

# On the Calculation of Henry's Law Constants of Chlorinated Benzenes in Water from Semiempirical Quantum Chemical Methods

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The Henry's law constants for all 12 polychlorinated benzene congeners were calculated using semiempirical quantum chemical solvation models (SM2, SM2.1, and SM3), and their performances are discussed. The values obtained by the SM3 method are underestimated compared with the experimental values and those calculated by SM2 and SM2.1 methods. This underestimation is larger as the degree of chlorination of the benzenes increases. This bad performance of SM3 to calculate Henry's law constants is attributable to the PM3 Hamiltonian, due to its incapacity to give a good description of electron density in chlorinated benzenes. The best results, within the 95% confidence limit of error of the experimental mean, are obtained using SM2 method. The discussion includes analysis of the different contributions to the free energy of solvation, namely, polarization free energy, cavitation, dispersion, and structural rearrangement of the solvent effects as well as partial atomic charges.

## INTRODUCTION

It has been found experimentally that the solubility of a gas over a given solvent increases with an increase in the partial pressure of the gas over the solution. The law that relates the solubility of a gas to its pressure was proposed in 1803 by the English physician and chemist, William Henry.<sup>1,2</sup> Henry's law states that the concentration of dissolved gas in a given solvent is directly proportional to the partial pressure of the gas, temperature remaining constant. The proportional constant is known as Henry's law constant  $H_{i,S}$  of the solute  $i$  in the solvent  $S$ .

$H_{i,S}$  determines how a chemical substance will partition between air and a given solvent. Henry's constant is also related to the infinite dilution residual chemical potential,<sup>3–5</sup>  $\mu_i^\infty$ , which also makes it readily amenable to molecular level investigations. From an environmental point of view,  $H_{i,S}$  is a key parameter used to model the diffusive exchange of chemicals between aqueous phases and the atmosphere. Accurate knowledge of Henry's law constants is essential to predict the environmental behavior, transport, and fate of many types of pollutants.<sup>6–8</sup>

Unfortunately, the lack of accurate  $H_{i,S}$  measurements is a major limitation in predicting the environmental distribution and transport of pollutants. The difficulty to obtain accurate experimental values arise from the limitations of analytical techniques to measure the solute concentration in both phases in equilibrium. Most of the reported values of  $H_{i,S}$  were obtained by dividing vapor pressure data by solubility data, a method which sometimes leads to significantly reduced accuracy. In general, for reasons of cost, time, safety, and availability of techniques to measure  $H_{i,S}$ , it is useful to be able to predict it rather than measure it. Even though such a predictive model should be based on empirical information, it is more useful to develop models based on the 3D

molecular structure, since this allows the model to be used to the prediction of  $H_{i,S}$  for unavailable or new compounds only from structural information.

Quantitative structure–property relationships (QSPR)<sup>9–11</sup> studies have provided accurate models for the prediction of  $H_{i,S}$ . However, the nature of the relationship between Henry's law constant and molecular structure is difficult to interpret due to the number of parameters involved in the correlation. On the other hand, for this kind of study to be successful demands what is not available, i.e., accurate experimental data. In this way this type of study falls into sort of a vicious circle since they require the property value of what they precisely want to predict.

The evolution of quantum chemical methods for solutions,<sup>12</sup> instead, has allowed the prediction of molecular properties from the first principles, and therefore they do not require to know the property experimental value in advance, and moreover their results have a more transparent physical meaning allowing a clear interpretation of the phenomena. In a recent paper, Schüürmann<sup>13</sup> calculates Henry's law constant for 30 benzene derivatives, using quantum chemical continuum-solvation models. In this paper, the author stressed the need to check the performance of dielectric continuum-solvation models in predicting free energy of solvation and Henry's law constant for more hydrophobic compounds such as higher chlorinated benzenes, biphenyls, and pesticides as well as other more persistent xenobiotics.

In this article, we predict Henry's law constants for all 12 polychlorinated benzene congeners using quantum chemical continuum-solvation models (SM2, SM2.1, and SM3), and their performances are discussed.

