Vapor Pressure Measurements by the Gas Saturation Method: The Influence of the Carrier Gas

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Supporting Information

ABSTRACT: The influence of the carrier gas on vapor pressure ($p_{\text{sat}}$) measurements by the gas saturation method was studied. Eicosane ($C_{20}H_{42}$) was used as the test compound. Helium (He), nitrogen (N$_2$), carbon dioxide (CO$_2$), and sulfur hexafluoride (SF$_6$) were chosen as the carrier gases. The apparent $p_{\text{sat}}$ of eicosane was determined repeatedly in each of the four carrier gases at 323.15 K, and was found to increase with carrier gas in the order He < N$_2$ < CO$_2$ < SF$_6$. On average, the apparent $p_{\text{sat}}$ was 26% higher when measured with SF$_6$ than when measured with helium, which shows that the assumption of ideal-gas behavior for gas saturation measurements can lead to large errors.

INTRODUCTION

The gas saturation method (also known as the transpiration method or gas current method) is a common measurement technique for the determination of vapor pressures below ~1 kPa.$^{1-10}$ It is an indirect method in which a carrier gas stream is saturated with the vapor of a condensed phase of the compound of interest. The vapor pressure ($p_{\text{sat}}$) is then calculated from the quantity of vapor solute in a known amount of carrier gas. This measurement method has several important advantages: The effect of impurities is relatively small and predictable; therefore samples of limited purity can be measured. Calibration with compounds of known vapor pressure is not required. Apparatus design and construction are relatively simple and inexpensive.

The gas saturation method also has drawbacks. The most relevant drawback for this work is that this method does not measure the true vapor pressure of a substance, which is defined as the pressure of a pure vapor in equilibrium with its pure condensed phase at a specified temperature. Obviously, for this method, the vapor phase is not pure and consists primarily of the carrier gas. Any nonideality in the vapor-phase mixture will influence the measurement and will cause a systematic error in the data unless a correction is made.

Many decades ago, a method was described that corrects for the interaction of carrier gas with the vapor solute.$^6$ This method requires measurements with two carrier gases at multiple pressures. This is a sound approach, but it is laborious and it requires an instrument that is capable of operating at multiple pressures. Consequently, it has not been adopted by the measurement community. Instead, ideal-gas behavior is assumed in the overwhelming majority of vapor pressure determinations by the gas saturation method. Occasionally, this assumption of ideal-gas behavior has been considered as a source of uncertainty,$^{4,11}$ has been tested with experimental measurements,$^{3,6}$ or the vapor nonideality has been considered as a correction,$^{3,12}$ but such cases are rare.

The purpose of this work is to test the influence of carrier gas on vapor pressure measurements by the gas saturation method. Eicosane ($C_{20}H_{42}$) was chosen as the test compound because it has a well-known vapor pressure, which has been measured with a variety of techniques,$^{5,8,13-17}$ and correlated.$^{18,19}$ It is also chemically stable and available commercially in good purity. Helium (He), nitrogen (N$_2$), carbon dioxide (CO$_2$), and sulfur hexafluoride (SF$_6$) were chosen as the carrier gases because they have widely varying polarizabilities. The equilibrium vapor mole fraction of eicosane was measured at 323.15 K in each of the four carrier gases. A companion paper interprets these same data in terms of virial coefficients derived from molecular models.$^{20}$

EXPERIMENTAL SECTION

Chemicals. Eicosane was obtained from a commercial source and was used as received. Our analysis by gas chromatography with flame ionization detection (GC-FID) indicated a mass fraction purity of 0.998, which is consistent with the manufacturer’s purity statement. A single impurity in the eicosane accounted for about $\frac{1}{3}$ of the total integral area for impurities. This impurity eluted after eicosane, which suggests that it has a higher molecular mass than eicosane. Octadecane, used as an internal standard for GC-FID analysis, was obtained from a commercial source and was used as received. Our analysis by GC-FID indicated a mass fraction

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purity of 0.992, which is consistent with the manufacturer’s purity statement. Reagent-grade acetone and octane, used as solvents in this work, were obtained from commercial sources and used as received. Our analysis by GC-FID indicated mass fraction purities $\geq 0.99$, which is consistent with the manufacturer’s purity statements.

