

Calculations of Henry's law constants for organic species using relative Gibbs free energy change[☆]



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ABSTRACT

An effective approach is established to estimate Henry's law constant values (H) using density functional theory (DFT) at the level of B3LYP/6-311+G(d,p) along with a polarizable continuum model (PCM). The 319 H values for the eight categories of small organic molecules (43 alcohols, 50 amines, 24 aldehydes, 32 ketones, 33 organic fluorides, 72 organic chlorides, 32 organic bromides and 33 organic nitrates) are estimated, respectively. The Henry's law constant values estimated by this procedure are in good agreement with the experimental results with the standard deviations of 1.38 $\ln H$ unit for alcohols, 1.94 $\ln H$ unit for amines, 1.55 $\ln H$ unit for aldehydes, 1.18 $\ln H$ unit for ketones, 1.24 $\ln H$ unit for organic fluorides, 1.44 $\ln H$ unit for organic chlorides, 1.49 $\ln H$ unit for organic bromides and 0.95 $\ln H$ unit for organic nitrates, respectively.

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1. Introduction

Henry's law constant (HLC) describes an ability of a chemical molecule to distribute between gaseous and aqueous phase, and plays a key role in physical chemistry [1]. It is a key property in the process of describing a chemical substance's environmental behavior [2–4]. So many attentions have been devoted to seeking the estimation methods of HLC values. Conventionally, the most important property–property relationships (PPR) [5] for the estimation of HLC values are given by the vapor pressure/aqueous solubility ratio. This method has a thermodynamical background and therefore a broad range of applicability. However the results obtained by this approach depend strongly on the measured quality of the vapor pressure and aqueous solubility data. Unfortunately such data is often unavailable or not reliable.

In 1975 Hine and Mookerjee reported the group contribution method [6], however, this method only can be used to a part of compounds owing to missing fragment constants. The EPICS (Equilibrium Partitioning in Closed Systems) method, which proposed by Gosset in 1987, involves carefully weighing the amount

of the volatile compound added to both of the sealed bottles and working with ratios of masses [7]. This method needs ascertain the exact ratio of the masses added to both bottles, so it would be impossible to accurately determine the Henry's law constants. In 1993 Robbins reported the static headspace method [8], in which the exact concentration of the volatile compound need not to be known. Experimentally, this method involves the measurement of the equilibrium headspace peak areas of one or more compounds by gas chromatography from aliquots of the same solution in three separate enclosed vials with different headspace-to-liquid volume ratios. In addition the bond method by Meylan and Howard [9] can be applied to some compounds with distinct experimental HLC values. However, there are some shortcomings in this method. One is the missing differentiation of isomers, which is an inherent problem of all fragment methods. Another point is the comparably bad performance for the most of the organochlorines. Perhaps the experimental HLC data presented here could be used for a further improvement of the bond method by introducing additional class specific correction factors [5]. Usually, LSER method (Linear solvation energy relationship) by Dearden [10] is also used to estimate HLC values for more compounds. In 2009 H. S. Simon Ip [11] performed offline analysis of aliquots of glyoxal solution by ion chromatography (IC), and glyoxylic acid and glycolic acid solutions by high performance liquid chromatography. In 2013, J. Duncan Kish [12] presented an improved method by coupling a bubble column

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system with a gas cell in an infrared spectrometer. This method can be applicable to different classes of atmospheric organics regardless of the presence of heteroatoms or aqueous phase dissociation.

Nowadays by means of computers with high computing power theoreticians can also use thermodynamic methods in conjunction with the advanced computational algorithm to calculate the HLC values. Density functional theory (DFT) is a reliable tool which can be used to theoretically study thermodynamic processes, such as surface adsorption and chemical equilibrium. In our previous study [13], pK_a values of carboxylic acids in aqueous solution were calculated using density functional theory methods. In this work, we report theoretically estimation of Henry's law constants for 319 compounds covering eight categories (alcohols, amines, aldehydes, ketones, organic fluorides, chlorides, bromides and organic nitrates) in aqueous solution with density functional theory, and the polarizable continuum model (PCM) [14] used to describe the solvent effect.

2. Theory and computational methods

2.1. Thermodynamic theory

The Henry's law constant H is a way of describing the solubility in water. Usually H is defined as:

$$H = \frac{P_D}{C_D} \quad (1)$$

where, C_D is the concentration of specie D in the aqueous phase, P_D is the partial pressure of species D in the gas phase. The solvation equation of species D into aqueous solution is



From Eq. (2), we can get the relationship of Henry's law constant H and solvation standard Gibbs free energy change, ΔG_D^0 , as follow:

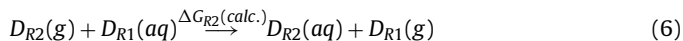
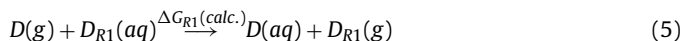
$$\Delta G_D^0 = -RT \ln K_C = -RT \ln \frac{C_D}{P_D} = RT \ln H \quad (3)$$

Then

$$\ln H = \frac{\Delta G_D^0}{RT} \quad (4)$$

where R is gas constant and T is temperature.