## THERMODYNAMICS

Let a solution with many components, with mole fractions  $x_i$ , be at equilibrium with its vapor. At equilibrium the

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affinities for the conversion of liquid to gas phase are zero for each component  $i$ , i.e., for each component, the chemical potentials in the two phases are equal<sup>14</sup>

$$\mu_{i,l} = \mu_{i,g} \quad (1)$$

$$\mu_{i,l}^0(P,T) + RT \ln a_i = \mu_{i,g}^0(P,T) + RT \ln f_i \quad (2)$$

where the subscripts  $l$  and  $g$  indicate the liquid and gas phases and  $a_i$  and  $f_i$  are the activity and fugacity of the component  $i$ , respectively. After rearrangement eq 2 takes the form

$$\frac{f_i}{a_i} = K_i \quad (3)$$

where

$$K_i = \exp\{(\mu_{i,l}^0(P,T) - \mu_{i,g}^0(P,T))/RT\} \quad (4)$$

From the nature of  $\mu_{i,l}^0(P,T)$  and  $\mu_{i,g}^0(P,T)$  it follows that  $K_i$  is independent of composition, and it is a function only of  $P$  and  $T$ , but since  $\mu_{i,l}^0(P,T)$  changes little with  $P$ , it is essentially a function of  $T$ .

For any component when  $x_i = 1$ , it is evident that  $K_i$  is the same as  $P_i^0$ , the vapor pressure of pure component  $i$ . Thus eq 3 is the same as Raoult's law. On the other hand, for a minor component, when its mole fraction  $x_i \ll 1$ ,  $K_i$  is not equal to the vapor pressure of the pure substance and eq 3 is known as Henry's law. The constant is called the Henry's law constant  $H_{i,solvent}$  and is defined by<sup>15</sup>

$$H_{i,solvent} = \lim_{x_i \rightarrow 0} \left( \frac{f_i}{a_i} \right) \quad (5)$$

where the activity  $a_i$  is defined as  $a_i = \gamma_i x_i$ , where  $\gamma_i$  is the activity coefficient and  $x_i$  is the mole fraction. The value of the activity coefficient  $\gamma_i$  depends on the choice of reference system. In the case of solutions in which the mole fraction of some components cannot be varied up to unity without change of phase, e.g. aqueous solutions of solids or aromatics compounds, it is convenient to distinguish between the solvent and the solutes. The former is a component which is present in excess and whose mole fraction can be varied up to unity without change of phase. For the solvent, the activity coefficient is taken as approaching to unity as the mole fraction approaches unity:  $\lim_{x_i \rightarrow 1} \gamma_i = 1$ . For the solutes, the activity coefficients are taken as approaching unity at infinite dilution:  $\lim_{x_i \rightarrow 0} \gamma_i = 1$ . This approach is known as unsymmetrical criterion or convention II.<sup>14</sup>

However, for solutes that both are only very slightly soluble in water and have very low pressures, eq 5 may be approximated by the following equation

$$H_{i,solvent} = \frac{p_i}{x_i} \quad (6)$$

where  $p_i$  is the vapor pressure of the solute  $i$  in equilibrium with a liquid solution whose molar fraction is  $x_i$ . In other words, Henry's law constants are true equilibrium constants and therefore may be connected to the standard Gibbs free energy of solvation. Equation 6 is a good approximation when the solute is sparingly soluble, the partial pressure is

very low, and the temperature is much less than the critical temperature of the solvent. The limits of solubility and partial pressure vary from one system to another, but in general, the partial pressure must not exceed 5–10 bar and solubility must be less than 3% in moles.<sup>15</sup>

Many studies have estimated Henry's law constants using this equation assuming the following two assumptions:<sup>10</sup> (1) the vapor pressure of the water-saturated compound is approximately equal to that of the pure compound and (2) the activity coefficient of the solute does not vary appreciably with concentration and can be neglected.

