Measuring the Aqueous Henry's Law Constant at Elevated Temperatures Using an Extended EPICS Technique

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Experimental data for Henry's law constant of organic solutes at temperatures between (313.15 and 363.15) K are unavailable or scarce. A method is presented to measure Henry's law constant of organic solutes in water at these temperatures known as extended Equilibrium Partitioning in Closed Systems (extended EPICS). Extended EPICS rely upon liquid concentration sampling rather than the gas-phase headspace analyses required by the basic EPICS method. The results for four selected organic chemicals (benzene, methylbenzene, chlorobenzene, and bromobenzene) agree well with values calculated from literature solute vapor pressure and solubility data and from correlations.

Introduction

Partitioning of hazardous organic chemicals between air and water phases is an important subject in environmental science. The linear equilibrium relationship between a dilute organic chemical in a water solvent and the equilibrium vapor phase above it can be described by Henry's law constant, H_{ci}. Two widely used forms of Henry's law are

$$\hat{f}_i^{G} = x_i H_{ci} \tag{1}$$

$$H_i = \frac{C_G}{C_L} \tag{2}$$

where eq 1 is known as the thermodynamic and eq 2 as the environmental forms. In eq 1, $\hat{f}_i^{G}$ is the fugacity of i in the gas mixture; H_{ci} is Henry's law constant; and x_i is the liquid mole fraction. In eq 2, H_i is Henry's law constant; C_G is the gas concentration; and C_L is the liquid concentration.

The value of H_{ci}, especially at higher temperatures, is needed in the design of water treatment equipment. Since many organic chemicals are very volatile, determining the H_{ci} value becomes difficult, especially at high temperatures. Therefore, high temperature H_{ci} data are often unavailable or scarce in the published literature. Several researchers have attempted to develop models correlating high-temperature H_{ci} values for various organic chemicals. However, development and verification of these models requires experimental data; therefore, a good experimental technique for determining high-temperature H_{ci} values is necessary.

Several researchers have previously developed new experimental methodologies to measure H_{ci} values at ambient temperature. A summary of their methods is shown in Table 1. One of the advantages of using the EPICS methodology[1] over the other methods is that no mass transfer limitations occur during the experiment, in comparison to other methods such as batch air-stripping.[2] The EPICS method is also easy to implement as it requires a simple apparatus.[3] With EPICS, results are obtained by measuring only the ratio of either the gas or liquid concentrations of the two systems.[3]

Table 1. Previous Experimental Methods for Determining Henry's Law Constant

method	researcher
equilibrium batch gas stripping	Mackay et al.[2]
equilibrium partitioning in closed systems (EPICS)	Lincoff and Gossett[1] Gossett[3]
wetted-wall column technique	Fendinger and Glotfelty[43]
static cell headspace gas chromatography	Hussam and Carr[44]
gas−liquid chromatography	Orbey and Sandler[45] Tse et al.[46]

The unique feature of the extended EPICS method presented herein is the higher temperature application up to 362 K. Unlike the traditional EPICS method, which measures the ratio of the gas concentrations, liquid concentrations are measured instead. This method eliminates the sampling error due to vapor loss via condensation.

Background and Theory

The method of Equilibrium Partitioning In Closed Systems (EPICS)[1] consists of two binary solute−solvent equilibrium systems with different liquid volumes. The liquid- or gas-phase concentrations of the two systems are measured, and the ratio of these values is used to compute the dimensionless Henry's law constant via the combined mass balance equations of the two systems.

In 1984, Lincoff and Gossett were the first to use the original EPICS equation to determine the H_i value of five chlorinated organic chemicals in the temperature range of (283.15 to 303.15) K.[1] The original EPICS equation was applied to equal masses of chemical introduced into the two closed systems. However, this equal mass constraint can lead to low precision for H_i values.

In 1987, Gossett modified the method by using the mass ratio of added solute to calculate H_i. He measured 13 volatile C1 and C2 chlorinated organic chemicals in the temperature range of (283.15 to 308.15) K.[3] In 1988, Ashworth et al. used the