The carrier gases were obtained from commercial sources and used as received. Two grades of nitrogen gas were used—industrial grade (mole fraction purity $\geq 0.995$) was used for the first three vapor pressure measurements with nitrogen, and ultrahigh purity grade (mole fraction purity 0.999995) was used for subsequent measurements in nitrogen. Use of the better grade of nitrogen did not significantly change the measured vapor pressure. The stated mole fraction purities of the other carrier gases were 0.99997 for carbon dioxide, 0.999 for sulfur hexafluoride, and $\geq 0.995$ for helium. Before use, each of the carrier gases was transferred into a small evacuated aluminum cylinder to facilitate mass determinations (see below).

**Concatenated Gas Saturation Apparatus.** The concatenated gas saturation method, as a concept, was invented at NIST. The measurements described herein were done with a new apparatus that was designed and constructed at NIST. The design of the new apparatus is similar to an earlier apparatus for which a detailed description has been published. However, as described below, a number of small changes have been made to improve the performance of the new apparatus.

The principal components of the apparatus were a carrier gas supply system, a series of saturators and adsorbers, and a temperature-controlled chamber (Figure 1). The carrier gas supply system included an aluminum gas cylinder filled with carrier gas, a pressure regulator, an ultralow-flow mass flow controller, an adsorber, and a pressure gauge. The cylinder-regulator assembly was removed between vapor pressure measurements to determine the mass of carrier gas that was used. To facilitate this procedure, the cylinder-regulator assembly was connected to the mass flow controller by a 25 cm section of stainless steel tubing (0.76 mm inside diameter) with a valve at each end. Closing these two valves allowed the cylinder-regulator assembly to be removed with the loss of $<1$ mg of carrier gas. The electronic mass flow controller had a range of (0.1 to 10) cm$^3$ min$^{-1}$ with a built-in totalizer function that determined the total amount of carrier gas used in a specified interval. After exiting the mass flow controller, the carrier gas passed through an adsorber (see below) packed with the porous polymer adsorbent poly(2,6-diphenyl-1,4-phenylene oxide), which was intended to remove impurities from the carrier gas. The last component of the carrier gas supply was a Bourdon-tube pressure gauge (located just upstream from the first saturator–adsorber pair), which was used to determine the pressure drop along the series of saturator–adsorber pairs. Unless otherwise indicated, the various components were plumbed together with stainless steel tubing with an outside diameter of 1.59 mm and an inside diameter of 0.76 mm.

The carrier gas then flowed through a series of saturator–adsorber pairs before it vented into the laboratory at ambient pressure. As many as 18 saturator–adsorber pairs can be plumbed in series in this apparatus. However, for this work, only six saturator–adsorber pairs were used. The use of fewer saturator–adsorber pairs decreased the volume of the carrier gas in the apparatus and minimized the pressure drop across the apparatus. The saturators were located inside a temperature-controlled forced-air chamber, while the adsorbers were located on a manifold above the chamber (at room temperature, approximately 294 K). Each saturator was made from a PTFE tube with an outside diameter 0.635 cm, an inside diameter of 0.476 cm, and a length of either 33 or 61 cm. Except for 4 cm sections on each end, the saturators were packed with 1 mm glass beads that were held in place by PTFE inserts. Compression fittings were used to mount the saturators, in the form of a hanging loop, inside the temperature-controlled chamber. The shorter saturators had an average void volume of 3.4 mL, and the longer saturators had an average void volume of 5.5 mL (determined by filling each saturator with acetone with a volumetric syringe). The series of saturator–adsorber pairs alternated short saturators with long saturators for a total of six (Figure 1).

