Vapor Pressure and Viscosity of 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione

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The viscosity and vapor pressure of the reactive chelating ligand, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (H^+hfac) have been determined. The viscosity of liquid H^+hfac was determined to be $(1.39 \pm 0.19) \times 10^{-3}$ Pa·s at 24 °C and $(8.35 \pm 0.25) \times 10^{-4}$ Pa·s at 35 °C. The vapor pressure of H^+hfac was found to range from 4 kPa at 0 °C to 49.5 kPa at 57 °C. The viscosity was measured using a capillary tube viscometer, and the vapor pressure was measured using a mass transfer gas saturation apparatus. These methods were employed because conventional methodologies would have produced unreliable data due to the formation of the tetrol hydrate of H^+hfac inside the apparatus and potentially exposed laboratory personnel to hazardous working conditions.

Introduction

1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (H^+hfac) is a potential vapor-phase cleaning agent for removing trace transition metals from silicon wafer surfaces and for in situ removal of spurious bulk copper in Cu CVD chamber cleaning applications (Ivankovits et al., 1992; George et al., 1995; Beck et al., 1996). Liquid H^+hfac is corrosive and toxic (Sato and Kammori, 1969; Lenga and Voltoupal, 1996). The corrosive nature of H^+hfac requires special consideration in the selection of materials used to make physical measurements. Two methods have been used to deliver H^+hfac to the surface cleaning reactor. The first method utilizes an inert carrier gas bubbled through a vessel of liquid H^+hfac. A second approach involves the direct injection of a known amount of liquid H^+hfac into a vaporization chamber or directly into the reaction chamber. Direct liquid injection (DLI) of H^+hfac for cleaning has the advantage of improved control of source delivery. However, DLI of H^+hfac requires a more complex hardware setup, largely due to concerns with material compatibility issues with that hardware. As part of our program to develop reliable quantitative delivery of H^+hfac by these methods, we have determined the viscosity and vapor pressure of H^+hfac.

The measurement of the physical properties of H^+hfac challenges the techniques used for both viscosity and vapor pressure because H^+hfac is known to aggressively react with some metals, e.g., stainless steel, copper, etc. (Sato and Kammori, 1969), metals typically used in viscosity and vapor pressure measuring devices. For example, we have observed a change in appearance of liquid H^+hfac from clear and colorless to orange-brown and cloudy when placed in contact with stainless steel. This change is presumably due to the dissolution and complexation of the surface metal oxides of stainless steel. After H^+hfac exposure, the stainless steel exhibited dark corrosion marks on its surface. Therefore, due to the reactive nature of H^+hfac, standard methodologies for determining physical properties are likely unreliable since H^+hfac will corrode stainless steel valves, tubing, pressure transducers, and many other process components, thus modifying the composition of the liquid being analyzed. Additionally, safety considerations while working with H^+hfac demand that the possibility of personal contact with this substance be minimized—another shortcoming of traditional procedures. Therefore, a method similar to a DLI system was developed and used to determine the viscosity of H^+hfac, and a gas saturation/mass transfer method was used to determine its vapor pressure near ambient temperature.

This paper reports values for the viscosity of liquid H^+hfac at 24 °C and 35 °C and the vapor pressure of H^+hfac in the temperature range from 0 °C to 57 °C. The viscosity is previously unreported, while the vapor pressure results extend the useful range of that originally reported by Mousa, who measured vapor pressures near the critical point. The critical point for H^+hfac from Mousa's work was determined to be T_C, 485.10 K and P_C, 2767 kPa (Mousa, 1981).

