insoluble material scavenged by a drop of water evaporating to dryness. This model predicts that the volume of organic liquid left behind increases slightly as the relative humidity approaches 100%.

1. Introduction

The reports by Glotfelty et al. (1987, 1990) described large violations of Henry's law with respect to pesticide scavenging by fog drops. These reports prompted us to conduct laboratory experiments looking into the gas scavenging of the simulated pesticides methyl salicylate (MS), (Seaver et al. 1992) and dimethyl methyl phosphonate (DMMP) (Seaver and Peele 1992). These two species simulate an "insoluble" and a soluble organic species, respectively. For MS, whose water solubility is $1 \text{ g (1500 g)}^{-1}$, we have shown that evaporative cooling provides a mechanism whereby water drops can circumvent Henry's law when pesticide vapors approach their saturation vapor pressures (Seaver et al. 1992). However, lack of knowledge about activity coefficients for DMMP-water mixtures and the possibility of liquid-phase chemical changes precluded any definite conclusion with respect to our model for the scavenging of soluble vapors (Seaver and Peele 1992). In this report, we present data on the scavenging of 1-propanol vapor by water drops at different water and propanol partial pressures including relative humidities of 94%. The propanol is a soluble organic whose activity coefficients in water mixtures are well known and will not undergo liquid phase chemical changes. Our results demonstrate that accurate knowledge of the liquid-phase activity coefficients, of which Henry's law rep-

resents a limiting case, allows our model to account for the liquid-phase concentration of propanol at all partial pressures over most of a drop's history. Because our model is a steady-state model, the small differences between our model and the propanol results assess the importance of dynamic effects in the scavenging process. We also take this opportunity to investigate the model predictions with respect to the scavenging of insoluble species for drop sizes and relative humidities representative of fog conditions.

2. Experimental

The apparatus has been described in detail (Seaver et al. 1989). Briefly, single drops of water, approximately 3 mm in diameter, are levitated with an acoustic standing wave near the center of a small horizontal wind tunnel. The gas flow starts as dry nitrogen, with water and organic vapor added to separate gas streams. These streams are mixed prior to passage through a heat exchanger that establishes the wind tunnel temperature. Drop evaporation or growth is monitored through a video telemicroscope. Backlit drop images are digitized and their surface area and volume measured at 3–5-s time intervals. Typically, we monitor a single drop for 500 or more seconds.

For these experiments, the gas temperature is $20.3^\circ \pm 0.2^\circ\text{C}$, the wind speed is $90 \pm 5 \text{ cm s}^{-1}$, and the relative humidity is set at 14% or 94%. Propanol partial pressures are about 7 torr with its saturation vapor pressure at 20°C equal to 17 torr. The water is ultrapure from a Milli-Q purification system and has a resistivity

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of 18.2 MΩ cm. The 1-propanol is certified grade and is cleaned and dehydrated by passage through an activated alumina column prior to use.

Throughout the course of each experiment, the partial pressure of propanol in the gas stream is monitored with a resonant optoacoustic spectrophone (Kliger 1983), which is built into the wind tunnel. The spectrophone monitors the strength of the propanol vapor absorption at 10.23 μm (R18 in the 10.6-μm band of a continuous wave CO₂ laser). There is no detectable water vapor absorption at this wavelength. The spectrophone is calibrated prior to incorporation into the wind tunnel by immersing a sidearm containing liquid propanol in a constant-temperature bath and measuring the microphone output. We vary the bath temperature between 4° and 20°C. A plot of microphone signal versus the propanol saturation vapor pressure at bath temperature provides the calibration that enables us to convert microphone signal to propanol partial pressure. The propanol saturation vapor pressure versus temperature data comes from the *Handbook of Chemistry and Physics* (Weast 1987).

3. Transport model

a. Nonideal liquids

The size of our drops (0.5–3.0-mm diameter), the fact that we operate at atmospheric pressure, and the timescale of our experiment dictates the use of a steady-state continuum model for gas–liquid transport. By analogy with the discussion in Pruppacher and Klett (1978), the evaporation or condensation of a two-component liquid drop in moving air, (*dm/dt*), is described by

$$\left(\frac{dm}{dt}\right)_v = \left(\frac{dm_1}{dt}\right)_0 \bar{f}_{v,1} + \left(\frac{dm_2}{dt}\right)_0 \bar{f}_{v,2}. \quad (1)$$

