Extending the Solid-Phase Microextraction Technique To High Analyte Concentrations: Measurements and Thermodynamic Analysis

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The solid-phase microextraction (SPME) technique has been used historically to quantify analytes present at the parts per million level. However, the nonintrusive nature of SPME lends itself to other applications involving analytes at higher concentration. In the current work, the possibility of using the SPME technique to measure concentrated gaseous samples was examined. Pentane concentrations between 0 and 100% saturation were studied, over a temperature range of 20−45 °C. The results showed that, up to a critical mole fraction in the solid phase, the concentrations of pentane in the polymeric extracting solid and vapor phases were related by a constant, equal to Henry's constant. The temperature dependence of Henry's constant was shown to follow the predicted trend with temperature, as determined from rigorous thermodynamic calculations. Above the pentane concentration in the polymeric phase, the response deviated from linearity. The nonideality was captured in an activity coefficient. An activity coefficient model developed to describe the nonideality was found to be a function of the swollen volume of the SPME polymer phase. The results indicate that the SPME technique can be applied to high analyte concentrations, although difficulties may be encountered when multiple analytes are absorbed.

Solid-phase microextraction (SPME) is a solvent-free analytical technique developed for dilute systems. In this method, a polymer-coated fiber is exposed to the gas or liquid phase containing the analytes of interest. Generally, a minimum analysis time is imposed so that equilibrium conditions are established between the solid and fluid phases, with respect to the measured species. However, this is not necessary, provided the exposure time and conditions are kept constant.[1−3] Following exposure, the contents of the fiber are desorbed and quantified using gas chromatography. Through knowledge of the equilibrium relationship between the polymer and fluid phases, the concentration of analytes in the original fluid can be determined.

Application of the SPME technique has focused exclusively on quantifying dilute solutions of the compound of interest.[4,5] The method has been, and continues to be, focused on systems where the upper concentration of the range of interest is on the parts per million level.[5−8] However, many of the attributes of the technique make it an attractive option for quantifying systems of higher concentration. The miniscule sample size required, the lack of a need for an internal standard in many instances, and the elimination of extracting solvents from the methodology are a few of the obvious benefits afforded by SPME.[9] Furthermore, the SPME technique has been automated and provides the basis for a number of analyzers and integrated analysis techniques.[10−13] There are numerous applications involving concentrated solutions that could make use of these benefits. For example, in equilibrium studies, concentrations of the compounds of interest are typically varied from 0 to 100% saturation. In these studies, a minimum disturbance of the system is required, making the SPME method an obvious candidate. These benefits have already been realized in equilibrium studies of systems at low concentrations but have yet to be applied to vapor−liquid equilibrium problems where concentrations on the order of grams per liter are generated.[14−16]

The focus of the current study was to determine the applicability of the solid-phase microextraction technique to concentrated systems. A gaseous pentane−air system was used for this purpose.

EXPERIMENTAL SECTION

Chemicals. HPLC grade pentane (99.4% purity) was obtained from Fisher Chemicals (Fisher Scientific, Fair Lawn, NJ).

Materials. SPME fibers were obtained from Supelco Inc. (Oakville, ON, Canada). The fibers consisted of a solid core,

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coated with a polymer. The polymer phase used in this study was poly(dimethylsiloxane) (PDMS). The majority of the experiments were performed with fibers having a 7-μm polymer thickness. However, Polymer phases of 30- and 100-μm thickness were also used, where indicated. The polymer phase extended 1 cm in the axial direction, for all fibers used.

Analytical Methods. All analyses were carried out using a Varian 3800 gas chromatograph (GC), coupled with a Varian Star workstation. The GC was equipped with a 30-m Supleco SPB-5 column, with an internal diameter of 0.32 mm, and a film thickness of 0.25 μm (Supelco Inc.). Samples were detected using a flame ionization detector (FID). The injector (Varian 1177 type 1 EFC) was equipped with a low-volume insert designed specifically for analysis by SPME (Supelco Inc.).