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10.1021/je100701w

Table 2. Summary of Previous EPICS Experiments

researcher	chemicals studied	phase of the concentration ratio	($T_{\min}$ to $T_{\max}$)/K
Lincoff and Gossett[1]	1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, chloroform, methylene chloride	gas	283.15 to 303.15
Gossett[3]	1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, chloroform, 1,1-dichloroethylene, *cis*-1,2-dichloroethylene, *trans*-1,2-dichloroethylene, vinyl chloride, 1,1-dichloroethane, chloroethane, carbon tetrachloride, dichloromethane, chloromethane	gas	283.15 to 308.15
Ashworth et al.[4]	45 volatile organic chemicals of various classes	gas	283.15 to 303.15
Robbins et al.[47]	benzene, methylbenzene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, *tert*-butyl ether	gas	298.15 to 323.15
Dewulf et al.[48]	chloroform, tetrachloromethane, 1,1-dichloroehtane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, benzene, methylbenzene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene	gas	275.15 to 298.15
Heron et al.[5]	trichloroethylene	gas	283.15 to 363.15
Ayuttaya et al.[49]	isopropyl alcohol, acetone, 1,2-dichloroethane, methylbenzene	liquid	298.15

same method to measure H_i of 45 chemicals covering a wider range of chemical structures and volatilities in the temperature range of (283.15 to 303.15) K.[4] Heron et al. in 1998 applied this method by measuring the ratio of the gas concentrations to obtain H_i of trichloroethylene in water between (283.15 and 363.15) K.[5] In 2001, Ayuttaya et al. applied a similar method by measuring the ratio of the liquid concentrations to obtain H_i of four organic solutes at a single temperature. Table 2 summarizes the previous EPICS experiments by various researchers.

For this study, the authors used an extended EPICS equation for elevated temperatures based on the liquid concentration ratio of two closed systems.[6] At equilibrium in a closed vessel, the total mass of solute can be expressed as

$$M = C_L V_L + C_G V_G \tag{3}$$

By applying the dimensionless Henry's law constant, H_i, eq 3 becomes

$$M = [C_L V_L + (H_i C_L) V_G] = C_L [V_L + H_i V_G] \tag{4}$$

where M is the total organic mass; C_L is the liquid-phase concentration; C_G is the vapor-phase concentration; V_L is the liquid volume; and V_G is the gas volume.

If two systems are prepared within the solute's Henry's law concentration range using two different liquid volumes

$$M_1 = C_{L1}[V_{L1} + H_i V_{G1}] \tag{5}$$

$$M_2 = C_{L2}[V_{L2} + H_i V_{G2}] \tag{6}$$

Solving eq 5 and eq 6 for H_i gives

$$H_i = \frac{V_{L2} - \phi V_{L1}}{\phi V_{G1} - V_{G2}} \tag{7}$$

where

$$\phi = \frac{\left(\dfrac{M_2}{M_1}\right)}{\left(\dfrac{C_{L2}}{C_{L1}}\right)} \tag{8}$$

Table 3. Suppliers and Grades for Chemicals

chemical	grade	suppliers
benzene	benzene CHROMASOLV plus for HPLC $w \geq 0.999$	Sigma Aldrich
methylbenzene	$w \geq 0.998$ Certified ACS Reagent	Fisher Scientific
chlorobenzene	ACS Reagent $w \geq 0.995$	Sigma Aldrich
bromobenzene	Reagent Plus $w \geq 0.99$	Sigma Aldrich

For the closed systems 1 and 2 in eqs 5 and 6, C_{L1} and C_{L2} are the liquid-phase concentrations; M_1 and M_2 are the total organic masses; V_{L1} and V_{L2} are the liquid volumes; and V_{G1} and V_{G2} are the gas volumes. The ratio of liquid concentrations can be obtained from UV absorbances from a UV spectrometer or from any other suitable analytical method.

Experimental Section

The four chemicals selected for experiment (benzene, methylbenzene, chlorobenzene, and bromobenzene) are aromatic, as this is an important class of water contaminant. These chemicals are also volatile organic compounds found in the petroleum industry, which are harmful to human health, especially the central nervous system. In addition, the selected chemicals have intermediate volatilities that are suitable for experimental measurement. They also provide a good UV signal, which can be detected by a spectrometer. The details of the grades and sources of chemicals are shown in Table 3.

The distilled and deionized water used in the experiments was obtained by passing in-house distilled water through a Mega-Pure water purification system (model MP-190 LC, Corning Scientific Products). The experimental setup for the EPICS experiments is shown in Figure 1.

All glassware was washed with distilled water and dried in an oven for 24 h. At each temperature, six vials were prepared: three filled with "*a*" amount of distilled/deionized water and three with "*b*" amount. The vials were each closed with a screw top-hole cap with a PTFE (polytetrafluoroethylene) lined silicone septa. A Mettler Toledo AB304-S analytical balance was used to measure the mass of the water. A different vial size was chosen for each chemical, as listed in Table 4, to ensure accurate mass measurements without exceeding the solubility limit.