In this expression, (*dm/dt*)₀ is the mass change rate in still air and $\bar{f}_{v,i}$ is the average mass ventilation coefficient for species *i*. The ventilation factor accounts for the effects of forced convection. This factor has been measured experimentally (Beard and Pruppacher 1971; Wedding et al. 1986). The Beard and Pruppacher (1971) correlation for Re ≥ 2.5 is

$$\bar{f}_{v,i} = 0.76 + 0.302 (Sc_i)^{1/3} (Re)^{1/2}, \quad (2)$$

where Sc_{*i*} is the Schmidt number for species *i* and Re is the drop Reynolds number. In still air, the mass change rate is

$$\left(\frac{dm_i}{dt}\right)_0 = \frac{4\pi a D_{v,i} M_i}{R} \left(\frac{p_{i,\infty}}{T_\infty} - \frac{p_{i,d}}{T_d}\right), \quad (3)$$

where *m* is the mass (g), *a* is the drop radius (cm), *D_v* is the diffusivity of the vapor in air (cm² s^{−1}), *M* is the molecular weight (g mol^{−1}), *p* is the partial pressure (dyn cm^{−2}), *R* is the gas constant (erg mol^{−1} K^{−1}), *T*

is the temperature (K), and subscript *i* refers to species 1 or 2. The subscripts ∞ and *d* refer to locations in the gas well away from the drop and in the gas just above the drop surface, respectively.

For volatile species, the latent heat of evaporation cools (heats) the drop as that species evaporates (condenses). Thus, the drop temperature will differ from ambient. In this case, we calculate the drop temperature by iterating

$$T_\infty - T_d = \frac{D_{v,1} M_1 L_1}{Rk_a} \left(\frac{p_{1,\infty}}{T_\infty} - \frac{p_{1,d}}{T_d}\right) \left(\frac{\bar{f}_{v,1}}{\bar{f}_{h,1}}\right) + \frac{D_{v,2} M_2 L_2}{Rk_a} \left(\frac{p_{2,\infty}}{T_\infty} - \frac{p_{2,d}}{T_d}\right) \left(\frac{\bar{f}_{v,2}}{\bar{f}_{h,2}}\right). \quad (4)$$

New parameters in this equation include *L*, the latent heat of vaporization (cal g^{−1}), *k_a*, the thermal conductivity of air (cal cm^{−1} K^{−1} s^{−1}), and $\bar{f}_{h,i}$, the mean thermal ventilation coefficient. The mean thermal ventilation coefficient obeys the same correlation as $\bar{f}_{v,j}$ provided we substitute the Prandtl number (Pr) for the Schmidt number (Pruppacher and Klett 1978):

$$\bar{f}_{h,i} = 0.76 + 0.302 (Pr_i)^{1/3} (Re)^{1/2}. \quad (5)$$

The two terms on the right-hand side of (1) form a set of coupled differential equations where the coupling terms are the vapor pressures of each species at the drop surface. For nonideal mixtures, the equilibrium vapor pressure of species *i* above the liquid is given by

$$p_{i,d} = \gamma_i x_i p_i^0(T_d), \quad (6)$$

where γ is the activity coefficient at mole fraction *x* and $p^0(T_d)$ is the saturation vapor pressure at drop temperature. Our model integrates the two mass terms using a fourth-order Runge–Kutta routine (Press et al. 1986) and then sums them to get *m_{tot}* versus time. We convert the total mass to a volume to compare with our experimental data through the use of the molar volume formula, $V_m = x_1 V_{1,m} + x_2 V_{2,m}$, and the partial molar volumes *V_{*i,m*}* (Atkins 1978). The partial molar volumes are derived from the data listed in Timmermans (1960).

b. Immiscible liquids

As for miscible liquids, (1)–(5) describe the drop’s mass history. In this case, we assume that the presence of liquid MS does not change the water partial pressure near the drop surface, and vice versa. This assumption relies on the fact that the diffusive flux through a thin layer obeys Fick’s law and therefore varies inversely with the layer thickness. In our previous work (Seaver et al. 1992) we demonstrate that this assumption is valid for most of the lifetime of an evaporating water drop. Thus, we set $p_{i,d} = p^0(T_d)$. The model tracks the individual masses and converts them to volumes via their densities. The volumes are then summed to com-

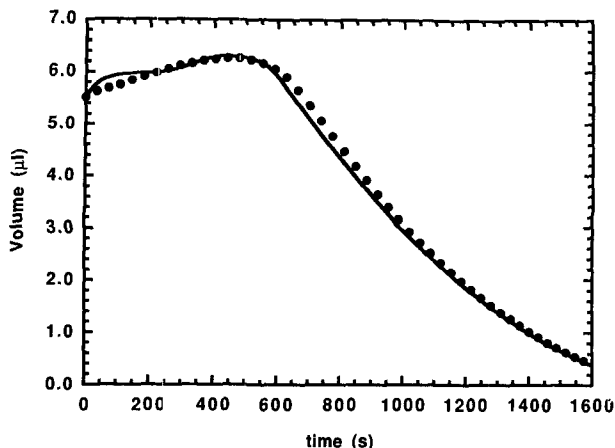


FIG. 1. Volume history for an initially pure water drop at $p_{\text{wat}} = 2.6$ torr and $p_{\text{prop}} = 7.3$ torr. Ambient temperature is 20.4°C and the wind speed is 90 cm s^{-1} . The solid points are every eighth experimental data point. The solid line is our model calculation.

pare with experimental data. The total volume provides the coupling term via the drop radius a in (3) and the Reynolds number in (2) and (5). Again, we numerically integrate the coupled differential equations using a fourth-order Runge-Kutta algorithm.