Preparation of Gaseous Standard. Experiments were performed using air−pentane systems. Glass bottles were used in all cases. The volume of each bottle was determined by weight using liquid water of a known density. The average volume was determined to be 161.0 mL, with a standard deviation of 0.7 mL ($n = 6$). The bottles were first heated to the experimental temperature in an incubator. The equilibration process was carried out in the presence of ambient air. Once a uniform temperature was attained, each bottle was capped with a septum. All septa were equilibrated at the experimental temperature prior to use. Bottles were then removed from the incubator, and a volume of pentane (<0.7 mL at 20 °C) was added using a syringe. The standards were then returned to the incubator until thermal equilibrium at the desired temperature was reestablished. The temperature was kept constant to within 0.5 °C of the set point. Using the ideal gas law, the partial pressure of the hydrocarbon in each bottle was then calculated from the equation

$$p_H = y_H P = n_H^G RT / V^G \tag{1}$$

where n_H^G, y_H, and p_H are the number of moles, mole fraction, and partial pressure of the pentane hydrocarbon in the gas phase, respectively. The partial pressure was easily calculated, as n_H^G, the volume of the gas phase (V^G), and the equilibrium temperature (T) were all known. It is apparent from this equation that the number of moles of air and water vapor present does not affect the partial pressure of pentane. The increase in pressure arising from the addition of moles of air or water vapor is offset exactly by an equivalent decrease in the pentane mole fraction. The presence of any humidity in the air was not expected to affect the absorption characteristics of the fiber, based on previous findings.[5] The total pressure in the system varied from standard to standard, depending upon the amount of pentane added. The pressure associated with the maximum amount of pentane injected was less than 200 kPa.

Prior to exposure to the hydrocarbon, the SPME fiber and assembly were equilibrated in the incubator. Once the fiber had reached incubation temperature, while still in the oven, the needle was inserted through the septum and exposed to the gaseous standard for 20 min. This exposure time was sufficient for establishing equilibrium conditions, as determined by preliminary experimentation (data not shown).

Following equilibration, the fiber was retracted into the assembly sleeve and quickly (<1 s) transported to the gas

chromatograph. Desorption of the fiber contents was carried out for 0.75 min, at a temperature of 200 °C. The system was operated in splitless mode for 5 min to ensure that all of the desorbed analyte entered the column. The temperature program used was as follows: hold at 30 °C for 1.2 min, ramp to 240 °C at 40 °C/min, and hold for 2.5 min. The detector was operated at 320 °C. Helium was used as the carrier gas, at a flow rate of 1.5 mL/min.

RESULTS AND DISCUSSION

SPME fibers can be classified as either adsorption or absorption type, depending on the nature of the polymer phase.[17−19] The mechanism of analyte uptake dictates how the data obtained are interpreted. There has been some debate in the literature as to whether analyte uptake into a PDMS polymer phase occurs by adsorption or absorption. However, for the polymer−analyte system used in this study, the experimental evidence supports an absorption mechanism.[17,19,20] As such, the analyte, pentane, dissolves in the solid phase, and a homogeneous mixture results at equilibrium. From basic thermodynamics, the fugacity of the hydrocarbon in both the vapor and solid phases must be equal, at equilibrium. It is usually more convenient to work with the fugacity coefficient, $\hat{\phi}_H^G$, in the gas phase, and the activity coefficient, γ_H^S, in the solid phase. Thus, the equilibrium relationship can be written

$$y_H \hat{\phi}_H^G P = x_H \gamma_H^S f_H^{S,o} \tag{2}$$

where x_H and $f_H^{S,o}$ are the mole fraction and standard-state fugacity of pentane in the fiber, respectively. As no direct measure of the fugacity or activity coefficients exists, appropriate assumptions must be applied in order to make use of this relationship. Separate assumptions are required for the gas and solid phases. If the gas phase can be considered ideal, then $\hat{\phi}_H^G$ is equal to unity. For the solid phase, a definition of the standard state is required. According to Henry's definition

$$\lim_{x_H \to 0} \frac{\hat{f}_H^S}{x_H} = f_H^{S,o} \equiv k_H \tag{3}$$

where $\hat{f}_H^S$ is the fugacity of pentane in the fiber and k_H is referred to as Henry's constant. If eq 3 is used to define the standard state, then for a real solution, as $x_H \to 0$, the solution behaves as ideal in Henry's sense, and γ_H^S is equal to unity. Under these conditions, eq 2 reduces to

$$y_H P \equiv p_H = k_H x_H \tag{4}$$

The linearity of the detector response was established by injecting known quantities of liquid pentane into the GC under splitless conditions. The detector was found to exhibit linear