Experimental Section

The H^+hfac used in these experiments was 99+% pure. This purity was achieved by distilling 95.8% pure H^+hfac (supplied by Fairfield Chemical) on a batch basis using a 2 kg charge of H^+hfac. The reboiler was controlled at a pressure of 101.3 kPa and the H^+hfac at a temperature of 71.5 °C, while the condenser was operated at 62 °C. The distillation was completed in approximately 135 min, giving 604 g of purified product at the condenser. Previous work has shown the concentration of most metallic contaminants (such as aluminum, copper, iron, nickel, and sodium) in the H^+hfac after distillation to each be less than 1 ppb as characterized by an inductively coupled plasma/mass spectrometer (Beck et al., 1994). The major volatile organic contaminant both before and after distillation was ethyl trifluoroacetate. The normal boiling point of ethyl trifluoroacetate has been reported to be 61.6 °C (Macey, 1960);

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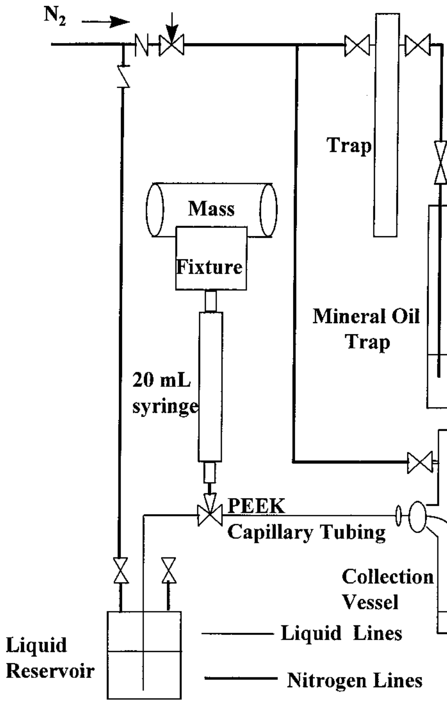

Figure 1. Experimental apparatus used to measure viscosity of D.I· H_2O, Methanol, Toluene and H^+hfac.

therefore, the condenser temperature of 62 °C might not have been sufficient to separate this impurity from the H^+hfac.

Viscosity Measurement. The viscosity experimental apparatus, shown schematically in Figure 1, was constructed to maximize the safety of the operator without compromising the integrity of the viscosity measurements. H^+hfac is a corrosive material, harmful in both its liquid and gas phases (Lenga and Votoupal, 1996). It is known to be extremely destructive to tissue of the mucous membranes and upper respiratory tract, as well as to eyes and skin (MSDS, 1995). Additionally H^+hfac rapidly forms a crystalline tetrol hydrate when exposed to moisture (Bouwman et al., 1992). Traditional methods for measuring viscosity, such as the use of an open-ended Ostwald viscometer, would have exposed H^+hfac to the moisture in the atmosphere and jeopardized the safety of the experimenter. Use of a precision syringe pump to provide a more exact flow rate and pressure, such as the Isco Model 2350 reciprocating pump, was discounted because it has stainless steel components, which are incompatible with H^+hfac. With the apparatus shown in Figure 1, all measurements of the viscosity of H^+hfac can be made without exposing it to air while minimizing the possibility of personal exposure to H^+hfac. Since H^+hfac is known to react with metals and some polymers, all wetted components of the system were constructed of glass, tetrafluoroethylene (TFE), or poly (ether ether ketone) (PEEK), materials that have shown compatibility with H^+hfac in our experimental work.

Deionized water, methanol, and toluene were used as calibration standards. The liquid of interest (water, methanol, toluene, or H^+hfac) was kept under nitrogen in the glass liquid source reservoir. A three-way valve at the base of the 20 mL syringe allowed the liquid to be transferred from the reservoir to the syringe through TFE tubing when the plunger was withdrawn. When 10 to 15 mL of liquid had been transferred to the syringe, the three-way valve was turned so that all connections were isolated from one another. To supply a known force to the system, a (1.093 ± 0.001) kg fixture was secured to the plunger either alone or in conjunction with a (2.012 ± 0.001) kg mass, thus creating pressures of (134 000 ± 100) and (197 000 ± 200) Pa on the syringe, respectively. The empty glass collection vessel was then weighed. A 3 or 5 ft length of PEEK capillary tubing with manufacturer specified internal diameters of 5.10×10^{-4} m or 7.60×10^{-4} m was then connected to the three-way valve at one end; the other end was fed into the collection vessel, and the valve was opened. After a predetermined time had elapsed (typically 10 to 120 s), the valve was turned so that all connections were isolated, ending the flow into the collection vessel. Finally, the vessel was again weighed.