The main body of each adsorber consisted of a stainless-steel tube 7.5 cm in length with an outside diameter of 0.953 cm and an inside diameter of 0.635 cm. These were packed with the porous polymer adsorbent poly(2,6-diphenyl-1,4-phenylene oxide).
oxide). PTFE inserts and plugs of glass wool at either end held the adsorbent in place. Reducing unions at each end of the adsorber allowed the connection to 1.59 mm stainless steel tubing. The 1.59 mm tubing on the inlet side was an integral part of the adsorber—it was a “stinger” that went through the roof of the temperature-controlled chamber and penetrated into the outlet end of the saturator. The stinger prevented the loss of solute vapor as the carrier gas flowed from the temperature-controlled saturator to the room-temperature adsorber. The outlet end of the adsorber directed the carrier gas into the next saturator. The average void volume of the adsorbers (determined by filling each adsorber with acetone with a volumetric syringe) was 1.8 mL.

There were several changes in the design of this apparatus compared to a previously reported apparatus. One important change was the use of an electronic mass flow controller with a totalizer function, instead of the manual flow controller used previously. The electronic mass flow controller provided an independent (albeit lower accuracy) method for determining the amount of carrier gas used for a vapor pressure measurement (in addition to weighing the carrier gas supply cylinder), and it facilitated controlled changes to the flow rate. Another important design change in the new apparatus involved the use of saturators of different lengths for each sample, which provided an internal check that the flow rate of carrier gas was slow enough to allow for equilibration. A third change was the use of a single pressure gauge to determine the pressure drop across the apparatus (instead of having a pressure gauge for each saturator–adsorber pair). This eliminated substantial dead volume in the system and simplified the plumbing. Other changes were made to reduce the internal volume of the saturator–adsorber chain. The saturators were shorter overall and were filled with smaller glass beads, and the adsorbers had a smaller internal diameter. This reduced the void volume of each saturator–adsorber pair from about 16 mL in the previous apparatus to about 7 mL (for the longer saturators) or 5 mL (for the shorter saturators). Reducing the internal volume of the saturator–adsorber chain is particularly desirable for this work because the carrier gas was changed between each measurement. A small internal volume allowed the previously used carrier gas to be flushed from the system with a negligible volume of the new carrier gas. For the measurements reported here, the internal volume of the system was ≤ 0.5 % of the volume of carrier gas used for the measurement. Therefore, the effect of the previously used carrier gas was negligible.

Measurement of the Mass of Eicosane Vapor and the Mass of Carrier Gas. Each saturator was coated with eicosane in the following way. First, a 10% (mass/mass) solution of eicosane in hexane was made. The glass beads in each saturator were wetted with ~1.5 mL of this solution, and the excess was poured out. Then the hexane was removed by a gentle flow of helium through the adsorber at room temperature for ≥0.5 h. The coated saturators were installed in the temperature-controlled chamber of the apparatus. At one point during the course of these measurements, more of the eicosane solution was applied to the saturators (this was done after a measurement in which two of the saturator–adsorber pairs yielded abnormally low values for the vapor pressure).

Before each measurement, the starting mass of the carrier gas supply cylinder was determined on a high-accuracy electronic balance with a 10 kg capacity by use of a double-substitution weighing design. This method comprised four separate weighings: (1) a reference cylinder and standard masses, (2) the sample cylinder and (different) standard masses, (3) the sample cylinder and standard masses used in weighing 2 plus a 20 g sensitivity mass, and (4) the reference cylinder and standard masses used in weighing 1 plus a 20 g sensitivity mass. The standard masses were chosen to give approximately the same total balance loading for weighings 1 and 2. A key advantage of this approach is that the air buoyancy effect reduces to the small differences in volumes of the tare and sample cylinders and the standard masses. A buoyancy correction was made by measuring the ambient pressure, temperature, and humidity in the balance chamber and using those data to calculate the air density with the equation of Picard et al.26

After being weighed, the carrier gas supply cylinder was placed in an enclosure on the gas saturation apparatus, which served to protect the cylinder from dust. The adsorbers were installed. Then temperature was set and, after 10 min for thermal equilibration, the totalizer was zeroed and the flow of carrier gas was initiated. The flow rate of carrier gas was set to 1.0 cm³·min⁻¹, which resulted in a residence time of the carrier gas in a saturator of about 5 to 7 min. Most measurements were done with a total flow period of about 7 days, but periods as long as 21 days were used. There was no significant difference in the apparent vapor pressures for longer flow periods. At the end of this period, the flow of carrier gas was stopped and the carrier gas supply cylinder was weighed again to determine the mass of carrier gas used.

