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Technical Notes

Measurement of Aqueous Henry's Law Constants for Oxygenates and Aromatics Found in Gasolines by the Static Headspace Method

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A simple equilibrium vessel made from a large stopcock was used in conjunction with the static headspace method to measure the aqueous Henry's law constants for methyl *tert*-butyl ether (MTBE) and other potential oxygenates as well as certain of the aromatics found in gasoline. The present method involves using only one aqueous solution whose concentration is not necessarily known. The only quantity that must be known is the phase ratio. Plotting a series of peak areas of the analyte in the headspace after each equilibrium change against the initial peak area of the analyte found in the headspace leads to a linear relationship whose slope is dependent on the analyte's unitless Henry's law constant and the phase ratio. This new method is found to yield unitless aqueous Henry's law constants in the range from 0.02 to 0.2, which are especially applicable to the oxygenates and aromatics found in gasolines.

The knowledge of Henry's law coefficients is highly desirable when the concentrations of volatile organic compounds are determined using the static headspace method. The Henry's law coefficient describes the partitioning of a compound between a condensed phase (normally an aqueous solution) and the gaseous phase above it. Knowledge of the Henry's law coefficients for analytes in a specific analytical system gives the analyst the ability to accurately predict the limitations of an analysis, as well as the conditions necessary to make an analysis feasible. In addition, Henry's law coefficients are useful to environmental scientists when considering possible remediation technologies, such as air stripping methods.

There has been a great deal of interest in the health effects and environmental impact of the various oxygenates being added to automotive gasolines. These compounds, in 1996, were being blended into 30% of the nation's fuels with the intention of increasing the amount of oxygen in the fuel, thereby enhancing the efficiency of combustion in automobile engines. The increased oxygen content results in more complete combustion of the fuel to decrease hydrocarbon emissions, as well as decreasing the formation of carbon monoxide, nitrogen oxides, and ozone.[1] This assumption, however, was recently disputed by a National Research Council report that claims oxygenates do little to reduce ozone formation and may in fact increase nitrogen oxide emissions.[2] The percentage of gasoline which will have methyl *tert*-butyl ether (MTBE) or other oxygenates blended into it is projected to increase to 70% by the year 2000, which implies that the concern over the potential environmental and health effects of this compound can be expected to increase.[3] A 1998 study reported that 78% of the groundwater samples taken around leaking underground fuel tanks in California were contaminated with MTBE at levels of 5 ppb, suggesting that over 10 000 sites could be affected.[4] In addition, it was recently discovered that MTBE is being found in diesel fuel as well as home heating oil at concentrations as high as 30 ppm.[5] When this is combined with the fact that there may now be far more leaking home heating oil tanks than leaking storage tanks at gasoline stations, the need for research in these areas is obvious.

The determinations of Henry's law coefficients for the oxygenates methyl *tert*-butyl ether, ethyl *tert*-butyl ether (ETBE), ethyl butyl ether (EBE), diisopropyl ether (DIPE), and *tert*-amyl methyl ether (TAME) and for several aromatic compounds were studied using a variation on the equilibrium partitioning in closed systems (EPICS) method described by Gossett in 1987.[6] The EPICS method is experimentally demanding in that it requires the preparation of multiple samples containing different phase ratios but the same number of moles of analyte. The present method represents a further improvement over existing techniques, including that of our past report, in that results could be obtained using only one aqueous solution, whose concentration is not necessarily known.[7,8] The only quantity that must be known in

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this method is the phase ratio, which is easily obtained from the experimental apparatus. Plotting a series of peak areas of the analyte in the headspace after each equilibrium change against the initial peak area of the analyte found in the headspace leads to a linear relationship whose slope is dependent on the analyte's unitless Henry's law constant and the phase ratio. This new method is found to yield accurate unitless aqueous Henry's law constants especially in the range for those of the oxygenates and aromatics found in gasolines.

THEORETICAL BASIS

Henry's law describes the distribution of a discrete amount of solute between a dilute solution and the gaseous phase above it. This relationship has been exploited in the experimental procedure described here, where the initial amount of solute is varied systematically. The initial number of moles of solute is lowered after each successive equilibrium by an amount equivalent to the number of moles of analyte present in the headspace at equilibrium. This is demonstrated mathematically below.