The effect of the friction of the plunger in the syringe was accounted for by finding the minimum mass, $M_{\rm min}$, needed to initiate plunger movement through the syringe against the outlet pressure of the capillary, $P_{\rm outlet}$. Movement of the plunger during experiments was slow enough that this frictional force was assumed to be constant. The inlet pressure, $P_{\rm inlet}$, was determined by subtraction of this mass from the mass of the fixture ($M_{\rm fixture}$), multiplying by the gravitational constant (g), and dividing the result by the cross-sectional area of the syringe plunger ($A_{\rm s}$), as shown in eq 1. This minimum mass was measured several times during a set of experiments.

$$P_{\rm inlet} = \frac{(M_{\rm fixture} - M_{\rm min})\cdot g}{A_{\rm s}} \qquad (1)$$

The viscosity, η, in units of Pascal·seconds (Pa·s), was calculated using the data generated by the syringe pump and capillary tubing apparatus by the Hagen−Poiseuille equation. This equation is often used to calculate the experimental viscosity of a liquid by measuring the pressure drop and volumetric flow rate through a tube of known length and internal diameter for steady flow and negligible end effects (McCabe and Smith, 1976; ASTM Standard D 2162, 1991).

Capillary viscometers have an inherent error associated with the data they generate because of the time taken to establish fully developed laminar flow (ASTM Standard D 446-89a, 1991). These effects were compensated for in our experiments by the following equation

$$\eta = Ct - E/t^2 \qquad (2)$$

where

$$C = \frac{\Delta P\cdot d^4\cdot\pi}{128\cdot V\cdot L}\, t \ (\mathrm{Pa})$$

$$E = \frac{1.66\cdot V^{3/2}\cdot\rho}{L\cdot\sqrt{\dfrac{\Delta P\cdot d^5\cdot\pi}{128\cdot V\cdot L\cdot\rho}}} \qquad \text{correction term}$$

(ASTM Standard D 446−89a, 1991)

ρ = density of fluid (kg/m^3)

$\Delta P = P_{\rm inlet} - P_{\rm outlet}$ (Pa)

d = i.d. of capillary tubing (m)

L = length of tubing (m)

V = volume of liquid passed through the tube in time t (m^3)

Table 1. Tubing Internal Diameter As Determined by Equation 2 Using Data Generated from Experiments with Deionized Water at 20 °C[a]

manufacturer stated internal diameter/m	calculated diameter with standard deviation/m
7.6×10^{-4} (0.03 in. ± 0.005 in.)	$(7.44 \pm 0.0327) \times 10^{-4}$
5.10×10^{-4} (0.02 in. ± 0.005 in.)	$(5.34 \pm 0.006\ 29) \times 10^{-4}$

[a] Bath temperature was maintained at (20 ± 1) °C.

The manufacturer's stated tolerance for capillary tubing internal diameter ($\pm 1.3 \times 10^{-4}$ m) required that we determine the internal diameter experimentally. The apparent internal diameter was found by making measurements with deionized water (18.1 MΩ) using the well-established viscosity of water and substituting the experimental data into eq 2 to determine *d*. The temperature varied from 19.0 °C to 21.0 °C, and the corresponding literature viscosities of water at these temperatures were taken from Lide (1994). The experimentally determined diameters are given in Table 1. Note that the 5.10×10^{-4} m internal diameter (i.d.) tubing and the 7.60×10^{-4} m tubing both gave different internal diameters than their specifications would indicate, but within the manufacturer's tolerance. These internal diameters of the capillaries, along with data generated with spectroscopic grade methanol (EM Science) and class 1B toluene (Fisher Scientific), were used in eq 2 to determine the error in our viscosity measurements.

During the H^+hfac experiments, the liquid source reservoir, syringe, and the TFE and PEEK tubing were submerged in an ethylene glycol bath. After two or three trials with H^+hfac in the water bath or after about six trials in the ethylene glycol bath, the flow rates would decrease as the components of the system would begin to clog with the hydrate of H^+hfac (presumably due to the permeation and reaction of moisture through the tubing walls). This effect was not observed with any of the other liquids since they do not react with moisture. The system was cleaned in three steps: (1) rinsing the PEEK tubing and glass components with acetone to dissolve the H^+hfac hydrate, (2) rinsing with methanol to remove any organic residue, and (3) purging with dry nitrogen for at least 1 h to minimize the surface moisture content of the components.