Even though the second assumption is right, the first one is not quite correct since the vapor pressure of the solute must be measured under conditions of equilibrium with a liquid solution of composition  $x_i$ . This oversight had led to a great dispersion in the reported experimental values of the Henry's law constants as well as to ambiguous conclusions in theoretical studies.

### SEMIEMPIRICAL QUANTUM CHEMICAL SOLVATION MODELS

The standard-state free energy of solvation  $\Delta G_s^0$  is a fundamental quantity characterizing the interaction of a solute molecule with a given solvent. In addition to its fundamental interest,  $\Delta G_s^0$  may be combined with other thermodynamic data to predict a variety of equilibrium constants, the most important of which are solubility and the partitioning of a solute between immiscible phases.

The self-consistent reaction field (SCRF)<sup>12,16</sup> approach considers the solvent as a uniform polarizable medium with a dielectric constant  $\epsilon$ , with the solute placed in a suitable shaped hole in the medium and combines the following three elements<sup>17</sup> to calculate  $\Delta G_s^0$ : (1) explicit inclusion of electrostatics with a distributed monopole charge representation and a molecular shape approximated by an all-atom superposition of van der Waals spheres; (2) self-consistent polarization of the solute electronic charge distribution by the solvent reaction field; and (3) explicit inclusion of first solvation shell effects by parametrized atomic surface tensions using solvent accessible surface areas. Elements (1) and (2) together are known as electrostatics part of the calculation, and element (3) is called the nonelectrostatic part.

All these three effects are taken into account in the parametrized solvation models developed by Cramer and Truhlar called SMx.<sup>18–21</sup> In these approaches the Gibbs free energy of solvation is calculated as<sup>19</sup>

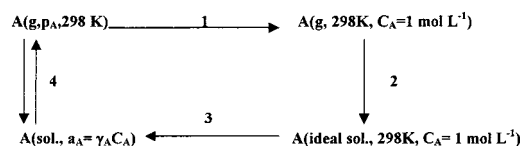
$$\Delta G_s^0(aq) = \Delta G_{ENP}(aq) + G_{CDS}(aq) \quad (7)$$

where  $\Delta G_{ENP}$  includes the change in the electronic and nuclear internal energy of the solute and the electric polarization free energy of the solute–solvent system upon insertion of the solute in the solvent, and  $G_{CDS}$  contains the free energy effects of the solvent cavitation, modified dispersion interactions, and structural rearrangement of the solvent that takes place in the first solvation shell. The standard state for both phases, gas and solution, is 1 mol L<sup>-1</sup>, and the temperature is taken as 298 K.

### STANDARD GIBBS FREE ENERGY OF SOLVATION AND HENRY'S LAW CONSTANT

The Henry's Law constant may be calculated from the Gibbs free energy of solvation considering the following

thermodynamic cycle:



For the cycle  $\Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 = 0$  where  $\Delta G_1$  is the change in the Gibbs free energy on going from gas at pressure  $p_A$  to gas at concentration  $1 \text{ mol L}^{-1}$ ;  $\Delta G_2$  is the Gibbs free energy of solvation;  $\Delta G_3$  is the free energy change on going from an ideal solution ( $1 \text{ mol L}^{-1}$ ) to a solution of activity  $a_A$ ; and  $\Delta G_4 = 0$  is condition of thermodynamic equilibrium.

The free energy changes for each step are given by the expressions

$$\Delta G_1 = RT \ln(RT/p_A) \quad (8)$$

$$\Delta G_2 = \Delta G_s^0 \quad (9)$$

$$\Delta G_3 = RT \ln(\gamma_A C_A) \quad (10)$$

where  $\gamma_A$  is the activity coefficient of the solute  $A$  in the molarity scale, and  $C_A$  is the concentration of the solute  $A$ , at the liquid solution, in equilibrium with  $A$  in the gas phase at partial pressure  $p_A$ .

After rearrangement

$$\ln H = \ln RT + \frac{\Delta G_s^0}{RT} \quad (11)$$

where  $H = p_A/\gamma_A C_A$  is the Henry's law constant.