The vapor collected in each adsorber was prepared for analysis by GC-FID in the following way. After each run, a standard octadecane solution was prepared (by mass) in a 30 mL glass vial with octane as the solvent. The octadecane concentrations ranged from about 0.3 % to 0.5 %. About 0.5 g of the octadecane solution was weighed into each of 12 GC autosampler vials, which were then loosely capped. The eicosane vapor that had collected in each adsorber was eluted into the autosampler vials in the following way. The adsorber (including the stinger) was removed from the apparatus and connected to a syringe pump filled with acetone. The syringe pump was set to deliver acetone at a rate of 0.25 mL·min⁻¹, and the first ~1 mL of eluent from the adsorber was collected into one of the autosampler vials, which was then capped. The flow rate of acetone from the syringe pump was then increased to 0.5 mL·min⁻¹ and the next ~1 mL of eluent was collected in a second autosampler vial, which was then capped. The flow rate was increased to 2 mL·min⁻¹ and the next 8 mL of eluent was discarded. Finally, the adsorber was dried with a flow of helium before using it for the next measurement.

The eluent fractions (with octadecane as an internal standard) were analyzed by GC-FID. Research-grade nitrogen was used as the carrier and makeup gas. The split/splitless injection inlet was used in the splitless mode and maintained at 300 °C. The samples were separated on a 30 m capillary column coated with a 0.25 μm film of (5 %-phenyl)-methylpolysiloxane. The temperature program consisted of 1 min at 100 °C, followed by a 100 °C·min⁻¹ gradient to 130 °C, followed by a 20 °C·min⁻¹ gradient to 210 °C, with a 4.7 min hold at 210 °C.

The relative sensitivity of the FID to eicosane and the internal standard (octadecane) was determined by analyzing known mixtures. Four mixtures were made with eicosane/octadecane ratios from approximately 1:10 to 1:1. These mixtures were dissolved in octane and analyzed by GC-FID as
described above, and a plot of the peak area ratio versus the mass ratio was made. The slope of a linear fit to the data was 0.999 (with an R² value of 0.9999). Hence, as expected, the FID is equally sensitive to eicosane and octadecane on a mass basis.

**Calculation of Apparent Vapor Pressure.** Apparent vapor pressures were calculated from the raw data by a form of the ideal gas law that contains the Poynting correction, eq 1,

\[
p_{\text{sat}} = \frac{(mRT)}{(VM\Phi)}
\]

where \(p_{\text{sat}}\) is the apparent vapor pressure of eicosane, \(m\) is the recovered mass of eicosane vapor, \(R\) is the gas constant, \(T\) is the temperature of the saturator, \(V\) is the volume of carrier gas at the temperature and pressure of the saturator, \(M\) is the molar mass of eicosane, and \(\Phi\) is the Poynting correction. Assuming that the condensed phase is incompressible, and knowing that \(p_{\text{sat}}\) is negligible compared to the experimental pressure (\(p\)), then \(\Phi = \exp(p v/(RT))\), where \(v\) is the molar volume of liquid eicosane. This is a small correction, which lowers all values of apparent \(p_{\text{sat}}\) by \(\sim 1\ %\), so it did not significantly change discrepancies among carrier gases. The volume of carrier gas, \(V\), was determined from a high-accuracy equation of state for each carrier gas\(^{29-32}\) as implemented in REPROP\(^{33}\). For these measurements the effect of the eicosane on the vapor volume could be ignored because its mole fraction was very small compared to that of the carrier gas. The pressure in the saturators was taken to be ambient, which is 83.2 kPa (with a standard deviation of 0.6 kPa) on the NIST site in Boulder, Colorado. This was determined by continuous on-site monitoring of the local atmospheric pressure for one year.