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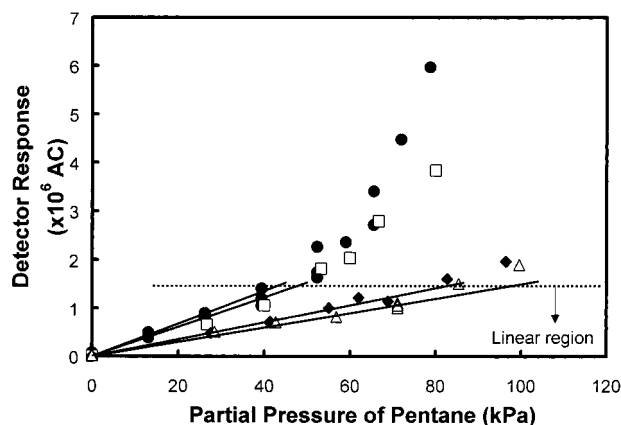
Figure 1. Relationship between the partial pressure in the gas phase and the concentration in the solid phase. The detector response is measured in area counts (AC). Data were collected using 7-μm fibers at 20 (●), 25 (□), 35 (◆), and 45 °C (△). Replicate measurements are shown, where preformed. Lines represent the results of linear regressions.

behavior for quantities of pentane less than 0.4 μL (3.5 × 10^{-12} mol) (data not shown). This corresponded to a detector response of ~1.5 × 10^9 area counts. Therefore, for a detector response less than this critical value, the area count is synonymous with moles of pentane absorbed by the fiber at equilibrium. To convert the area counts into a mole fraction, the number of moles of polymer in the fiber is required. This number was not readily available, and it was more convenient to work in units of moles of pentane per mole of polymer, $\tilde{x}_H$. This was preferred as the number of moles of polymer is constant. Furthermore, the detector response varies linearly with $\tilde{x}_H$ and not with x_H. With this definition, eq 4 becomes

$$p_H = k_H \frac{\tilde{x}_H}{1 + \tilde{x}_H} \tag{5}$$

If it is further assumed that $\tilde{x}_H \ll 1$, and then the equilibrium expression can be written

$$p_H \cong k_H \tilde{x}_H \tag{6}$$

Henry's definition of ideality is exact in the limit as $x_H \rightarrow 0$. Thus, in the system under study, eq 4 applies only when small amounts of analyte are absorbed into the solid phase. These assumptions have been found to hold for most applications of SPME to date. In the current study, a wider range of concentrations was explored. At temperatures between 20 and 45 °C, the concentration of pentane in the vapor phase was varied between 0 and over 100% saturation. These concentrations are several orders of magnitude larger than those previously measured using the SPME technique. From the data collected, it appears that Henry's law applies to the solid phase at detector responses of less than ~1.5 × 10^6 area counts (Figure 1), as the data deviate from linearity in this region. It should be noted that these data are all well within the region of linear detector response, where $\tilde{x}_H$ can be used interchangeably with area counts. Although eq 4 suggests reversing the *ordinate* and *abcissa* definitions used in Figure 1, the current choice was

Table 1. Concentration of Pentane in the Vapor Phase at the Dew Point, as a Function of Temperature[a]

temperature (°C)	saturation pressure (kPa)
20	56.5
25	68.3
35	97.6
45	136.0

[a] Values were estimated using the Antoine equation, where the constants were obtained from Reid et al.[28]
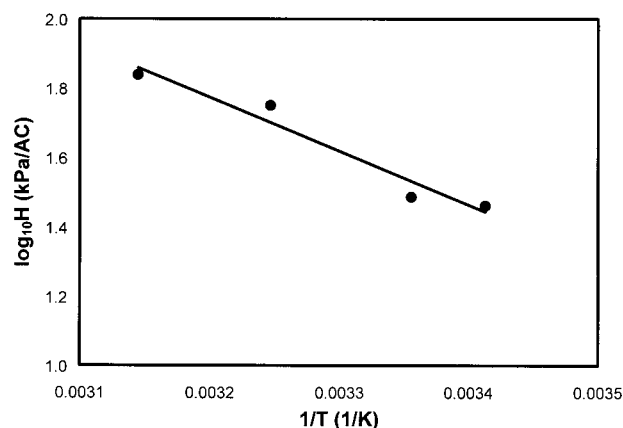