The distribution of an analyte between a dilute solution and its associated headspace is described by Henry's law as shown in the following equation:

$$H = c_{\rm hs}/c_{\rm aq} \tag{1}$$

where H is the unitless Henry's law constant, $c_{\rm hs}$ is the concentration of analyte in the headspace, and $c_{\rm aq}$ is the concentration of analyte in the aqueous phase. Since the concentration of an analyte is defined as the number of moles (n) of analyte per unit volume (V), eq 1 becomes

$$H = \frac{n_{\rm hs}/V_{\rm hs}}{n_{\rm aq}/V_{\rm aq}} = \frac{n_{\rm hs}}{n_{\rm aq}}\left(\frac{V_{\rm aq}}{V_{\rm hs}}\right) \tag{2}$$

When the equilibrium is established, mass balance dictates that the amount of analyte in the headspace and aqueous phase at equilibrium equals the number of moles initially present in the aqueous phase such that

$$n_{i_{\rm aq}} = n_{i\,+\,1_{\rm aq}} + n_{i\,+\,1_{\rm hs}} \tag{3}$$

where $n_{i_{\rm aq}}$ is the number of moles present in the aqueous phase initially, $n_{i\,+\,1_{\rm aq}}$ is the number of moles present in the aqueous phase at equilibrium, and $n_{i\,+\,1_{\rm hs}}$ is the number of moles present in the headspace at equilibrium. Equation 2 can be rearranged to describe the number of moles of analyte in the aqueous phase as a function of the number of moles of analyte in the headspace, as follows:

$$n_{\rm aq} = n_{\rm hs}\left(\frac{V_{\rm aq}}{HV_{\rm hs}}\right) \tag{4}$$

The results of eqs 3 and 4 can be combined to give the following equation:

$$n_{i_{\rm hs}}\left(\frac{V_{\rm aq}}{HV_{\rm hs}}\right) = n_{i\,+\,1_{\rm hs}}\left(\frac{V_{\rm aq}}{HV_{\rm hs}}\right) + n_{i\,+\,1_{\rm hs}} \tag{5}$$

Which reduces to

$$n_{i_{\rm hs}} = n_{i\,+\,1_{\rm hs}}\left(1 + \frac{HV_{\rm hs}}{V_{\rm aq}}\right) \tag{6}$$

In this equation, $n_{i_{\rm hs}}$ corresponds to the number of moles of analyte present at equilibrium during the analysis which was performed immediately prior to the current analysis. Since the number of moles of analyte is proportional to chromatographic peak area (PA), $n_{\rm hs}$ can be replaced by (PA)k, giving

$$(PA)_{i_{\rm hs}}k = (PA)_{i\,+\,1_{\rm hs}}k\left(1 + \frac{HV_{\rm hs}}{V_{\rm aq}}\right) \tag{7}$$

Dividing both sides of this equation by the proportionality constant k yields

$$(PA)_{i_{\rm hs}} = (PA)_{i\,+\,1_{\rm hs}}\left(1 + \frac{HV_{\rm hs}}{V_{\rm aq}}\right) \tag{8}$$

This equation indicates that a plot of (PA)$_{i_{\rm hs}}$ versus (PA)$_{i\,+\,1_{\rm hs}}$ should yield a straight line through the origin with a slope of $1 + (HV_{\rm hs}/V_{\rm aq})$.

EXPERIMENTAL SECTION

All experiments were performed using a Hewlett-Packard model 5890A gas chromatograph (Hewlett-Packard, Wilmington, DE) that was equipped with an OI model 4430 photoionization detector (PID; OI Analytical, College Station, TX) which was serially connected to an OI model 4410 flame ionization detector (FID). The column used is this study was a J&W DB-MTBE, of 0.53 mm i.d., 30 m length, and 3.0 μm film thickness (J&W Scientific, Folsom, CA). The serial arrangement of the detectors allowed the entire column eluent to be subjected to each detector, producing two independent detector responses. Two separate HP 3396A integrators (Hewlett-Packard, Wilmington, DE) handled the data collection. The GC conditions used in these experiments were dependent on the standard that was being analyzed. For all analyses, the injector temperature was set at 180 °C and the detectors were set at 200 °C. Detection was provided by both the FID and the PID, operated at 10.0 eV and a current of 1.30 mA.

For the ether compounds, the oven was programmed to run isothermally at 40 °C for 3.50 min, then to be increased in temperature at 12 °C/min to 100 °C, and finally to remain at 100 °C for 30 s. This resulted in a 9.00 min run to completely separate all compounds.

For the aromatic compounds benzene, toluene, ethylbenzene, and *o*- and *m*-xylene (BTEX), the oven was programmed to run isothermally for 1.50 min at 80 °C and then to be increased in temperature at 10 °C/min to 140 °C, where it remained for 1.50 min. This resulted in a 9.00 min run to separate all five aromatic compounds.

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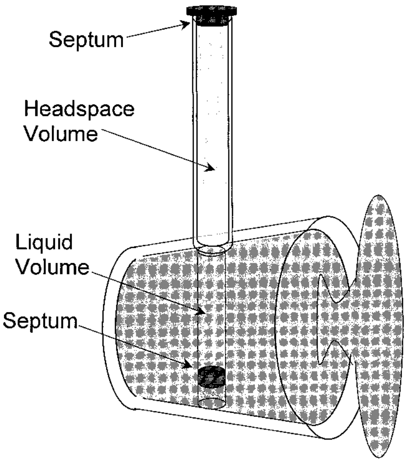

Figure 1. Illustration of the experimental apparatus.