**Possible Systematic Errors in the Measurement of \(p_{\text{sat}}\).** For this study, it is important to rule out sources of systematic error other than gas-phase nonideality. With the concatenated apparatus, which had a large number of connections along the carrier gas stream, a potential source of systematic error would be a leak of the carrier gas. Downstream from a leak, less carrier gas would flow through the saturators, which would result in systematically low values of \(p_{\text{sat}}\). Fortunately, the concatenated method also makes such a situation easy to identify. Since six simultaneous determinations of \(p_{\text{sat}}\) were done for each eicosane measurement, a comparison of \(p_{\text{sat}}\) values measured in different parts of the apparatus can be used to detect any leaks within the saturator–adsorber chain. The only evidence of leakage anywhere in the system occurred when helium was the carrier gas. For all of the measurements with helium, there was a decline in the apparent \(p_{\text{sat}}\) along the saturator–adsorber chain. The apparent \(p_{\text{sat}}\) decreased by an average of 0.0013 Pa for each saturator–adsorber pair. Tightening or changing the fittings in the saturator–adsorber chain had no effect on this behavior. We believe that this was a manifestation of the well-known permeability of PTFE to helium (i.e., some of the helium carrier gas was leaking through the PTFE tubing used to make the saturators).\(^{34}\) In the tables and figures, the values of \(p_{\text{sat}}\) with helium carrier gas have been corrected for this effect by adding 0.0013 Pa to the apparent \(p_{\text{sat}}\) measured in the first saturator–adsorber pair, 0.0026 Pa to the apparent \(p_{\text{sat}}\) measured in the second saturator–adsorber pair, and so forth.

Another possible source of systematic error would be a carrier gas flow rate that was too fast or too slow. A flow rate that was too fast would result in a lower apparent \(p_{\text{sat}}\) due to insufficient equilibration time in the saturators. In addition to lengthening the measurement time, a flow rate that was too slow would result in a higher apparent \(p_{\text{sat}}\) due to significant diffusional mass transfer.\(^{3,35}\) Two tests for such flow rate effects were employed. First, saturators of two different lengths were used for each experiment (see above). Both types of saturators yielded the same values of \(p_{\text{sat}}\) within the repeatability of the measurement, which is excellent evidence that the equilibration time was sufficiently long. Second, we did replicate measurements at half the normal flow rate. Again, the same values of \(p_{\text{sat}}\) were obtained within the repeatability of the measurement, which is excellent evidence against flow rate effects.

**Uncertainties in the Measurement of Vapor Pressure.** A detailed analysis of the uncertainties in the measurement of \(p_{\text{sat}}\) with a concatenated gas saturation apparatus of similar design has been published.\(^{11}\) Except for vapor nonideality (which we consider separately), temperature control is the principal source of uncertainty for these measurements. Temperature gradients and temperature fluctuations in the temperature-controlled chamber were measured with an ITS-90 calibrated platinum resistance thermometer (PRT). During the course of the vapor pressure measurements, the calibration of the PRT was checked with both a water triple-point cell \((T = 273.16 \text{ K})\) and a gallium fixed-point cell \((T = 302.9146 \text{ K})\). The temperatures measured by the PRT deviated from the two fixed points by \(\leq 0.014 \text{ K}\). With a temperature set-point of 323.15 K, the PRT was placed in 12 different locations (at the bottom/middle of each saturator loop and near the exit end of each saturator) and temperature fluctuations were recorded at each location. Generally, temperature fluctuations in a particular location were relatively small, typically less than \(\pm 0.05 \text{ K}\). A larger source of uncertainty comes from temperature gradients in the chamber, which increased in magnitude with temperature settings farther from ambient. Considering both temperature gradients and temperature fluctuations, we estimate that the standard uncertainty in temperature is 0.36 K at a setting of 323.15 K. By use of a literature value for the slope of eicosane’s vapor pressure curve at 323.15 K,\(^{19}\) this uncertainty in the temperature results in relative standard uncertainty in the measured \(p_{\text{sat}}\) of 4.6 % with He as the carrier gas, 4.5 % with \(N_2\), 4.4 % with \(CO_2\), and 3.7 % with \(SF_6\). Temperature gradients were also the primary source of scatter in the measured data for a given carrier gas.