Figure 2. Temperature dependence of Henry's constant, k_H. Estimates of k_H were calculated from data collected in the linear region of Figure 1, using eq 4. The line is the result of statistical analysis.

made, as partial pressure is the independent variable. In the manner presented, the slope of the linear section is the reciprocal of Henry's constant, in units of detector response per kilopascal.

For the pentane−air system used in this study, the pentane partial pressures associated with saturation conditions are shown in Table 1. These data were calculated by assuming that the gas phase was ideal and that all other species in the gas phase behaved as inert gases. From these data, comparing with Figure 1, deviation from Henry's law appears to occur at partial pressures approaching the saturation pressure of pentane. The partial pressures measured at 20 and 25 °C even slightly exceeded the corresponding saturation pressures (Table 1). However, formation of a liquid phase was not observed in any of the experiments performed.

In a previous work, it was shown that if the standard state fugacity of pentane in the fiber, $f_H^{S,o}$, is defined in terms of the Lewis−Randall rule, then the distribution coefficients can be shown to follow a semilogarithmic dependence with the reciprocal of the temperature. This relationship arises from the functionality of the Clausius−Clapeyron equation, which can be linked to $f_H^{S,o}$ through a number of assumptions.[5] In the current work, the standard-state fugacity is defined in terms Henry's law (eq 3). Estimates of Henry's constant were obtained from the linear regions from the data in Figure 1. As shown in Figure 2, these values also exhibit a semilogarithmic dependence on the reciprocal of temperature. In this case, the temperature dependence does not follow from the Clausius−Clapeyron equation, as the saturation pressure does not appear in the equilibrium relationship. A more general approach must be followed to derive the temperature dependence of Henry's constant. The standard-state fugacity of

pentane varies with temperature according to the equation

$$\left(\frac{\partial \ln f_H^{S,o}}{\partial T}\right)_P = -\frac{h_H' - h_H^o}{RT^2} \quad (7)$$

where h_H' is the molar enthalpy of pentane in the ideal gas state and h_H^o is the molar enthalpy of pentane in its standard state.[21] Both quantities are evaluated at the temperature and pressure of the system. The activity coefficient of pentane in the fiber varies with temperature according to the following relationship:

$$\left(\frac{\partial \ln \gamma_H^S}{\partial T}\right)_{P,x} = -\frac{\bar{h}_H^S - h_H^o}{RT^2} \quad (8)$$

where $\bar{h}_H$ is the partial molar enthalpy of pentane in the fiber.[21] In the limit as $x_f \to 0$, Henry's definition of ideality becomes valid, as defined in eq 3. Under these conditions, the activity coefficient is unity, and the partial derivative defined in eq 8 is equal to zero. This condition requires that $\bar{h}_H^S = h_H^o$. Furthermore, $\bar{h}_H^S$ assumes the value of $\bar{h}_H^\infty$, which is the partial molar enthalpy when $x_H \to 0$. Therefore, in the region where Henry's law is an exact description of the system, eq 7 becomes

$$\left(\frac{\partial \ln k_H}{\partial T}\right)_{P,x=0} = -\frac{h_H' - \bar{h}_H^\infty}{RT^2} \quad (9)$$

From this equation, at constant pressure the natural logarithm of k_H is expected to vary with the reciprocal of temperature. However, as discussed above, each standard was at a different pressure, depending upon how much pentane was added. Therefore, eq 9 is not strictly applicable to the data presented in Figure 1 and Figure 2. Through a derivation similar to the one above, it can be shown that the pressure dependence on Henry's constant is given by the equation

$$\left(\frac{\partial \ln k_H}{\partial P}\right)_{T,x=0} = \frac{\bar{v}_H^\infty}{RT} \quad (10)$$

where $\bar{v}_H^\infty$ is the partial molar volume of pentane in the fiber.[21] The value of this derivative is typically insignificant, except in the critical region.[21] Therefore, the pressure effect is assumed negligible in the experimental region studied.