Vapor Pressure Measurements. The vapor pressure of H^+hfac was found from the mass transfer of H^+hfac through a gas saturation apparatus. The following equation was used (Middleman and Hochberg, 1993)

$$\frac{dM}{dt} = \frac{P}{P_{\text{total}} - P}\cdot\frac{M_W}{R}\cdot Q \qquad (3)$$

where dM/dt = time rate of change of bubbler mass, $P_{\text{total 1}}$ = bubbler head pressure, P = saturated vapor pressure, M_W = source molecular weight, R = gas constant, Q = carrier flow rate. The saturated vapor pressure is determined by solving eq 3 for *P*. The experimental set up used is shown schematically in Figure 2.

As with the viscosity experiments, the vapor pressure experiments were designed such that no metal components were used in the apparatus and operator exposure to H^+hfac was minimized. When the initial mass of the H^+hfac in the bubbler was found, the H^+hfac was held at a constant temperature below room temperature. Both the nitrogen flow rate and its temperature were controlled as it bubbled through the H^+hfac. The nitrogen flow rate was controlled using a Brooks 5850 Mass Flow Controller and was typically about 30 $cm^3 \cdot min^{-1}$ at STP. The path length of the nitrogen gas bubbles through the H^+hfac was about 9 cm from entry point to the surface of the liquid. Vapor pressures for H^+hfac were measured at temperatures ranging between 0 °C and 57 °C. For trials conducted above room temperature, the delivery lines were heated to prevent H^+hfac condensation in the lines. Each trial was 60 min or more in duration. The mass of the transferred H^+hfac was determined by subtracting the final mass of the bubbler from the initial mass. This method, which is suggested in ASTM E1194-87 as the standard test method for determining vapor pressure (ASTM Standard E1194-87, 91), is superior in this instance to the more common static cell method because it does not require a pressure transducer with metallic components, which could fail upon exposure to the H^+hfac. The nitrogen was saturated in our experiments since the vapor pressure measurements were reproducible even as the volume of H^+hfac was depleted in the bubbler and the depth of the liquid (or contact time between a bubble and the liquid) decreased.

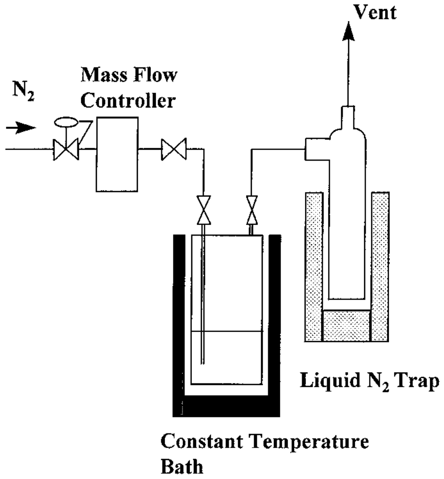

Figure 2. Experimental apparatus used to determine the saturated vapor pressure of H^+hfac.

Results

Table 2 gives our experimental results for the viscosity of methanol and toluene. Our experimentally determined viscosity of methanol is $(6.61 \pm 0.54) \times 10^{-4}$ Pa·s for the 5.10×10^{-4} m tubing and $(6.23 \pm 0.45) \times 10^{-4}$ Pa·s for the 7.60×10^{-4} m tubing at 20 °C. These standard deviations are a result of variations from run to run. According to *The Properties of Gases and Liquids* (Reid et al., 1987), the viscosity of methanol at 20 °C is expected to be 5.78×10^{-4} Pa·s. Trials were also conducted with toluene. Our experimentally determined viscosities with the 7.60×10^{-4} m i.d. tubing are presented in Table 2. A viscosity of $(6.37 \pm 0.33) \times 10^{-4}$ Pa·s was obtained for toluene at 21 °C as compared to the literature value of 5.8×10^{-4} Pa·s (Reid et al., 1987; Miller et al., 1976).