For benzene, methylbenzene, and chlorobenzene, the vials were turned upside-down before the pure organic solute was injected using a Hamilton 0.1 mL gastight syringe (810 RN 100 μL SYR). For the neat organics, the mass injected into the six vials was measured to four significant figures using a Mettler Toledo AB304-S analytical balance to weigh the vial before and after the injection. For bromobenzene, a saturated stock solution of bromobenzene in water was prepared and pipetted into the vials. The concentration of the solute was under the

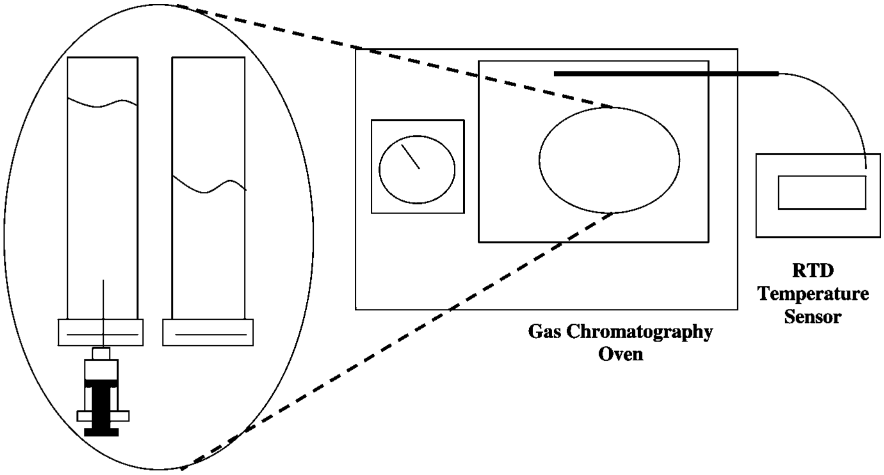

Figure 1. Diagram of extended EPICS experimental apparatus. Two vials contain different volumes of water and the same amounts of organic solute mass.

Table 4. Chemicals Studied at Temperature *T* with Water Volumes *V*(H_2O), Total Organic Mass *M*, Equilibration Time *t*, and Wavelength *λ*

		T[a]		*V*(H_2O) "*a*"	*V*(H_2O) "*b*"	M	*t*	*λ*
case	chemical	K	vial type	cm^3	cm^3	mg	h	nm
1	benzene	322.00, 342.00, 362.00	Supelco 40 mL clear vial	25 ± 0.5	15 ± 0.5	18.3 ± 0.3	∼24	238
2	methylbenzene	322.00, 342.00, 362.00	Pyrex 70 mL culture tube	60 ± 0.5	40 ± 0.5	17.6 ± 0.6	∼24	245
3	chlorobenzene	323.15, 333.15, 343.15	VWR Boston round bottles, amber, narrow mount	60 ± 0.5	40 ± 0.5	22.4 ± 0.4	∼72	264
4	bromobenzene	303.15, 323.15, 343.15	Supelco 40 mL clear vial	25 ± 0.5[c]	10 ± 0.5[c]	n/a[b]	∼48	264

[a] The RTD (resistance temperature detector) has a display accuracy of ± 0.01 K. [b] Prepared via saturated stock solution. [c] Volume of saturated stock solution of bromobenzene in water pipetted into the vials.

Table 5. Extended EPICS Experimental Values of H_{ci}/MPa with 95 % Confidence Intervals

	T/K		
chemical	322.00	342.00	362.00
benzene	70.7 ± 2.5	112.3 ± 15.9	160.0 ± 7.4
methylbenzene	85.5 ± 1.8	138.8 ± 8.2	214.9 ± 17.2
	T/K		
	323.15	333.15	343.15
chlorobenzene	43.5 ± 3.6	53.3 ± 5.2	55.1 ± 4.4
	T/K		
	303.15	323.15	343.15
bromobenzene	15.9 ± 0.8	32.3 ± 2.4	48.4 ± 5.1

solubility limit in the system. All six vials were heated to the desired temperature in a GC oven for temperature control. Incubation times of all chemicals were checked to ensure enough time for the system to reach equilibrium, and these times are listed in Table 4. Each chemical was investigated at a different set of discrete temperatures, which are reported in Table 5, to verify existing published data and to make Henry's constant measurements at higher temperatures than those reported previously, up to the limitation of the equipment.

