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Infinite dilution activity coefficients and Henry's law constants of compounds in water using the inert gas stripping method

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ABSTRACT

Henry's law constants and infinite dilution activity coefficients were measured for toluene, 1-butanol, anisole, 1,2-difluorobenzene, 4-bromotoluene, 1,2,3-trichlorobenzene, and 2,4-dichlorotoluene in water using the inert gas stripping method at ambient pressure (approximately 86.2 kPa) and at temperatures between 281.15 K and 323.15 K. Fugacity ratios, required to determine infinite dilution activity coefficients for the solid solutes, were calculated from literature values for the heat of fusion and the liquid and solid heat capacities. Chemicals were chosen based on missing or conflicting data from the literature.

1. Introduction

The fate and transport of chemicals in the environment as well as the health and safety risks associated with chemical exposure are growing global concerns. The U.S. Environmental Protection Agency has developed a process to estimate risks associated with chemicals to ensure chemical commercialization will not pose unreasonable risks [1]. Properties used in these risk assessments include aqueous solubility (x_i^{aq}) and the aqueous Henry's law constant (k_H). In environmental impact studies, k_Hs are used to determine the fate and transport of chemicals in air and water by determining volatilization or absorption tendencies [2,3]. Additionally, k_H values have pharmaceutical, medical, and food science applications [4]. The design and optimization of air-stripping columns also use k_Hs. These types of columns are often used to remove volatile contaminants from groundwater.

The definition of k_H is

$$k_H \equiv \lim_{x_i \to 0} \frac{\hat{f}_i}{x_i} \tag{1.1}$$

where $\hat{f}_i$ is the partial fugacity of compound i in solution, and x_i is the mole fraction in the liquid phase [5–7]. When experimental values are not available, k_H can be estimated from independent pure component vapor pressure (P_i^{sat}) and x_i^{aq}:

$$k_H = \frac{P_i^{sat}}{x_i^{aq}}. \tag{1.2}$$

Assumptions for using Eq. (1.2) are that the solubility of water in the organic chemical is negligible so the solute vapor pressure is unaffected by the presence of water and that the activity coefficient does not change with concentration [2,8,9]. These assumptions are valid for the hydrophobic compounds studied in this work.

The inert gas stripping (IGS) method has been used to measure both k_Hs and infinite dilution activity coefficients (γ_i^{∞}s) [10,11]. In this study, k_Hs and γ_i^{∞}s were measured for various compounds at temperatures between 8 °C and 50 °C using the IGS method. Compounds in this study were selected based on the absence of experimental data or inconsistencies between reported experimental values. Some of the inconsistencies occur between experimentally determined k_Hs and calculated k_Hs (Eq. (1.2)).

2. Experimental methods

2.1. Materials

The compounds used as solutes are listed in Table 1 with the suppliers and stated purities. Chemicals were used as received without further purification. Deionized distilled water was used as the solvent.

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List of symbols

a	slope obtained from plotting $\ln(A/A^{\circ})$ versus time (s^{-1}) Eq. (2.5)
A	peak area
B_{ii}	second virial coefficient (m^3/mol)
Cp	heat capacity (J/mol K)
f	pure component liquid phase fugacity (kPa)
$\hat{f}$	partial fugacity in solution (kPa)
F	volumetric flow rate (m^3/s)
FID	flame ionization detector
GC	gas chromatography
H	enthalpy (J/mol)
$\Delta H_{fus,Tm}$	heat of fusion at the melting point (J/mol)
IGS	inert gas stripping
k_H	Henry's law constant (kPa)
n	moles in stripping cell
N	number of measurements
P	pressure (kPa)
P^{sat}	vapor pressure (kPa)
R	universal gas constant (8.3145 J/mol K)
s	standard deviation
V_g	volume of the headspace in the stripping cell (m^3)
x	mole fraction in liquid phase
y	mole fraction in vapor phase
T	temperature (K)

Greek letters

γ	activity coefficient
$\hat{\phi}$	fugacity coefficient in solution
ϕ^{sat}	pure component vapor-phase fugacity coefficient at its saturation pressure
Ψ	fugacity ratio

Superscripts

0	initial
∞	infinite dilution
aq	aqueous solubility
L	liquid
S	solid
V	vapor

Subscripts

CG	carrier gas
i	solute
in	total entering stripping cell
solv	solvent

2.2. Inert gas stripping theory

The IGS method uses gas chromatography (GC) to analyze the change in composition with time of the vapor phase produced from stripping a dilute solution. The theory for the IGS method has been outlined in detail by Krummen et al. [12]. The general theory is outlined here with further discussion of the application to a solid solute.

