Technical note

An improved approach for measuring Henry's law coefficients of atmospheric organics

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ARTICLE INFO

ABSTRACT

In this work, we present an improved method for Henry's law constant, K_H, measurements by coupling a bubble column system with a gas cell/infrared spectrometer. To demonstrate the feasibility of this approach, we measured K_H of atmospheric organics from three different classes, namely, toluene (hydrocarbon), sec-butylamine (amine), and cineole (ether). We also reported temperature and ionic strength effects on the K_H values of sec-butylamine for the first time. As shown in this work, the method is highly capable of determining K_H of atmospheric organic species regardless the presence of heteroatoms and the occurrence of hydration in water. It is very versatile, easy to use, reliable, and efficient. It is also well-suited for undergraduate students to conduct environmental chemical science research during academic semesters.

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1. Introduction

Henry's Law, the relationship between the solubility of a gas and its partial pressure above the liquid, plays a pivotal role in regulating the partition of myriads of volatile organic compounds (VOCs) between the gas phase and the aqueous phase, in turn affecting their participation in both aerosol and cloud formation processes, and their contribution to various environmental issues including air pollution, climate change, and public health. Currently, Henry's law constants, K_H, of many VOCs, including those closely related to atmospheric chemistry, are not available from direct measurements, instead, they are only estimated from thermodynamic data. Moreover, temperature dependences of Henry's law constants are often unavailable (Staudinger and Roberts, 1996; Betterton, 1992). As a result, estimated temperature dependent $K_H(T)$ values were used in models for studying atmospheric organic cloud chemistry and formation of secondary organic aerosols (SOA) (Couvidat and Seigneur, 2011; Karl et al., 2009; Mouchel-Vallon et al., 2013; Tilgner and Herrmann, 2010). Evidently, there is a scientific need in the direct measurements of temperature dependent Henry's law constants of organics of atmospheric interest.

There are several different methods for Henry's law constants determinations, including the static and dynamic equilibrium approaches (Staudinger and Roberts, 1996). The bubble column technique, which is based on a dynamic equilibrium, has been the most frequently used method for Henry's law constants measurements (Betterton and Hoffmann, 1988; Ip et al., 2009; Mackay et al., 1979; Lee et al., 2012; Roberts, 2005). In the experiments, the solute of interest moves up from the bottom of a column containing a liquid into the headspace, where changes in concentrations of the gaseous solute are analyzed. Unlike the static equilibrium method, which requires direct measurements of the absolute concentrations of the solute in the gas and aqueous phases, only relative concentrations of the solute, over time, are necessary for Henry's law constant determination. This greatly minimizes uncertainties resulting from the absolute concentration measurements (Staudinger and Roberts, 1996). The concentrations of the solutes can be measured either online or offline, however, the solutes may require different detection methods due to sensitivity of individual instruments, and data collection procedures could be time consuming and tedious. For example, Lee et al. (2012) recently set up a gas chromatography (GC) system equipped with a flame ionization detector (FID) to measure online concentration of hydrocarbons from manual discrete injections of the solutes in the gas phase for every minute. In a similar manner, Roberts (2005) determined Henry's law constant of peroxyacetic nitric anhydride

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(PAN) using GC/ECD. Whereas, Ip et al. (2009) performed offline analyses of aliquots of glyoxal solution by ion chromatograph (IC), and glyoxylic acid and glycolic acid solutions by high performance liquid chromatography. Sampling time intervals in their studies range from 30 min to 6 h.

In this work, we present an improved method for Henry's law constant measurements by coupling a bubble column system with a gas cell in an infrared spectrometer. We measured K_H values of toluene, sec-butylamine, and cineole to demonstrate the feasibility, versatility, usability, reliability, and efficiency of this approach. We reported the K_H of cineole and temperature and ionic strength effects on the K_H of sec-butylamine for the first time.

2. Experimental

Toluene (99%, Fisher), sec-butylamine (99%, Alfa Aesar), and cineole (99%, Alfa Aesar) were used as delivered without further purification.

Henry's law constants were measured using a temperature-controlled bubble column system (Fig. 1). Details about the system have been discussed elsewhere (Betterton and Hoffmann, 1988; Ip et al., 2009; Mackay et al., 1979; Lee et al., 2012; Roberts, 2005). Briefly, it is made up of two double-jacketed bubble columns. The first one (35 cm long) was for organic vapor generation by bubbling organic liquids in the column with nitrogen gas. The exiting gaseous mixture was then passed through water in the second column (80 cm long) for organic vapor absorption and for establishing equilibrium between the solutes in the exiting gas and the solutes in the aqueous phase. Low flow rates of N_2 (50–100 mL min^{-1}) and high liquid depth (500–1000 mL) were used to achieve the gas–liquid equilibrium. Two 3-way valves were used to switch the N_2 so it either passed through the first column or bypassed it. When the 3-way valves were set to the bypass position, the dissolved organic species in the second column were purged with N_2 at different flow rates (500–1000 mL min^{-1}). Concentrations of organic solutes in the headspace were monitored as a function of time. The concentration decay of organic solutes in the gas phase can be utilized to derive Henry's law constants based on the following equation (Lee et al., 2012):