4. Experimental results and discussion

a. 1-propanol gas scavenging

The points in Fig. 1 report the volume history measured for a drop that starts as pure water. In this experiment, the water and propanol partial pressures are 2.6 and 7.3 torr, respectively. (These numbers represent 14% and 43% of the respective saturation vapor pressures.) What we see is that the drop grows by about 10% during the first 500 s and then begins to evaporate. The “bump” seen prior to 100 s in the model calculation is determined by variations in the partial molar volumes (Atkins 1978). There is one noteworthy observation associated with this data that cannot be shown in the figure. Visually, after about 100 s we see striations in the drop. These striations presumably arise from concentration gradients produced when internal circulation in the drop mixes the propanol condensing on the drop surface with the water. The striations disappear near the maximum in the volume curve.

The solid line in Fig. 1 is the drop volume calculated using our model and the measured initial drop volume of $5.52\text{ }\mu\text{L}$. Because of our observation of nonuniform mixing, it is not surprising that the early stages of the model predict growth rates that differ from our measurements. It is interesting to note that despite the nonuniform mixing, our model gives good agreement as to the maximum drop size. Once the drop becomes uniformly mixed, near 500 s, a steady-state description should be appropriate and we see good agreement as

the drop evaporates. During this portion of the drop history our model predicts constant liquid composition as the drop comes into equilibrium with the vapor. This behavior is similar to but not the same as an azeotrope, since an azeotrope has the same mole fraction composition in both the liquid and vapor phases (Atkins 1978).

Figure 2 shows the results for a drop of water at 94% relative humidity. In this figure, the partial pressures of water and propanol are 16.7 and 6.3 torr, respectively. Here we see a 20% increase in volume rather than the 10% seen in Fig. 1. This difference arises because of the reduced water evaporation rate, while the propanol condensation rate remains nearly constant. Again, we see that the model does a good job of describing the volume history. The difference between the measured and calculated volumes at times greater than 600 s arises from slow drifts in the propanol partial pressure during the experiment as evaporation changes the surface area in the flask of propanol exposed to the dry nitrogen stream.

b. Dynamic effects assessment

Gas scavenging of soluble organic vapors by water drops can be described as a two-step process. The first step condenses the organic vapor on the liquid surface. The second step disperses the organic liquid throughout the water drop. Dynamic effects will appear when these two steps have similar rates. If either step is rate limiting, we can ignore the fast step and describe the process with a steady-state model. An example of such a case is seen in the early time, $t < 200$ s, behavior shown in Fig. 1. Here the liquid phase diffusion is rate limiting and our model overpredicts the amount of liquid propanol in the drop.

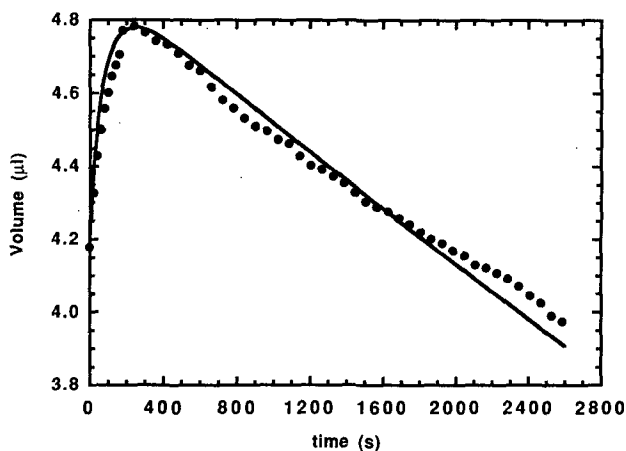


FIG. 2. Volume history for an initially pure water drop at $p_{\text{wat}} = 16.7$ torr and $p_{\text{prop}} = 6.3$ torr. Ambient temperature is 20.4°C and the wind speed is 90 cm s^{-1} . The solid points are every eighth experimental data point. The solid line is our model calculation.