Determination of the mass of recovered vapor solute by GC-FID with an internal standard had an estimated relative standard uncertainty of 3 %. This includes uncertainties in the preparation and use of the internal standard solution, uncertainties associated with adsorber efficiency and adsorber elution, and the repeatability of the chromatographic analysis. The determination of the mass of helium by weighing the supply cylinder resulted in a relative standard uncertainty of 1 % in the measured \(p_{\text{sat}}\) of eicosane. The determination of the mass of the other carrier gases by weighing the supply cylinder resulted in relative standard uncertainties of \(\leq 0.1 \%\) in the measured \(p_{\text{sat}}\) of eicosane. A confirmatory measurement of the mass of carrier gas was obtained from the mass flow controller (with a larger uncertainty). The mass flow controller has a range of (0.1 to 10) standard cm³/min⁻¹ with a manufacturer-
claimed accuracy of (0.4 % of reading + 0.2 % of full scale). Therefore, at a flow rate of 1.0 cm³·min⁻¹, the manufacturer-estimated relative uncertainty is 2.4 %. The difference between the two methods of mass determination never exceeded the manufacturer’s uncertainty estimate for the mass flow controller.

The pressure in the saturators was not directly controlled. There was a slight pressure drop across the six saturator–adsorber pairs of ≤0.5 kPa for the carrier gases and flow rates used for this work, which we treat as an uncertainty in the experimental pressure. Additionally, since the carrier gas exited the apparatus at ambient pressure, barometric variability contributed a standard uncertainty of approximately 0.6 kPa to the experimental pressure. Both of these effects caused some uncertainty in the volume of carrier gas that passed through a saturator. The combined standard uncertainty in the experimental pressure leads to a relative standard uncertainty of 0.9 % in the measured vapor pressures.

There was also an uncertainty caused by impurities in the eicosane. In an ideal-mixture approximation, the partial pressure of each component of a sample is equal to the product of its mole fraction and its vapor pressure. Based on the GC-FID analysis of eicosane, we know that the mass fraction purity of the eicosane was 0.998 (see above) and that the molecular mass of the principal impurity was somewhat higher than that of eicosane. Therefore, the expected shift in the measured vapor pressure due to impurities is unlikely to exceed 0.2 %. We have no reason to suspect that the eicosane would react or decompose under the mild conditions of these measurements, and there was no evidence of decomposition from the GC-FID analysis of the trapped vapor, so we do not believe that the purity of the eicosane decreased significantly during the measurements. The solubility of each carrier gas in the eicosane (which is a liquid at 323.15 K) causes a shift in the measured p_sat in the same way that impurities do. The mole fraction solubility of SF₆ in long-chain n-alkanes is approximately 0.008 at 298.15 K and 0.1 MPa, hence, the expected shift in the measured p_sat of eicosane is <0.8 % because the p_sat measurements were done at a higher temperature (323.15 K) and lower pressure (0.0832 MPa). Similarly, the solubility of the other carrier gases can be estimated from literature data as 1 % for carbon dioxide, 0.1 % for nitrogen, and 0.03 % for helium. However, because of the need to extrapolate to different temperature, pressure, or alkane solvent, we treated this effect as an uncertainty in the measurements (instead of attempting to correct the measurements for this effect).

Additional miscellaneous effects were also considered as uncertainties in the data. At the beginning of each measurement, the apparatus still contained the previously used carrier gas. The effect of this retained gas on the subsequent measurement is estimated to be 0.1 % or less (based on the observed differences between measurements in the different carrier gases). A correction was made for helium leakage through the PTFE saturators (see above). This correction is estimated to have a relative standard uncertainty of 2.7 % for the measured apparent p_sat in helium. Any nonideality of saturated solute vapor is expected to be negligible because the vapor pressures are low and there is no reason to suspect an effect like dimerization. Of course, the most important nonideality is the interaction of the solute vapor with the carrier gas, but this is considered separately from the uncertainty budget because it is the quantity under investigation.

The quadrature sum of relative standard uncertainties associated with the measurement of apparent p_sat yields a combined standard uncertainty of 5.5 % for measurements with SF₆ carrier gas, 6.1 % with CO₂, 6.1 % with N₂, and 6.7 % with He. However, much of the uncertainty for these measurements is systematic, so there is less uncertainty in the observed differences among carrier gases.