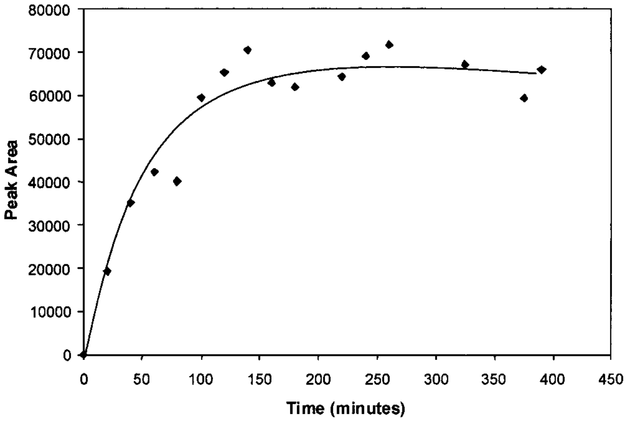

Figure 2. Determination of equilibration time for methyl *tert*-butyl ether.

Chemical Standards. Standards were prepared by weight by diluting 5 μL each of MTBE, ETBE, DIPE, TAME, and EBE into 25.0 mL of distilled water to produce the concentrated ether standard. The high water solubility of the analytes allowed the standards to be prepared without the use of a cosolvent, preventing interference in determining the Henry's law coefficients. The concentrated BTEX standard was prepared by adding 5 μL each of benzene, toluene, ethylbenzene, *m*-xylene, and *o*-xylene into 5.00 mL of methanol. The concentrated ether standard was then diluted by a factor of 10 to produce a working solution with a final concentration of ~20 ppm for each analyte, while the concentrated BTEX standard was diluted 250 times in deionized water to a final concentration of 4.0 ppm.

Analysis Procedure. The apparatus used in these experiments consisted of a no. 10 standard taper stopcock modified to contain a liquid volume of 1.75 mL, as shown in Figure 1. This was accomplished by fitting a GC injector septum into the inner bore of the stopcock. The stem of the valve was capped with a tight-fitting septum that defined a 12.54 mL volume, which would contain the sample headspace. The volumes of the liquid cell and the headspace were measured gravimetrically by measuring the mass of water needed to completely fill each. After assembly, the valve handle was held vertically in place by a laboratory clamp. This allowed the liquid sample to be loaded into the liquid volume created in the valve and then the rest of the valve body attached, creating the closed system in which the experiment was to be run. After the sample was allowed to reach equilibrium, the outside valve housing was rotated, separating the liquid and gas volumes. A gastight locking syringe was then used to sample 250 μL of the gaseous phase for subsequent gas chromatographic analysis. After three separate samples were taken and analyzed, the septum capping the headspace was removed and the contents were expelled by a stream of humidified nitrogen. The humidified nitrogen was supplied by directing house nitrogen through a regulator to reduce the flow rate to approximately 450 mL/min. A length of 0.53 mm i.d. uncoated fused silica tubing was used to direct the nitrogen flow into the bottom of a septum-sealed 500 mL volumetric flask filled with deionized water. A second length of 0.53 mm i.d. uncoated fused silica tubing was used to transfer the nitrogen flow from the sealed volumetric flask to the headspace of the apparatus. Bubbling the humidified nitrogen through the headspace was found to completely purge the oxygenates from the headspace. This returned the system to nonequilibrium conditions, with the initial number of moles in the system equivalent to the equilibrium number of moles in the aqueous phase from the previous step. The septum capping the headspace was then replaced and the valve body rotated to place the headspace back in contact with the aqueous phase. Thereupon, a new equilibrium condition was established and the process repeated. It should be noted that this setup did not allow shaking of the sample due to the need to keep the liquid and headspace separate. This caused the time needed to achieve chemical equilibrium to be quite long, on the order of one to several hours.

After the chromatographic data had been obtained, the data were evaluated by plotting the average peak area generated after each equilibration versus the average peak area in the headspace of its prior equilibrium. To generate the unitless Henry's law constant, 1 was subtracted from the slope of the resulting curve and this value was then multiplied by V_{aq}/V_{hs} (see eq 8).