It can be seen that eq 9 adequately represents the dependence of Henry's constant on temperature (Figure 2). From this figure, it is apparent that the analyte has less of an affinity for the solid phase at higher temperatures, as k_H increases with temperature. Therefore, as the temperature is increased, the fiber exhibits ideal behavior in Henry's sense over a wider range of pentane partial pressures. This results in an extension of the linear region, as noted in Figure 1.

The focus of the remainder of the work was on explaining the observed nonlinearity in Figure 1. As the phenomenon was most prevalent at lower temperatures, the experimental temperature was fixed at 20 °C for the remaining experiments. At this
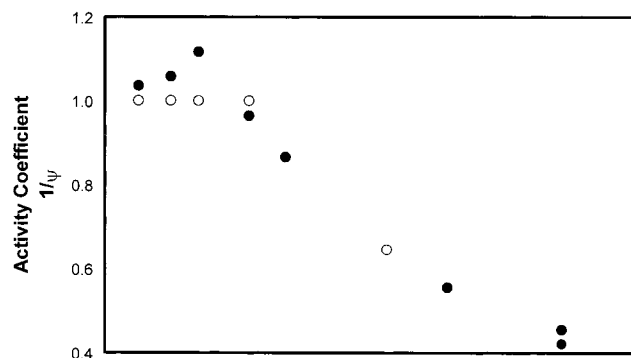
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Figure 3. Dependence of the activity coefficients (●) at 20 °C on $\tilde{x}_H$. The detector response, measured in area counts (AC), is used as a measure of $\tilde{x}_H$, as described in the text. Activity coefficients were calculated using eq 11. The reciprocal of the swelling factors associated with the same data set are also plotted (○).

temperature, eq 4 failed to adequately describe the equilibrium system above a response of $\sim 1.5 \times 10^6$ area counts. Above this concentration, the system started to exhibit nonideal behavior. This nonideality was most likely associated with the polymer phase, as the assumptions applied to the gaseous phase were still applicable. Reintroducing the activity coefficient into the equilibrium description yields

$$p_G \cong k_H \gamma_H^{S,*} \tilde{x}_H \quad (11)$$

where the superscript of the activity coefficient is used to identify that the standard state is based on Henry's law rather than the more common Lewis−Randall rule. The relationship is still only approximate, as $\tilde{x}_H$ is used instead of x_H, for the reasons discussed above. Using this equation, the activity coefficients associated with the data set collected at 20 °C were calculated. The activity coefficient was found to decrease below unity for data outside of the linear region (Figure 3).

For the system used, swelling of the polymer phase was suspected, based on preliminary experiments performed with a fiber with a 100-μm film thickness. When exposed to high partial pressures of pentane, considerable resistance was noted when the fiber was retracted into the protective metal sleeve of the fiber assembly. Under magnification, it was apparent that the polymer had been damaged (data not shown). These observations suggested that the pentane had caused the polymer to swell, making it too large for the sleeve of the assembly. This observation is consistent with the SPME literature that recognizes the potential incompatibility of low molecular weight hydrocarbons with the PDMS fibers.[22]

To explore the role of swelling on the system, a measure of the fiber volume was required. Initial attempts utilized a light microscope. Fiber diameters were measured directly on the view stand. A calibration curve was generated using fibers that had not been exposed to pentane. Pictures were taken of 7-, 30-, and 100-μm fibers at a magnification of 1000×. The polymer film was removed from one fiber, and a picture was taken of the solid supporting core. A photograph of a scale with 0.1-mm divisions was also taken, under the same magnification. Using these pic-