## COMPUTATIONAL METHODS

Quantum chemical calculations in the gas phase were performed using AMPAC 5.0<sup>22</sup> with AM1 parametrization and in aqueous solution were carried out using AMSOL. The AMSOL models installed in AMPAC (SM1, SM2, SM2.1, SM3) calculate the free energies of solvation of molecules in aqueous solution. Solvation models SM1, SM2, and SM2.1 are based on the AM1 semiempirical model<sup>23</sup> for the solute electronic Hamiltonian, and the SM3 solvation model is based on the PM3 semiempirical model<sup>24</sup> for the solute electronic Hamiltonian. The molecular geometries were optimized at the respective levels of theory.

## RESULTS AND DISCUSSION

Gibbs free energy of solvation,  $\Delta G_s^0$ , was calculated using the SM2, SM2.1, and SM3 continuum solvent models. These values for the 12 chlorinated benzenes are summarized in Table 1. These results show that SM2 and SM2.1 methods give values which are comparables between them; however, SM3 underestimates  $\Delta G_s^0$  (more negative values) even in some case by a factor 5. The difference observed increases steadily with the degree of chlorination.

To explain this behavior it is necessary to analyze several contributions to the free energy of solvation. In the SMx models the solvation free energy is partitioned as follows

$$\Delta G_s^0 = \Delta E_{EN} + G_P + G_{CDS}^0$$

**Table 1.** Free Energy of Solvation ( $\Delta G_s^0$ ) in Water

no.	compound	$\Delta G_s^0$ (kJ/mol) SM2	$\Delta G_s^0$ (kJ/mol) SM2.1	$\Delta G_s^0$ (kJ/mol) SM3
1	chlorobenzene	-4.833	-5.088	-5.502
2	1,2-dichlorobenzene	-7.112	-7.209	-9.845
3	1,3-dichlorobenzene	-6.000	-5.996	-9.791
4	1,4-dichlorobenzene	-5.774	-5.782	-9.682
5	1,2,3-trichlorobenzene	-8.213	-8.092	-14.397
6	1,2,4-trichlorobenzene	-6.950	-6.753	-14.154
7	1,3,5-trichlorobenzene	-6.020	-5.674	-13.983
8	1,2,3,5-tetrachlorobenzene	-7.100	-6.640	-18.878
9	1,2,4,5-tetrachlorobenzene	-6.983	-6.586	-18.757
10	1,2,3,4-tetrachlorobenzene	-8.188	-7.845	-19.163
11	pentachlorobenzene	-7.364	-6.782	-24.213
12	hexachlorobenzene	-6.904	-6.197	-30.075

**Table 2.** Free Energy of Polarization ( $G_P$ ) and Free Energy of Cavitation + Dispersion + Solvent Structure Rearrangement ( $G_{CDS}^0$ )

no.	SM2		SM2.1		SM3	
	$G_{Pol.}$ (kJ/mol)	$G_{CDS}^0$ (kJ/mol)	$G_{Pol.}$ (kJ/mol)	$G_{CDS}^0$ (kJ/mol)	$G_{Pol.}$ (kJ/mol)	$G_{CDS}^0$ (kJ/mol)
1	-10.288	3.715	-11.109	4.054	-12.703	4.385
2	-12.025	2.134	-12.874	2.594	-16.259	2.439
3	-9.008	1.456	-9.707	1.962	-15.075	1.523
4	-8.280	1.452	-8.950	1.962	-14.686	1.523
5	-11.845	0.582	-12.585	1.163	-20.242	0.494
6	-8.301	-0.121	-8.899	0.506	-18.753	-0.423
7	-5.966	-0.795	-6.389	-0.121	-17.552	-1.343
8	-6.724	-1.665	-7.130	-0.920	-23.405	-2.364
9	-6.230	-1.699	-6.699	-0.949	-23.163	-2.364
10	-9.598	-0.962	-10.167	-0.268	-24.723	-1.448
11	-6.243	-2.506	-6.607	-1.690	-30.041	-3.389
12	-4.732	-3.305	-5.017	-2.427	-37.581	-4.406