Our previous researches shown that there is a prodigious error when the thermodynamic properties (e.g., pK_a) of some equilibrium processes are directly computed by Gibbs free energy changes $\Delta G_D(\text{calc.})$ from density functional theory [13]. For this reason the relative Gibbs free energy change of two inter-change reactions can be used to calculate these thermodynamic properties [13]:



where D_{R1} and D_{R2} are two reference substances whose thermodynamic property is known.

The relative Gibbs free energy change, $\Delta G_r = \Delta G_{R1}(\text{calc.})/\Delta G_{R2}(\text{calc.})$, can be defined as

$$\begin{aligned} \Delta G_r &= \frac{\Delta G_{R1}(\text{calc.})}{\Delta G_{R2}(\text{calc.})} = \frac{\Delta G_D(\text{calc.}) - \Delta G_{D_{R1}}(\text{calc.})}{\Delta G_{D_{R2}}(\text{calc.}) - \Delta G_{D_{R1}}(\text{calc.})} \\ &= \frac{\ln H - \ln H_{R1}}{\ln H_{R2} - \ln H_{R1}} \quad (7) \end{aligned}$$

Then Henry's law constant H can be expressed by Eq. (8)

$$\begin{aligned} \ln H &= \left[\frac{(\ln H_{R2} - \ln H_{R1})}{\Delta G_{D_{R2}}(\text{calc.}) - \Delta G_{D_{R1}}(\text{calc.})} \right] \Delta G_D(\text{calc.}) \\ &+ \left[\ln H_{R1} - \frac{(\ln H_{R2} - \ln H_{R1})}{\Delta G_{D_{R2}}(\text{calc.}) - \Delta G_{D_{R1}}(\text{calc.})} \Delta G_{D_{R1}}(\text{calc.}) \right] \quad (8) \end{aligned}$$

when the selection of the two reference substances, D_{R1} and D_{R2} , is appropriate, the accurate Henry's law constant value H can be obtained from Eq. (8). With

$$A = \ln H_{R1} - \frac{(\ln H_{R2} - \ln H_{R1})}{\Delta G_{D_{R2}}(\text{calc.}) - \Delta G_{D_{R1}}(\text{calc.})} \Delta G_{D_{R1}}(\text{calc.}) \quad (9)$$

$$B = \frac{(\ln H_{R2} - \ln H_{R1})}{\Delta G_{D_{R2}}(\text{calc.}) - \Delta G_{D_{R1}}(\text{calc.})} RT \quad (10)$$

we finally arrive at

$$\ln H = \frac{B \Delta G_D(\text{calc.})}{RT} + A. \quad (11)$$

where A and B can be calculated from Eqs. (9) and (10) by $\Delta G_{D_{R1}}(\text{calc.})$, $\Delta G_{D_{R2}}(\text{calc.})$, and H_{R1} and H_{R2} of the two reference substances, D_{R1} and D_{R2} .

2.2. Theoretical calculations of Gibbs free energy changes, $\Delta G(\text{calc.})$

A total of 319 molecular systems with inclusion of 43 alcohols, 50 amines, 24 aldehydes, 32 ketones, 33 organic fluorides, 72 organic chlorides, 32 organic bromides and 33 organic nitrates, respectively, were initially optimized with DFT hybrid exchange-correlation energy density functional, B3LYP [15], which consists of the Becke's three parameterized exchange energy density functional and the Lee–Yang–Parr correlation functional. For both core and valence-shell electrons, we employed the People's basis set of split-valence triple-zeta plus (d,p)-type polarization, 6-311+G(d,p) [16]. The solvation effect was considered by using a polarizable continuum model (PCM) [17].

All calculations were performed with the Gaussian 09 Revision B.01 package [18]. The experimental Henry's law constant H taken from reference [5,19–22].

3. Results and discussion

3.1. Determine of the parameters A and B in Eq. (11)

It can be seen from Eqs. (9) and (10) that the determine of the parameters A and B depend on the choice of the two reference compounds, D_{R1} and D_{R2} , which is very important to the calculated accuracy. In our research the mathematical statistics, whose goal was the attain of the smallest standard deviation, was used to find out the most appropriate reference compounds in the same category using Origin Software. Our data analysis by the mathematical statistics for alcohols, amines, aldehydes, ketones, organic fluorides, organic chlorides, organic bromides and organic nitrates indicates that the most accurate calculated values of $\ln H$ can be obtained when $\text{CH}_2\text{OHCH}_2\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{CHOH}(\text{CH}_2)_2\text{CH}_3$ are chosen as the two reference substances for alcohols, 1-naphthylamine and $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}$ for amines, $\text{C}_6\text{H}_5\text{CHO}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ for aldehydes, $\text{C}_6\text{H}_5\text{COCH}_3$ and $p\text{-CH}_3\text{C}_6\text{H}_5\text{COCH}_3$ for ketones, $o\text{-C}_6\text{H}_4\text{F}_2$ and $\text{CH}_2=\text{CF}_2$ for organic fluorides, $\text{CH}_2\text{ClCH}_2\text{Cl}$ and C_6HCl_5 for organic chlorides, $\text{CH}_2\text{BrCH}_2\text{Br}$ and CH_3Br for organic bromides, 1,8-octanediol dinitrate and 1-butyl nitrate for organic nitrates. The parameters A and B in Eq. (11) can be calculated by inserting $\Delta G(\text{calc.})_B$ and $\ln H(\text{exp.})$ of the two reference compounds, which are listed in Table S-1 in

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