The viscosity of H^+hfac results are presented in Table 3. There is good agreement between the viscosities obtained from 5.10×10^{-4} and 7.60×10^{-4} m i.d. tubing for both lengths of tubing. At 24 °C the viscosity of H^+hfac was determined to be $(1.39 \pm 0.19) \times 10^{-3}$ Pa·s, and at 35 °C it was $(8.35 \pm 0.25) \times 10^{-4}$ Pa·s.

The vapor pressure of other compounds with established vapor pressures have been determined by the gas saturation apparatus described in the Experimental Section in

Table 2. Experimental Values for the Viscosity of Methanol and Toluene[a]

capillary internal diameter/m	methanol η (Pa·s)	toluene η (Pa·s)
$(7.44 \pm 0.0327) \times 10^{-4}$	$(6.229 \pm 0.4479) \times 10^{-4}$	$(6.371 \pm 0.3354) \times 10^{-4}$
$(5.34 \pm 0.006\,29) \times 10^{-4}$	$(6.607 \pm 0.5373) \times 10^{-4}$	

[a] Bath temperature was maintained at (20 ± 1) °C.

Table 3. Experimental Values for the Viscosity of H^+hfac at 24 and 35 °C

capillary internal diameter/m	H^+hfac η (Pa·s) (24 ± 0.2) °C	H^+hfac η (Pa·s) (35 ± 0.2) °C
$(7.44 \pm 0.0327) \times 10^{-4}$ (0.030 in.)	$(1.52 \pm 0.2016) \times 10^{-3}$	$(8.28 \pm 0.121) \times 10^{-4}$
$(5.34 \pm 0.006\,29) \times 10^{-4}$ (0.020 in.)	$(1.21 \pm 0.0664) \times 10^{-3}$	$(8.39 \pm 0.277) \times 10^{-4}$
average	$(1.39 \pm 0.19) \times 10^{-3}$	$(8.35 \pm 0.250) \times 10^{-4}$

Table 4. Temperature, Measured Vapor Pressure, and Deviation from Literature Value for TMP, TMB, and TEOS

compound/citation	t/°C	P/kPa	% deviation = $\{(P - P_{\text{lit.}})/P_{\text{lit.}}\}\cdot 100$
TMP/Dutt et al., 1982	29	3.86	−3.25
	60	16.66	−9.4
	111	106.63	+5.26
TMB/Christopher and Shilman, 1967	31	24.66	+2.78
	50	53.32	+0.73
	67	103.97	+3.04
TEOS/Kato and Tanaka, 1989	131	39.98	+0.33
	144	54.65	−3.95
	164	99.96	−1.48

Table 5. Temperature, Experimentally Determined Vapor Pressure, and Percent Deviation from the Calculated Vapor Pressure Using Equations 4 and 5

t/°C	P(kPa)	% deviation = $\{(P_{\text{calc}} - P)/P\}\cdot 100$	t/°C	P(kPa)	% deviation = $\{(P_{\text{calc}} - P)/P\}\cdot 100$
0	3.59	14.26	20	11.25	−1.28
0.9	4.07	6.12	26.5	14.84	−0.47
5.9	6.09	−8.14	50	35.72	9.53
10	8.01	−14.14	57	52.78	−3.77

order to determine the error associated with this method. Trimethyl borate (TMB), tetraethyl orthosilicate (TEOS), and trimethyl phosphite (TMP) have all been measured with this apparatus at various temperatures. Table 4 compares the results of these vapor pressure measurements to those found in the literature. These result are within 5% of the literature values and prove the validity of the technique. The vapor pressure data for H^+hfac is given in Table 5. The vapor pressure was found to vary from 4 kPa at 0 °C to 49.5 kPa at 57 °C. A linear relationship exists between natural log of pressure and inverse temperature as suggested by the Clausius−Clapeyron equation. A least-squares fit to the data in Table 5 using this relationship yielded

$$\ln(P/\text{kPa}) = -3.98\left(\frac{1000}{T/\text{K}}\right) + 15.97 \qquad (4)$$

The R^2 value of this fit is 0.9907. Percentage deviations of the experimental data from this line, defined as

$$\frac{P_{\text{calc}} - P}{P}\cdot 100 \qquad (5)$$

were calculated and are shown in Table 5.