(22) Shirey, R. E. In *Solid-phase microextraction: A practical guide*; Scheppers Wercinski, S. A., Ed.; Marcel Dekker: New York, 1999; pp 59−110.
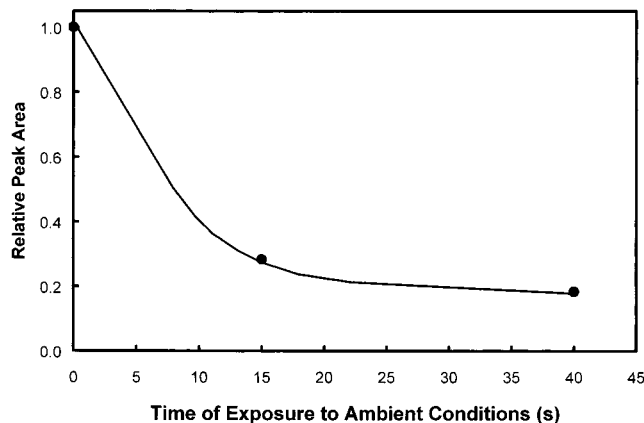
Figure 4. Relative amount of pentane remaining in the polymer fiber following exposure to ambient air. The fiber was first equilibrated with a pentane standard, as described in the text. The solid line is meant to indicate a trend only and is not the result of a statistical analysis.

Figure 5. Swelling factors (▲) associated with data collected at 20 °C. Values were calculated using eq 12. Peak area data (●), measured in area counts (AC), are the same as those presented in Figure 1. However, average values are presented. Lines show trends only.

tures, the volume of the polymer phase for each of fiber sizes was estimated. The values calculated were in good agreement with numbers published in the literature.[19] For the 30- and 100-μm fibers, the error was less than 3%. For the 7-μm fiber, the error was 15%.

The technique was then applied to fibers that had been exposed to gaseous pentane. However, no swelling was measured, under any experimental conditions. This finding contradicted the observations made regarding the 100-μm fiber, which was damaged presumably due to significant swelling. It was hypothesized that the pentane was desorbing from the fiber at room temperature prior to taking the picture under the microscope. To test this hypothesis, a 7-μm fiber was first equilibrated at 20 °C in a gaseous environment containing a partial pressure of 70 kPa pentane. These conditions placed the fiber in the nonlinear region (Figure 1). The fiber was then exposed to ambient air for a fixed period of time and then desorbed in the gas chromatograph. The experiment was repeated for various ambient exposure times. The results of this exercise indicated that over half of the pentane absorbed in the fiber was desorbed in less than 10 s, when exposed to ambient conditions (Figure 4). Following desorption, the concentration of analyte in the fiber was in the linear region of Figure 1. Thus, the swelling could not be measured adequately using this technique.

On the basis of the efforts with the light microscope, it was concluded that the measurements must be made in situ. The fiber was exposed to a gaseous standard, as described above. The fiber was then positioned so that it was in close proximity to the wall of bottle. The fiber diameter was then measured from the outside of the bottle, using a magnifying lens containing a calibrated scale. The scale had increments of 0.1 mm. Readings taken in this manner were expected to be distorted by the glass wall of the bottle. Thus, a calibration curve was required. This function was generated using fibers of 7, 30, and 100 μm that had not been exposed to pentane. Hence, they were not swollen. Measurements taken by the magnifying lens were plotted against the corresponding fiber volumes, as measured using the light microscope (data not shown). In theory, the calibration curve relating the diameter as measured by the lens and the volume of the fiber should be a second-order polynomial. Thus, a function of this type was fit to the data (data not shown).
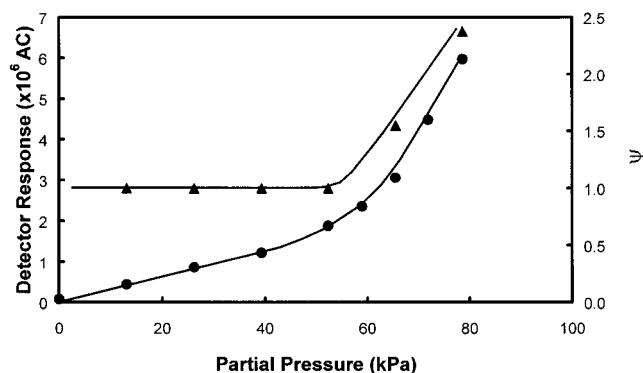
Using this method, swelling measurements were made at 20 °C. Swelling was quantified by means of a swelling factor, defined as

$$\psi = V_\infty^S / V_0^S \tag{12}$$

This definition has been used elsewhere to quantify polymer swelling.[23] Here, V_∞^S and V_0^S are the volumes of the solid phase at equilibrium with pentane and prior to exposure to the pentane environment. As can be seen, the swelling factors are unity in the linear region and increase proportionally with area count in the nonlinear region (Figure 5).