RESULTS AND DISCUSSION

Determination of Equilibrium Conditions. The establishment of equilibrium conditions is crucial in the performance of these experiments. Therefore, a study of the time needed to bring the system to equilibrium was undertaken. For this study, the apparatus was assembled as shown in Figure 1. As the system progressed toward equilibrium, 250 μL aliquots of the headspace were removed every 15 min with a locking gastight syringe and analyzed. Figure 2 shows that ~100 min was required for methyl *tert*-butyl ether to reach chemical and thermal equilibrium, while about 6 h was required for the aromatic (BTEX) standards to reach equilibrium under the static (nonshaking or stirring) conditions mandated by the experimental apparatus arrangement depicted in Figure 1. The length of time needed to establish equilibrium in this method was admittedly very long due to an inability to shake or stir the sample. It was felt that any attempt to agitate the sample would cause changes in the volume of the aqueous phase by splashing the aqueous phase into the headspace volume or pulling some of the aqueous solution into the ground-glass fitting by capillary action. For these reasons, the system was allowed to come to chemical equilibrium through diffusion only, without attempting to aid mass transport of the desired analytes.

Table 1. Henry's Law Constants for the Various Ether Compounds Studied

	MTBE	DIPE	ETBE	TAME	EBE
slope	1.169	1.668	1.696	1.306	1.255
R^2	0.9398	0.9637	0.9551	0.9570	0.9626
H (unitless)	0.0255	0.0932	0.0972	0.0776	0.0633
H (M/atm)	1.73	0.439	0.421	0.529	0.646
lit. values	1.6[7]	0.57[8]	0.37[9]	0.50[9]	N/A
	1.7[10]	0.31[9]			

Table 2. Henry's Law Constants for the Various Aromatic Compounds Studied

	benzene	toluene	ethylbenzene
slope	2.605	2.862	2.819
R^2	0.9841	0.9835	0.9985
H (unitless)	0.2241	0.2600	0.2539
H (M/atm)	0.1825	0.1573	0.1611
lit. values	0.19[7]	0.15[7]	0.13[7]
	0.21[11]	0.16[11]	0.15[11]

Determination of the Oxygenates' Henry's Law Coefficients. Analysis of the oxygenates is difficult owing to the relatively low Henry's law coefficients expected for these compounds.[7,9] The high water solubility of these compounds causes the equilibrium between the aqueous phase and headspace to strongly favor the aqueous phase. For this reason, the volume of the headspace used in these experiments was kept much larger than the volume of the aqueous phase, resulting in larger point to point changes in the data obtained. The results for the ether compounds can be found in Table 1. The data obtained here showed good agreement with reported literature values for all of the oxygenate species. It should be noted that the regression line was determined with the y intercept fixed at zero, as the theory dictates since the resulting equation fits the form $y = mx$ with no y intercept. Allowing the linear fit to incorporate a y intercept resulted in slopes of the lines which were slightly low and therefore generated data which did not match the reported literature values as well.

The BTEX compounds were analyzed, and the Henry's law coefficients were successfully determined for benzene, toluene, and ethylbenzene. The results of this experiment are given in Table 2. The coefficients generated for benzene and toluene were in excellent agreement with the literature values, while the ethylbenzene coefficient showed a slight deviation from the reported value. The analysis of alcohols such as ethanol, 2-propanol, and 1-butanol proved to be extraordinarily difficult by this method owing to their extremely low (0.0003) unitless Henry's Law constants. The Henry's law coefficients for these compounds are reported to be in the range 120−220 M/atm.[10,11] In order for this method to be successful, the purging of the headspace must significantly disturb the equilibrium previously established between the aqueous and vapor phases. This requirement is achieved only when a significant portion of the analyte, in this case an alcohol, is partitioned into the headspace. To accomplish this, the phase ratio V_{aq}/V_{hs} must be very small, between 1.8×10^{-4} and 3.4×10^{-4}, which is on the order of the unitless Henry's law coefficient. To achieve this, an aqueous solution volume of 15.0 μL would be required, since the headspace volume (12.54 mL) of the apparatus employed was not variable. The inability to create such a small cell to contain such a small volume of the alcohol standard (15.0 μL) would be difficult to construct and to be employed accurately. This difficulty and the exceedingly small volume of aqueous phase to be delivered and contained without evaporative or other losses are considered to be the most likely contributors to the lack of agreement between the data obtained for the alcohols and their literature values.

CONCLUSIONS

The method described here was demonstrated to be an improvement over the EPICS method, in which the experimental procedure was not dependent on the initial concentration of the analytes in the aqueous phase. The present method was not as sensitive to analytical errors as was that of our past report, which used a ratio of the slope and intercept to derive the Henry's law constant.[7,12] Our present method by virtue of its proportionality of one equilibrium concentration to its prior equilibrium headspace concentration was able to quickly show if experimental conditions had been reestablished. This improved method was utilized to generate aqueous Henry's law constants for various compounds having unitless Henry's law values in the 0.02−0.10 range that either are currently being used as oxygenates in reformulated gasolines or could be surrogates for their analysis.

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