## RESULTS

The apparent vapor pressure of eicosane was determined in four different carrier gases at 323.15 K. Over the course of about a year, these determinations were done repeatedly, switching back and forth among the four carrier gases to ensure that any observed differences were repeatable. For each determination, six simultaneous measurements were made with the same carrier gas stream (see the Experimental section for details). Figure 2 shows each determination as a function of the date of the measurement. The error bars in Figure 2 give the standard deviation of the six measurements. The solid line shows a reference value for the vapor pressure of eicosane; the dashed lines show the uncertainty interval for the reference value.

![Figure 2. Replicate determinations of the apparent vapor pressure (p_sat) of eicosane at 323.15 K in different carrier gases as a function of the date of the measurement. The four carrier gases used were He (◇), N₂ (○), CO₂ (□), and SF₆ (△). Each data point represents the average of six simultaneous measurements; the error bars give the standard deviation of the six measurements. The solid line shows a reference value for the vapor pressure of eicosane; the dashed lines show the uncertainty interval for the reference value.

The apparent vapor pressure of eicosane depends on the identity of the carrier gas. Helium tends to give the lowest values for p_sat and SF₆ the highest. In general, the apparent value of p_sat increases with carrier gas in the order He < N₂ < CO₂ < SF₆, however, not all of the differences are statistically

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significant. The data in Figure 2 demonstrate that these differences are repeatable and do not drift significantly over time. It is also worth noting that only the determinations in SF₆ yield values that are significantly different than the reference value.

Table 1 gives the average value for all the measurements with each carrier gas. The mole fraction of eicosane (y₁) in the vapor phase is included in Table 1 because it is obtained experimentally without any assumptions of ideality and is the same order that is observed in the apparent p_{sat} value.

<table>
<thead>
<tr>
<th>carrier gas</th>
<th>y₁10⁻⁷</th>
<th>apparent p_{sat}/Pa</th>
<th>σ(p_{sat})/Pa</th>
<th>u_c(p_{sat})/Pa</th>
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<tbody>
<tr>
<td>SF₆</td>
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<td>0.05656</td>
<td>0.00174</td>
<td>0.00313</td>
</tr>
<tr>
<td>CO₂</td>
<td>5.702</td>
<td>0.04707</td>
<td>0.00076</td>
<td>0.00287</td>
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<tr>
<td>N₂</td>
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<td>0.04578</td>
<td>0.00159</td>
<td>0.00279</td>
</tr>
<tr>
<td>He³</td>
<td>5.454</td>
<td>0.04485</td>
<td>0.00107</td>
<td>0.00302</td>
</tr>
</tbody>
</table>

“These values were calculated with eq 1.” These values have been corrected for the interaction of the solute vapor with the carrier gas (see the Experimental section for details).

### DISCUSSION

It is important to rule out some common difficulties with the gas saturation method that could cause a spread in the values of p_{sat} obtained in the different carrier gases. These effects include significant mass transfer by diffusion, insufficient equilibration time in the saturator, incomplete recovery of vapor solute, and leaks. Significant mass transfer by diffusion was ruled out by experiment (see the Experimental section) and by the fact that helium would be expected to give the most diffusional transfer (and SF₆ the least), which is the opposite of the observed trend for the carrier gases. Similarly, insufficient equilibration time was ruled out by experiment (see the Experimental section) and by the fact that helium would be expected to equilibrate the fastest (and give the highest p_{sat} in an equilibration-limited measurement), which is the opposite of the observed trend. Incomplete recovery of vapor solute is unlikely to account for the repeatable differences observed in Figure 2, especially since the procedure used and the quantity of vapor solute was similar for all of the measurements. It is also worth noting that, for a particular carrier gas, the measured p_{sat} did not depend on the amount of solute vapor collected (see Table S1 of the Supporting Information). Carrier gas leaks could cause shifts in the measured value of p_{sat}. Because of its relatively large molecular size, SF₆ is the least prone to leak, and helium is the most prone to leak, which is consistent with the values of p_{sat} obtained with the different carrier gases. However, the concatenated design of the gas saturation apparatus used for these measurements makes the detection of leaks straightforward. In fact, leaks were only detected when helium was the carrier gas, and the values of p_{sat} in Table 1 and Figure 2 have been corrected for the leak (see the Experimental section). Additionally, the measured value of p_{sat} in all of the carrier gases is equal to or greater than the reference value, which is good evidence against the presence of significant undetected leaks.