Comparing Figure 5 and Figure 3, it is apparent that the dependence of the activity coefficients on $\tilde{x}_H$ is inverse to that associated with the swelling factors. Thus, the inverse of the swelling factor was plotted against the detector response (Figure 3). From this figure, it is apparent that the activity coefficients and the inverse of the swelling factor have the same value. This suggests a simple activity model for the system studied, yielding the equation

$$p_H \cong k_H (1/\psi) \tilde{x}_H \tag{13}$$

Equation 13 suggests that the linear region identified in Figure 1 can be extended by dividing $\tilde{x}_H$ by the swelling factor. This hypothesis is verified in Figure 6.

From the previous analysis, it is apparent that the nonideality of the system can be described by a simple function of the swelling ratio. As discussed, the pressure varied slightly between each of the pentane standards. However, the temperature, and moles of polymer remained constant. Thus, the changes in the swelling factors resulting between standards can be expressed as

$$d\psi = \frac{d(n^S v^S)}{V_0^S} = \frac{1}{V_0^S} \left\{ \left(\frac{\partial (n^S v^S)}{\partial n_H^S} \right)_{T,P,n_P^S} dn_H^S + \left(\frac{\partial (n^S v^S)}{\partial P} \right)_{T,n^S} dP \right\} \tag{14}$$

where n_P^S is the number of moles of polymer in the solid phase,

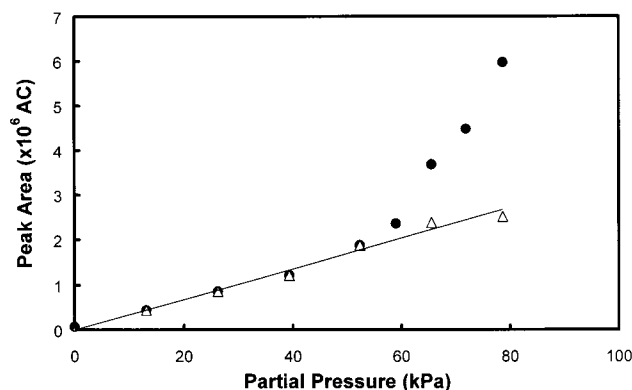(23) Singh, J.; Weber, M. E. *Chem. Eng. Sci.* **1996**, *51*, 4494−4508.

Figure 6. Data collected at 20 °C with a 7-μm fiber, adjusted using eq 13 to account for fiber swelling ($\triangle$). The unadjusted data also shown ($\bullet$). The solid line was extrapolated from Henry's region. The detector response is measured in area counts (AC).

n_H^S is the number of moles of hydrocarbon in the fiber phase, n^S is the *total* number of moles in the fiber phase ($n_P^S + n_H^S$), and v^S is the molar volume of the solid fiber phase. The second term in eq 14 is negligible and is therefore neglected. The first term is recognized as the partial molar volume of pentane in the solid phase, $\bar{v}_H^S$.[21] In terms of this quantity, the cumulative swelling factor, as measured experimentally, is given by

$$\psi|_{n_H^S} = \frac{1}{V_0^S} \int_0^{n_H^S} \bar{v}_H^S \, dn_H^S \qquad (15)$$

Equation 15 provides some insight as to the meaning of the activity function. Activity coefficients associated with PDMS fibers have been previously reported.[24] However, the data collected were associated with a system to which the infinite dilution approximation was valid. Under these conditions, a rigorous thermodynamic equation incorporating the Lewis−Randall rule predicted a dependence of the activity coefficient of the analyte in the solid on its pure molar volume. A molar volume dependence also appears in many commonly used activity models, such as the Wilson equation.[21] In the current work, where the mixture cannot be considered dilute, a dependence of the activity coefficient on the partial molar volume, and not on the pure liquid volume, was found. The reason for this is not entirely clear.