$$\ln(C_0/C_t) = [\Phi/(K_H RTV) + k]t \tag{1}$$

where C_0 and C_t are the concentration of the organic vapor at equilibrium and at time t (sec) after the equilibrium, respectively; Φ is the gas flow rate (mL min^{-1}); K_H is the Henry's law constant (M atm^{-1}); R is the gas constant (0.082 atm K^{-1} M^{-1}), T is the temperature (K); V is the water volume (mL); and k is the first-order hydrolysis loss rate (s^{-1}).

Throughout the experiments, both columns were temperature-controlled by a refrigerated circulator (VWR 1160S) and the entire system was under atmospheric pressure. Concentrations of toluene, cineole, and sec-butylamine in the headspace were measured by a FTIR spectrometer with a DTGS detector (Thermo Avatar 360) coupled to a Teflon gas cell (10 cm pathlength, and equipped with CaF$_2$ windows). Integrated absorbance peaks (3056–3016 cm^{-1}) for toluene (3000–2802 cm^{-1}) for sec-butylamine, and (1252–1190 cm^{-1}) for cineole as a function of time, which are proportional to gas phase concentrations of organics, were used to derive the Henry's law constants. In our experiments, all the spectral measurements were taken automatically by the macro function built in the OMNIC program in range of 650–4000 cm^{-1} over 4 scans with a resolution of 4 cm^{-1}. This substantially reduces the amount of repetitive operation. The macro function also allows users to set a delay time before each spectrum collection, so that the infrared spectra could be collected at designated time intervals. The delay time for organic species varies, depending on their individual Henry's law constants. For each sample, experiments were repeated under the same condition at least three times.

3. Results and discussion

3.1. Measurement validation

To accurately measure the Henry's law constants, it is critical to achieve an equilibrium between the rising bubbles and the surrounding solution. Since Henry's Law is a limiting law, in addition to the gas–liquid equilibrium requirement, it is also important to keep the concentration of the dissolved organic solution sufficiently dilute, and the partial pressure of organic vapor small relative to the total system pressure. Furthermore, the liquid should be under constant volume and temperature conditions. To validate the system, we first measured the Henry's law constant of toluene at 298 K in this work. Toluene, an aromatic hydrocarbon, has been well studied in both direct measurement and theoretical prediction, and literature values ranges from 0.13 to 0.21 mol L^{-1} atm^{-1} (Hoff et al., 1993; Linstrom and M.G, 2005; Lee et al., 2012; Mackay et al., 1979). Fig. 2 shows the decay of the peaks around 3042 cm^{-1}, which was assigned to =C–H stretching mode, over time. The integrated absorbance was used to measure relative concentrations of the solute in the gas phase, and in turn determine the Henry's law constant. Fig. 3a gives linear plots of $\ln(C_0/C_t)$ versus time for toluene at 298 K with different flow rates, Φ, as predicted by the Equation (1). With the slopes derived from curve fitting of the plots in Fig. 2a, d $\ln(C_0/C_t)$/dt versus Φ/V plots can be acquired (Fig. 3b). According to the Equation (1), d $\ln(C_0/C_t)$/dt versus Φ/V is expected to have a linear
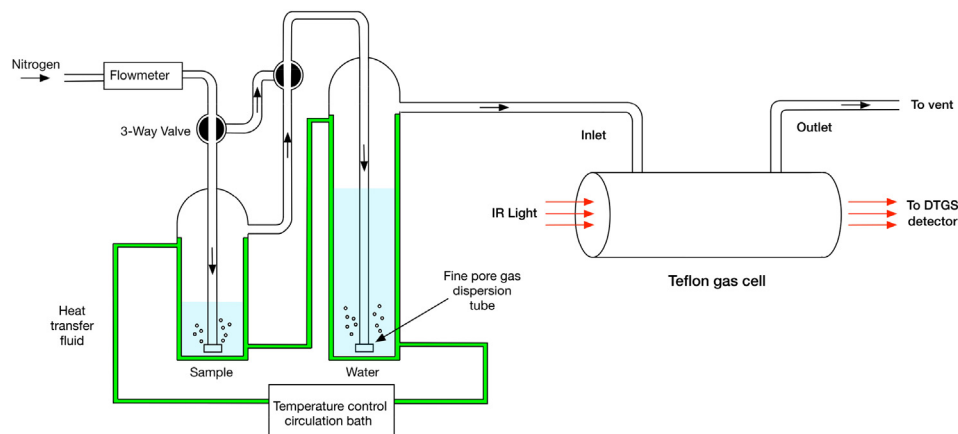

Fig. 1. A schematic diagram of bubble column-gas cell/IR system.