The experimental conditions used in this work enable us to assess the likelihood of dynamic effects in the gas scavenging of pesticide vapors. We have enhanced the condensation rate, relative to a pesticide, by working with an organic vapor at a moderately high partial pressure. In Fig. 1, we see that, even under conditions designed to create dynamic effects, the model only overpredicts the drop volume by a few percent during the earliest growth stages. To assess the likelihood of seeing dynamic effects in pesticide scavenging in the atmosphere, keep in mind that the partial pressure of propanol, approximately 7 torr, is at least an order of magnitude higher than the saturation vapor pressure of any typical pesticide near room temperature. Thus, the gas-phase flux of any pesticide will be more than ten times less than our flux of propanol. Since kinetic theory of gases tells us that liquid-phase diffusion will vary as $(1/m)^{1/2}$ (Atkins 1978) while pesticide partial pressures drop by orders of magnitude, we expect gas-phase diffusion to be the rate limiting step in most cases. As long as gas-phase diffusion is rate limiting, dynamic effects will not play a significant role in the gas scavenging of organic vapors.

c. Immiscible liquids predictions

The immiscible liquids version of our model accounts well for the scavenging of MS vapor by large drops at low relative humidities (Seaver et al. 1992). This agreement pinpoints the scavenging mechanism as condensation of the organic vapor on the drop cooled by evaporation. This mechanism will not change with relative humidity until the temperature of the drop exceeds the dewpoint of the air with respect to the organic vapor. Therefore, it is instructive to look at the model predictions as the relative humidity approaches 100%. For these calculations we use an initial drop radius of 11 μm , relative humidities of 80%, 90%, and 95%, a 90 cm s^{-1} wind speed, and gas saturated with MS vapor at 20°C ($p_{\text{MS}} = 0.9$ torr). In Fig. 3, we show the calculated results at 90% relative humidity. The important feature is the large volume of MS left after the water completely evaporates ($t \cong 3.7$ s). In this figure, the remaining MS represents 3.8% of the original drop volume. For MS, our model actually predicts a slight increase in the fractional volume collected with relative humidity. This increase arises because the MS vapor versus temperature curve has slightly less slope than its water vapor counterpart. For other organics this situation may be reversed. If we increase ambient temperature to 30°C, the condensed volume at 90% relative humidity rises to 7.8% of the initial drop volume. This agrees well with the expectation that vapor pressure versus temperature curves look exponential over short temperature ranges. The small saturation vapor pressure of MS, 0.9 torr, means that even when the MS drop encounters subsaturated air (with respect to MS vapor) its lifetime will be much longer than a water

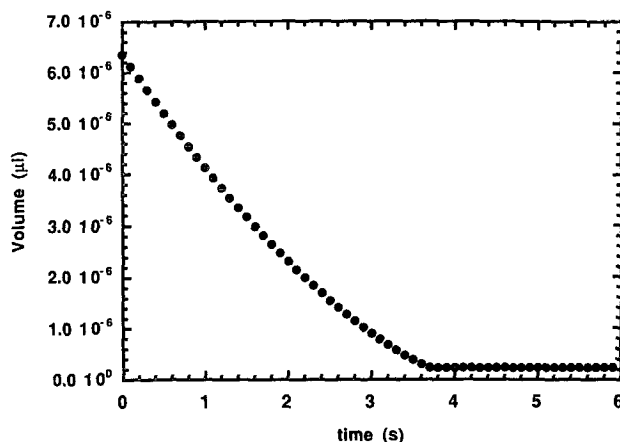


FIG. 3. Model calculation for an initially pure water drop collecting methyl salicylate. Conditions are $p_{\text{wat}} = 16.2$ torr (90% RH), $p_{\text{MS}} = 0.9$ torr (saturated), $T_{\text{air}} = 20.0^\circ\text{C}$, wind speed is 90 cm s^{-1} , and initial drop radius is 11 μm . The volume of MS left after complete evaporation of the water ($t = 3.7$ s) is 3.8% of the initial drop volume.

drop of corresponding size. Thus, a fog or cloud that has entrained air at relative humidities below 100% may contain drops of pure or nearly pure liquid pesticide. Because fog drops in the atmosphere will not be pure water, many will not evaporate to dryness. Thus, our numbers may overestimate the amount of MS that would be collected under atmospheric conditions. However, this scenario provides one possible explanation for the findings of Glotfelty et al. (1987, 1990).

5. Conclusions

Our results demonstrate that an accurate knowledge of the liquid-phase activity coefficients is sufficient to explain the gas-droplet partitioning of water soluble vapors. As long as gas-phase diffusion is the rate limiting step in the condensation–evaporation process, the Henry's law coefficient should provide all the information necessary since liquid-phase mole fractions will remain below a few percent. The small differences seen between our steady-state model and our experimental data for the 1-propanol–water system indicate that dynamic effects in gas scavenging of low vapor pressure organics (i.e., pesticides) are unlikely. In conjunction with our previous study of the gas scavenging of methyl salicylate (Seaver et al. 1992), our results indicate that the deviations from Henry's law reported by Glotfelty et al. (1987, 1990) may result from fog drops that have experienced brief encounters ($t \leq 10$ s) with subsaturated air.

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