A 5 mL Luer-Lok Tip Sterile Becton Dickinson syringe was used to sample the liquid solutions from each vial for absorbance measurements in the UV spectrometer. Each chemical was investigated at a specific wavelength. The absorbance of the liquid solution was measured by a Perkin-Elmer Lambda 35 UV/vis spectrometer. After obtaining absorbance readings from all six vials, the dimensionless Henry's law constant, H_i, was calculated for each pair of vials. Overall, H_i was determined using the average of the nine values calculated by pairing each of the three vials with the "*a*" volume of water with each of the three vials with the "*b*" volume of water. H_i was converted to Henry's law constant in pressure units (MPa), and the 95 % confidence interval was calculated from the nine values assuming a t-distribution function of errors. A detailed description of equipment and experimental conditions is given in Table 4.

Results and Discussion

The average of the nine H_i values for each temperature was obtained and converted to H_{ci} units. The measured H_{ci} values and their 95 % confidence intervals are presented in Table 5. For each chemical, the results were compared with vapor pressure and solubility literature data, which can be converted to H_{ci} through the equation[7]

$$H_{ci} = \frac{(1 - x_2^{\alpha})P_1^{s}\phi_1^{s}}{x_1^{\beta}} \tag{9}$$

where x_1^{β} is the solute mole fraction (solubility limit) in the water-rich phase; x_2^{α} is the water mole fraction (solubility limit) in the solute-rich phase; P_1^{s} is the vapor pressure of the solute; and ϕ_1^{s} is the saturation fugacity coefficient of the solute.

The four chemicals studied are all known to exhibit Henry's law behavior at near-ambient conditions up to their aqueous solubility limits.[2,8] For application at higher temperatures and pressures, eq 9 is based on the solute fugacity standard state, rather than the solute vapor pressure, and does not assume negligible water solubility in the organic chemical.

The saturation fugacity coefficient of the solute was calculated using the Peng−Robinson equation of state.[9] Critical properties and solute vapor pressures were obtained from the DIPPR 801 Database,[10] the DIPPR ESP Database,[11] and the Korean Thermophysical Properties Databank of the Chemical Engineering Research Information Center.[12] Solute solubility in the water-rich phase, x_1^{β}, and water solubility in the solute-rich phase, x_2^{α}, were obtained primarily from the NIST Solubility Database.[13]

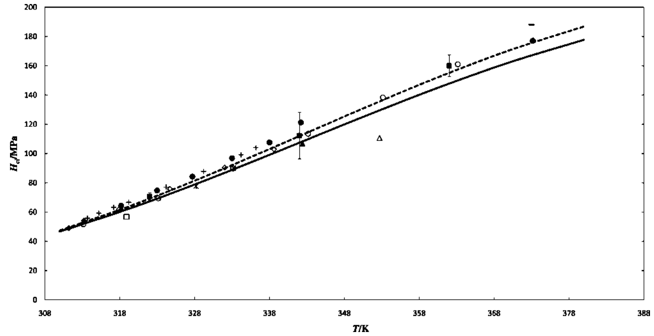

Figure 2. Henry's law constant experimental results of extended EPICS for benzene in comparison to literature data and models. ◇, ref 15; ●, ref 16; ▲, ref 17; ×, ref 18; ∗, ref 19; ○, ref 20; +, ref 21; −, ref 22; □, ref 23; ♦, ref 24; △, ref 25; ■, extended EPICS; −, bond contribution model, ref 7; - -, group contribution model, ref 7.

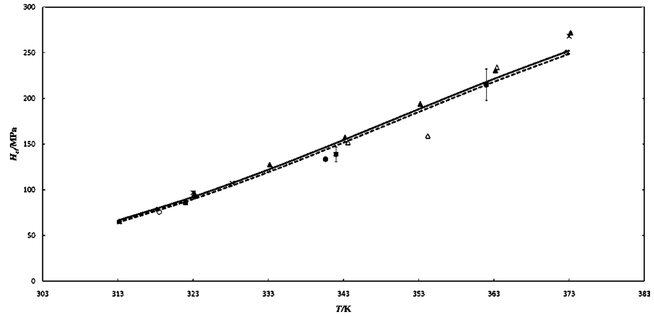

Figure 3. Henry's law constant experimental results of extended EPICS for methylbenzene in comparison to literature data and models. ◇, ref 26; ●, ref 27; ▲, ref 28; ×, ref 29; ∗, ref 22; ○, ref 23; +, ref 30; ♦, ref 31; △, ref 32; ■, extended EPICS; −, bond contribution, ref 7; - -, group contribution, ref 7.