Table 1
Compounds and purities.

Chemical	CAS	Supplier	Purity
Toluene	108-88-3	Sigma–Aldrich	99.8%
1-Butanol	71-36-3	Macron Chemicals	≥99.4%
Anisole	100-66-3	Sigma–Aldrich	≥99.0%
1,2,3-Trichlorobenzene	87-61-6	Sigma–Aldrich	99%
1,2-Difluorobenzene	367-11-3	Sigma–Aldrich	98%
4-Bromotoluene	106-38-7	Sigma–Aldrich	98%
2,4-Dichlorotoluene	95-73-8	Sigma–Aldrich	99%

In vapor–liquid equilibrium, the solute is described by

$$y_i \hat{\phi}_i^V P = \gamma_i x_i f_i^L \tag{2.1}$$

where y_i is the mole fraction in the vapor phase, $\hat{\phi}_i^V$ is the fugacity coefficient of species i in the vapor phase, P is the total pressure, γ_i is the activity coefficient relative to the pure-component standard state, x_i is the mole fraction in the liquid phase, and f_i^L is the fugacity of pure species i in the liquid phase. Since the solute concentration is very small, γ_i can be replaced by γ_i^{∞}.

For liquids, the liquid fugacity of pure species i is calculated at the system temperature using

$$f_i^L = \phi_i^{sat} P_i^{sat} \tag{2.2}$$

where P_i^{sat} is the vapor pressure of pure species i and ϕ_i^{sat} is the vapor-phase fugacity coefficient of pure species i at its saturation pressure. This equation assumes the Poynting factor is unity. The solvent can be described by

$$y_{solv} P = P_{solv}^{sat} \tag{2.3}$$

where y_{solv} is the mole fraction of water in the vapor phase and P_{solv}^{sat} is the vapor pressure of the solvent. This equation assumes that the Poynting factor and vapor-phase corrections are negligible and that the activity coefficient of solvent is unity which is valid because $x_{solv} \approx 1$.

The equations used to determine k_H and γ_i^{∞} using the IGS method are based on a mass balance around the stripping cell. The mass balance assumes that only solute is stripped from the stripping cell which is accomplished by saturating the stripping gas with solvent before it enters the stripping cell. Additionally, these balances assume ideal gas behavior, negligible dissolution of the carrier gas in the system, additive gas volumes (valid at constant temperatures and pressures in unreactive systems), and small concentrations of solute in the headspace ($y_i \approx 0$).

The only difference in mass balance equations used in this study and that of Krummen et al. [12] is the equation used to calculate the volumetric flow rate of solvent leaving the saturation cell and entering the stripping cell (F_{solv}):

$$F_{solv} = F_{in} y_{solv} = F_{in} \frac{P_{solv}^{sat}}{P} \tag{2.4}$$

where F_{in} is the total flow rate leaving the saturation cell and entering the stripping cell. Krummen et al. [12] use the flow rate of the carrier gas before it is saturated with solvent instead of F_{in} to calculate F_{solv}. Eq. (2.4) is consistent with the balance performed by Krummen et al. [12] around the stripping cell. The only variable that is a function of time in the mass balance is the concentration of solute which is related to GC peak area. Integrating the mass balance over the stripping time and rearranging gives the final equation for γ_i^{∞} which is

$$\gamma_i^{\infty} = \frac{-RT n_{solv}}{\phi_i^{sat} P_i^{sat} [V_g + F_{CG}/((1 - (P_{solv}^{sat}/P))a)]} \tag{2.5}$$

where V_g is the volume of the headspace in the stripping cell, n_{solv} is the moles of solvent in the stripping cell, R is the universal gas constant, T is temperature, and a is the slope obtained from plotting $\ln(A/A^{\circ})$ versus time. A is the GC solute peak area obtained from periodically sampling the vapor stream exiting the stripping cell and A° is the initial solute peak area. Eq. (2.5) is slightly different from that reported by Krummen et al. [12] due to the change in Eq. (2.4). Eq. (2.5) refers specifically to liquid solutes where the liquid fugacity of the pure species can be calculated using Eq. (2.2).