where  $\Delta E_{EN}$  is the difference between the solute electronic kinetic and electronic-nuclear Coulombic energies in the gas and solution phases.  $G_P$  is the polarization free energy associated with the solvation process, and  $G_{CDS}^0$  contains cavitation, dispersion, and solvent structural reorganization effects.  $\Delta E_{EN}$  is always positive, and, therefore, this term does not account for the tendency observed. On the other hand, even though the values of  $G_{CDS}^0$  decrease with the degree of chlorination, going from positive (chlorobenzene) to negative values (hexachlorobenzene), their magnitudes are comparable in the three methods (Table 2), and, therefore, this term does not account for the differences observed in the  $\Delta G_s^0$  values calculated by the three methods.

Table 2 also shows that the polarization free energy  $G_P$ , calculated by the SM3 method, decreases as the degree of chlorination increases; therefore, it is evident that this term is the responsible for the underestimation of  $\Delta G_s^0$ .  $G_P$ , in turn, depends on the partial atomic charges according to the generalized Born equation

$$G_P = -\frac{1}{2} \left( 1 - \frac{1}{\epsilon} \right) \sum_{k,k'} q_k q_{k'} \gamma_{kk'}$$

where  $\gamma$  is a Coulomb integral, which is modeled by the dielectric screening algorithm of Still et al.,<sup>25</sup>  $\epsilon$  is the dielectric constant of the solvent at 298 K, and  $q_k$  is the atomic charge on atom  $k$ . Therefore, an analysis of the partial atomic charges is essential to understand the dependence of  $G_P$  on the degree of chlorination observed in the SM3 calculations.

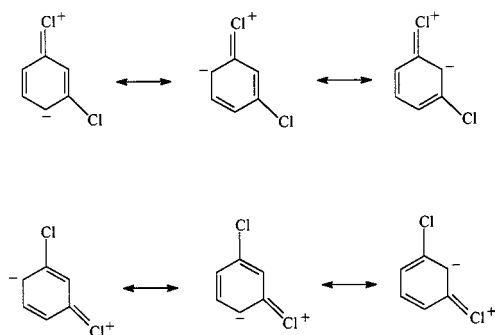


Figure 1. Resonance structures of 1,3-dichlorobenzene.

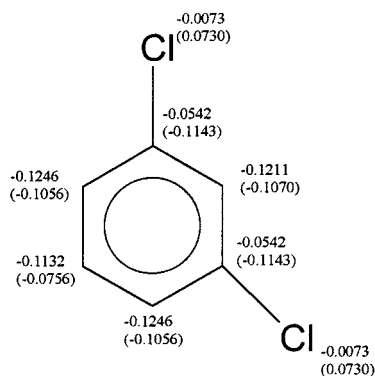


Figure 2. Partial atomic charges of 1,3-dichlorobenzene in gas phase. Figures in parenthesis refer to PM3 calculations; the other values refer to AM1 calculations.

**Inductive and Resonance Effects of Chlorine.** Classical physical organic chemistry<sup>26,27</sup> states that the substitution of a hydrogen atom by a chlorine atom in the benzene ring should lead to a decrease in the electron density or an increase of the positive character, on the carbon atom (ipso carbon) bonded to the chlorine atom. Thus, the chlorine atom is classified as electron-withdrawing group, i.e., it has an inductive effect (−I). This effect is expected to decrease with increasing distance.

On the other hand, by resonance effects the chlorine atom would be expected to increase the electron density in the ortho and para positions (resonance effect (+R)).

In a disubstituted molecule, like 1,3-dichlorobenzene, it is expected an increase in the positive charge of the ipso carbons caused by the inductive effects (−I) of the chlorine atoms. On the other hand, from a resonance point of view, it is expected an increase of electron density on carbons C2, C4, and C5 due to the character (+R) of the chlorine atoms, Figure 1.

**AM1 and PM3 Partial Atomic Charges.** To isolate from the solvation effects and more transparently analyze the performance of AM1 and PM3 methods, the partial atomic charges in gas phase were calculated. As example, the results for 1,3-dichlorobenzene are shown in Figure 2; figures in parentheses refer to PM3 partial atomic charges.