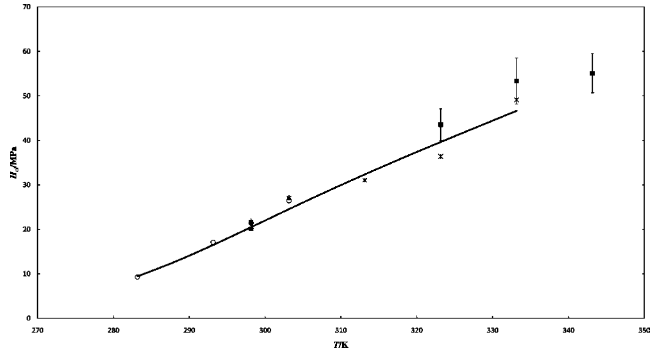

Figure 4. Henry's law constant experimental results of Extended EPICS for chlorobenzene in comparison to literature data and model. ◇, ref 33; ●, ref 34; ▲, ref 35; △, ref 36; ∗, ref 14; ○, ref 37; +, ref 38; ■, extended EPICS; −, fitted model, ref 39.

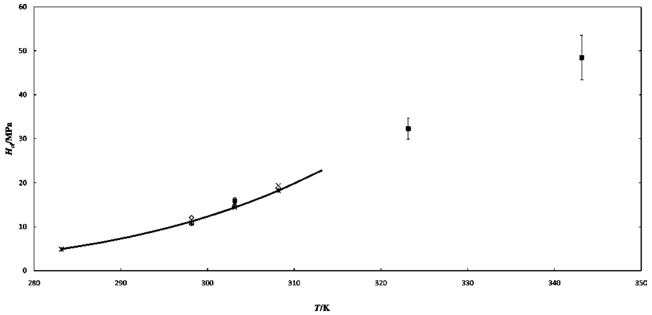

Figure 5. Henry's law constant experimental results of extended EPICS for bromobenzene in comparison to literature data and model. ◇, ref 33; ○, ref 40; △, ref 36; ×, ref 41; ∗, ref 38; +, ref ; ■, extended EPICS; −, fitted model, ref 39.

The authors chose to focus on the NIST and DIPPR critically evaluated databases since those sources assess data quality and internal data consistency.

The extended EPICS experimental data agreed well with the literature data. The error calculated using a 95 % confidence interval shows that the deviations increased with temperature due to the volatility increase of the chemicals.

The experimental results were also compared with an experimental data-fitted model and two correlating models developed by the authors.[7] Experimental data by extended EPICS agreed well with these models. Figures 2 to 5 show the experimental results for benzene, methylbenzene, chlorobenzene, and bromobenzene by extended EPICS in comparison to literature data and models. Experimental uncertainties based on 95 % confidence were calculated for all experimental measurements, and in no case was the uncertainty larger than 15 %. Note in Figure 4 for chlorobenzene that the extended EPICS measurements trend higher than the temperature-extrapolated literature data correlation shown; however, the single data point by Kisarov[14] at 333.15 K falls within the uncertainty limits of the extended EPICS measurement. Overall, the majority of the uncertainties for all four chemicals was within 10 % of the average measurements.

There are advantages and limitations of the method presented herein. Liquid sampling for UV absorbance readings is a better technique than gas sampling by syringe for GC analysis; the latter is error-prone due to vapor loss via condensation, especially at higher temperatures. However, in liquid sampling for UV absorbance readings, the concentration of the chemical solute in each vial needs to be high enough to provide a significant UV signal but not exceed the solubility limit. The volume of the solvent or mass input of the solute can be adjusted to meet this criterion. In addition, the analytical method presented herein also applies only to those chemicals that have significant UV absorbance. Chemicals that are not UV sensitive need to be investigated using gas chromatography (GC) or high-performance liquid chromatography (HPLC) with a refractive index (RI) detector.

Like original EPICS, due to the accuracy of the method, the application of extended EPICS is limited to chemicals which have H_{ci} values below about 400 MPa.[3] Therefore, extended EPICS is not recommended for extremely hydrophobic chemicals, such as the alkane family.

Conclusions

The proposed extended EPICS, which combines high-temperature application and liquid concentration sampling, has the capability to measure Henry's law constant in water up to at least 362 K. The experimental error increases with temperature due to the volatility increase of the organic chemical. Extended EPICS can be applied to UV-transparent chemicals by using chromatographic methods with appropriate detectors.

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Received for review June 30, 2010. Accepted August 17, 2010. The authors received support from the National Science Foundation through the Sustainable Futures IGERT project (DGE 0333401) and Michigan Tech's Sustainable Futures Institute (SFI). Collaboration with AIChE/DIPPR through Project ESP is also gratefully acknowledged.

JE100701W