In many SPME applications, the equilibrium between the solid and fluid phases is related through a partition (distribution) coefficient defined as

$$K = C_H^S / C_H^G \qquad (16)$$

where C_H^S and C_H^G are the concentrations of analyte in the fiber and gas phases, respectively.[25,26] By definition, K is dimensionless. Thus, the concentrations have the same units, usually moles per liter. The equilibrium description, as stated in eq 16, is only an approximation of the complete definition (eq 11). Using the ideal gas law, it is easily shown that p_H is equal to $C_H^G RT$. However,

description of the solid-phase concentration in units of moles per liter poses some problems, as the numerator and denominator both change as the polymer phase absorbs more pentane. Therefore, the nonideality noted in the current application is confounded with the definition of the solid-phase concentration. In historical applications of the SPME technique, the equilibrium definition described by eq 16 is entirely adequate. This is because, at low concentrations of analyte, the molar volume of the fiber, v^S, is constant and independent of n_H^S. This is equivalent to saying that the solution in the solid phase is ideal, based on the activity function determined in this work. Coupled with the approximation that $n_P^S \gg n_H^S$, it follows that $C_G^S \propto x_H$, and the partition coefficient adequately described the equilibrium condition. However, in the current work, at high analyte concentrations, this description is inadequate, and eq 11 must be used.

An important outstanding question involves the effect of swelling on multicomponent systems. Consider a system consisting of a single component (1). Assume that this component partitions according to eq 4. In this case, the relationship between the composition of component 1 in the fluid and solid phases is constant and is not a function of composition. Assume that another component (2) partitions with the solid phase according to eq 11. In this case, fluid and solid-phase concentrations are related by a function that is dependent upon concentration. Now consider a system consisting of both components. For a binary system at constant temperature and pressure, the Gibbs−Duhem equation reduces to[21]

$$x_1^S \, d \ln \gamma_1^S = - \, x_2^S \, d \ln \gamma_2^S \qquad (17)$$

It follows from this equation that if one component exhibits nonideality, then the other component must also. Thus, nonideal behavior by a single compound introduces composition dependence into the distribution coefficients for *all* species participating in the equilibrium. This is an unfortunate result, as it complicates the application of the SPME technique at high concentrations, where the assumptions of ideality do not hold. In the case where the partitioning of each component is governed by eq 4, then eq 17 is satisfied, and the partition coefficients are not functions of composition. This condition applies at low analyte concentrations, where SPME has been applied extensively, and was the intent of the original incarnation of the technique.[27]

In the current application, it was found that nonideal behavior was limited to lower temperatures. As the temperature was increased, the activity coefficients approached unity over the entire range of partial pressures (Figure 1). Thus, at higher temperatures, no composition dependence is expected to be introduced as a result of nonideal beahavour.

A further complication arising with multicomponent systems is related to the choice of the standard state. Where more than two components are present, the definition of Henry's constant given by eq 3 will be dependent upon the relative amounts of the other components. In this case, it would be more convenient to work with a solution-independent standard state, such as that given by the Lewis−Randall rule.

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Finally, it is important to try and generalize the findings of this study. The current work focused on a PDMS fiber with a film thickness of 7 μm. Fibers of 30 and 100 μm are also available in this material. However, the 7-μm fiber is stabilized through addition of a cross-linking agent, which also bonds the material to the silica fiber. The other sizes are not bonded.[22] Experimentation was restricted to the 7-μm fiber, since the larger sizes could not be retracted into the protective sleeve upon swelling. Therefore, although it was confirmed that swelling does indeed occur in both the nonbonded and bonded PDMS fibers, the effect of cross-linking could not be quantified.

CONCLUSION

Using a 7-μm-thick PDMS polymer phase, the SPME technique can be used to quantify the concentration of pentane in a gas phase over the entire range between 0 and 100% saturation. Above a certain critical concentration of pentane in the solid phase, the fiber swells, resulting in a nonlinear calibration curve between the concentration of pentane in the gas and fiber phases. This nonlinearity was captured in an activity coefficient model that is uniquely defined in terms of the swollen polymer volume. The results suggest that SPME technique can be extended to systems containing significantly higher analyte levels than have been measured traditionally using this method. However, difficulties are expected for multicomponent systems where the fiber has a strong affinity for multiple analytes, and nonideal behavior is exhibited by at least one species.