**AM1 Partial Atomic Charges.** For 1,3-dichlorobenzene, it is observed a decrease in the electron density of the ipso carbons, due to the inductive effect (−I) of chlorine. As well, an increase of the electron density on carbons C2, C4, and C5 is observed, as expected by resonance considerations. The negative partial charge on the chlorine atoms suggest that the inductive effect (−I) is dominant over the resonance effects (+R).

Table 3. Calculated and Experimental Henry's Law Constants

no.	<i>H</i> (Pa m <sup>3</sup> mol <sup>−1</sup> )			
	SM2	SM2.1	SM3	exptl <sup>a</sup>
1	352	318	269	383, 314, 398, 365, 367
2	140	135	47	193, 197, 159, 244
3	220	220	48	266, 289
4	241	240	50	240, 276, 321, 244
5	90	95	7	127
6	150	162	8	144, 195
7	218	251	9	
8	141	170	1	159, 160
9	148	174	1	
10	91	104	1	
11	127	160	0	
12	153	203	0	172

<sup>a</sup> Values compiled by Shiu et al.<sup>29</sup> and references therein.

**PM3 Partial Atomic Charges.** Partial atomic charges obtained from PM3 calculations indicate an increase in the electron density on the ipso carbons respect to C2, C4, and C5. In addition, the partial atomic charge on the chlorine atoms are positive. This results could be explained assuming a donate electron character for the chlorine atoms, i.e., an inductive effect (+I). This assumption is in opposition to what one could expect from the well-known chemistry of chlorine.<sup>28</sup>

Therefore, PM3 calculations give an inadequate picture of electron density in chlorinated benzenes. This deficient performance is enhanced in solution, leading to large errors in the free energy of polarization, and consequently in the free energy of solvation calculated by this method. Thus, this should be seen reflected in a property strongly dependent on the free energy of solvation as the Henry's law constant.

**Henry's Law Constant.** Before to discuss the performance of the semiempirical methods to calculate Henry's law constant, it is important to stress the great dispersion in the reported experimental values as it is evident from the data compiled by Shiu et al.,<sup>29</sup> therefore, any comparison between the calculated and experimental values and the conclusions derived from it should be taken with caution. On the other hand, the values recommended by Shiu are based on the direct ratio of vapor pressure and aqueous solubility. This assumption may be not always correct, as it may be concluded when these recommended values are compared with experimental values of *H* measured directly, for example, with the results reported by Bamford et al.<sup>30</sup> for PCBs measured directly using a gas-stripping technique.

The calculated Henry's law constants for the 12 chlorinated benzenes, eq 11, along with experimental values reported elsewhere are shown in Table 3. The values obtained by the SM3 method are underestimated compared with the experimental values and those calculated by SM2 and SM2.1 methods. This underestimation is larger as the degree of chlorination of the benzenes increases. This bad performance of SM3 to calculate Henry's law constant is attributable to the PM3 Hamiltonian, due to its incapacity to give a good description of electron density in chlorinated benzenes.

SM2 and SM2.1 results are in good agreement with the experimental values, having in mind the great dispersion of the reported values. To support this affirmation we have calculated the uncertainty in the mean value in those cases in which the number of values reported allows this statistical



analysis, namely, chlorobenzene and 1,2- and 1,4-dichlorobenzene. Thus, the 95% confidence limit of error using the student *t*-distribution was calculated. The results are as follows:  $366 \pm 39$ ,  $198 \pm 56$ ,  $270 \pm 60$ , for chlorobenzene and 1,2- and 1,4-dichlorobenzene, respectively. This allows for the confirmation that the Henry's law constant calculated by SM2 is within the confidence limit of error of the experimental mean. Therefore, the continuum solvation model SM2 can be used to predict Henry's law constant of chlorinated benzenes with a degree of confidence comparable to experimental determinations. However, the extensions of this procedure to other environmental important chemicals are currently being checked, and the results will be reported in future publications.

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