In the absence of these other effects, nonideality of the vapor phase mixture is the most likely cause of the observed differences in the apparent p_{sat}. In these gas saturation experiments, nonideality in the vapor phase manifests as higher apparent p_{sat}. On average, compared to helium, the apparent p_{sat} was 26% higher when measured with SF₆, 5% higher when measured with CO₂, and 2% higher when measured with N₂. The fact that helium is the most ideal carrier gas and SF₆ is the least ideal is no surprise, but the magnitude of the difference between the two is surprising. Published measurements with SF₆ carrier gas may need to be reassessed. In fairness to those earlier works, vapor phase nonideality was considered as a source of uncertainty, but SF₆ was used anyway because of the need for a high-density carrier gas.

We started this work with the hypothesis that the polarizability of the carrier gas would correlate with the magnitude of the nonideality for the vapor phase mixture, and the carrier gases were chosen so that they would have a range of polarizabilities. The average electric dipole polarizabilities of the four carrier gases (in units of 10⁻²⁴ cm³) are 0.2051 for helium, 1.7403 for N₂, 2.911 for CO₂, and 6.54 for SF₆. This is the same order that is observed in the apparent p_{sat} values (Table 1). On the basis of this result, polarizability may be a useful guide to predict how (non)ideal a carrier gas will be in the gas saturation experiment.

Of course, it is the interaction of the carrier gas with the vapor solute that creates nonideal behavior in the gas saturation measurement of p_{sat}. We did not vary the solute for these experiments, but it should be noted that polarizability generally scales with molecular size. Therefore, the influence of nonideality on measurements of p_{sat} is expected to increase for larger molecules and decrease for smaller molecules. This effect can be seen by comparing the present results for eicosane in SF₆ carrier gas with earlier measurements of tetradecane in SF₆: the apparent p_{sat} for the smaller tetradecane molecule exceeded the reference value by only 11%, compared to 23% for the larger eicosane solute. Similarly, the influence of nonideality on measurements of p_{sat} is expected to increase at lower temperatures (where the intermolecular forces are relatively strong compared to the thermal energy) and decrease at higher temperatures.

Choosing the best carrier gas is not necessarily as simple as choosing the one with the most ideal behavior. Helium’s tendency to leak (and to diffuse through polymers) and its low atomic mass, which increases the uncertainty of gravimetric determinations, can make its use impractical. SF₆ has many useful properties (e.g., it is inert, has a high density, and is not prone to leak), but its behavior is so nonideal that it will likely be a poor choice. Of the other gases tested, N₂ is a good overall choice—it’s behavior is close to ideal, it does not leak too readily, it is suitable for gravimetric determinations, and it is inexpensive. Although not tested here, argon might be superior to the commonly used N₂ as a carrier gas since its polarizability is slightly lower. Argon is also denser than N₂ and less prone to leak.

### CONCLUSIONS

Electric dipole polarizability correlates well with the observed nonideality of the vapor phase mixture in gas saturation measurements of p_{sat}. Further experimental tests of this correlation are merited. It would be interesting to test other
carrier gases, other types of vapor solutes (such as polar molecules), and to determine temperature trends. This is an area that is ripe for modeling studies such as the companion paper\(^2\) referenced in the Introduction. \(N_2\) appears to be a good all-around choice for a carrier gas, and argon may also be a good choice. Because of considerable vapor-phase nonideality, measurements with \(SF_6\) as the carrier gas should be avoided. In any case, for gas saturation measurements of \(p_{sat}\) we recommend including a term in the uncertainty budget for nonideal mixture behavior and, if possible, estimating a correction for the nonideality as discussed elsewhere.\(^2\)

**ASSOCIATED CONTENT**

**Supporting Information**

Table S1 contains the data for the individual determinations of apparent \(p_{sat}\) for eicosane in four different carrier gases at 323.15 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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