Discussion

The measured viscosity of methanol at 20 °C ((6.4 ± 0.6) × 10^{-4} Pa·s) is within 10% of the literature value of 5.78 × 10^{-4} Pa·s at 20 °C (*Handbook of Physical Properties of Liquids and Gases*, 1975). The *Handbook of Physical Properties of Liquids and Gases* and Miller et al. also give values for toluene; both report a viscosity of 5.80 × 10^{-4} Pa·s at 21.0 °C, which is within 10% of our experimentally determined value of (6.37 ± 0.33) × 10^{-4} Pa·s at the same temperature (Miller et al., 1976). Since the experimental values are within 10% of the accepted literature values, it was determined that the experimental apparatus and procedure were a valid means for finding the viscosity of H^+hfac within this range of error. The experimental viscosity of H^+hfac was found to be (1.39 ± 0.19) × 10^{-3} Pa·s at 24.0 °C and (8.35 ± 0.25) × 10^{-4} Pa·s at 35 °C.

Several interesting characteristics of H^+hfac were observed during the viscosity measurement. H^+hfac hydrated readily and rapidly to produce a white, adherent substance wherever it encountered moisture. The presence of moisture in the system was most likely due to permeation through the PEEK capillary. For this reason, an ethylene glycol bath was used instead of a water bath to control the temperature of the H^+hfac experiments. As noted previously, the tubing and glass components of the system had to be cleaned to ensure a repeatable flow rate over a series of runs. After several capillary cleans (discussed in the Experimental Section), the internal diameter was redetermined with deionized water and found to be unaffected by H^+hfac exposure.

In this study we report that the vapor pressure of H^+hfac in the 0 °C to 57 °C temperature region ranges from 4 to 49.5 kPa. Slight experimental error is possible due to some uncertainty in the measurement of bubbler headspace pressure during the experiment. Table 4 shows this error to be an error less than 5%. By extrapolating eq 4, the vapor pressure of H^+hfac at a particular temperature may be determined. When the experimental data are extrapolated to temperatures above 57 °C, the vapor pressures obtained agree reasonably well with those found by Mousa below the critical point of H^+hfac (Mousa, 1981). When the calculated vapor pressures at the normal boiling point of H^+hfac (70 °C) for both experiments are extrapolated, it is found that the method described here gives a vapor pressure much closer to atmospheric pressure than that reported previously; 76.1 kPa in this work versus 161.7 kPa at 70 °C (Mousa, 1981).

When the present data are analyzed and fitted to the Clausius−Clapeyron equation, eq 4, the heat of vaporization, ΔH_v, is calculated to be 33 kJ·mol^{-1}. This value is comparable to the value cited by Irving and da Silva, of 30.5 kJ·mol^{-1} (Irving and da Silva, 1975). The percent difference from our work to this value is 7.5. The vapor pressures determined by Mousa (Mousa, 1981) were near the critical point of H^+hfac and cannot be extrapolated with confidence to the subatmospheric pressures studied in the current work. The heat of vaporization from that work calculated from Mousa'a data is 34 $kJ \cdot mol^{-1}$. which is a 12.5% difference from the value reported by Irving and da Silva.

Conclusions

The viscosity of H^+hfac was found to be $(1.39 \pm 0.19) \times 10^{-3}$ Pa·s at 24 °C and $(8.35 \pm 0.25) \times 10^{-4}$ Pa·s at 35 °C. These data, determined using methods designed to compensate for the reactive and toxic nature of H^+hfac were obtained with an apparatus that utilized a known force on a syringe and varying lengths of capillary tubing much like a direct liquid injection system. Additionally, the vapor pressure of H^+hfac was determined to have values increasing from 4 to 49.5 kPa in the 0 °C to 57 °C temperature range. An equation based on the well-known Clausius−Clapeyron approximation describing this vapor pressure curve has been developed.

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