Fluid Phase Equilibria 281 (2009) 144–162

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Correlation and prediction of solute transfer to chloroalkanes from both water and the gas phase

Laura M. Sprunger[a], Sai S. Achi[a], William E. Acree Jr.[a,*], Michael H. Abraham[b], Albert J. Leo[c], David Hoekman[d]

[a] *Department of Chemistry, 1155 Union Circle Drive #305070, University of North Texas, Denton, TX 76203-5017, USA*
[b] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK*
[c] *BioByte Corp., 201W. Fourth St., Claremont, CA 91711, USA*
[d] *David Hoekman Consulting, Inc., 107 NW 82nd, Seattle, WA 97117, USA*

ARTICLE INFO

Article history:
Received 29 March 2009
Received in revised form 15 April 2009
Accepted 16 April 2009
Available online 24 April 2009

Keywords:
Carbon tetrachloride
Chloroform
Dichloromethane
1-Chlorobutane
Partition coefficients
Molecular solute descriptors

ABSTRACT

Data have been compiled from the published literature on the partition coefficients of solutes and vapors into chloroform, carbon tetrachloride, dichloromethane and 1-chlorobutane from both water and from the gas phase. The logarithms of the water-to-chloroalkane ($\log P$) and gas-to-chloroalkane partition coefficients ($\log K$) are correlated with the Abraham solvation parameter model. The derived correlations describe the observed $\log P$ and $\log K$ values within standard deviations of about 0.13–0.20 log units. For chloroform and carbon tetrachloride, the derived correlations were validated using training set and test set analyses.

1. Introduction

Solvent extraction provides a convenient means for separating and concentrating solutes from mixtures prior to chemical analysis. The method is based on the equilibrium distribution of the analyte(s) and unwanted impurities/interferences between the extraction solvent and sample that is to be analyzed. Large partition coefficients, P, defined as the ratio of the solute's molar concentration in the extraction solvent to that in the analytical sample:

$$P = \frac{\text{molar concentration of solute in extraction solvent}}{\text{molar concentration of solute in analyticalsample}} \quad (1)$$

favor solute transfer to the extraction solvent, whereas small partition coefficients would keep any unwanted impurities/interferences in the sample solution. Many of the biological and environmental samples involve aqueous solutions. The choice of organic solvent in water-to-solvent extractions is of ongoing importance.

The general solvation method of Abraham [1,2] is one of the more useful approaches for the analysis and prediction of free energies of partition in chemical and biological systems. The method relies on two linear free energy relationships (lfers), one for processes within condensed phases:

$$\mathrm{SP} = c + e\cdot\mathbf{E} + s\cdot\mathbf{S} + a\cdot\mathbf{A} + b\cdot\mathbf{B} + v\cdot\mathbf{V} \quad (2)$$

and one for processes involving gas-to-condensed phase transfer:

$$\mathrm{SP} = c + e\cdot\mathbf{E} + s\cdot\mathbf{S} + a\cdot\mathbf{A} + b\cdot\mathbf{B} + l\cdot\mathbf{L} \quad (3)$$

The dependent variable, SP, is some property of a series of solutes in a fixed phase, which in the present study will be the logarithm of solute partition coefficient between two immiscible (or partly miscible) phases. The independent variables, or descriptors, are solute properties as follows: **E** and **S** refer to the excess molar refraction and dipolarity/polarizability descriptors of the solute, respectively, **A** and **B** are measures of the solute hydrogen-bond acidity and basicity, **V** is the McGowan volume of the solute and **L** is the logarithm of the solute gas phase dimensionless Ostwald partition coefficient into hexadecane at 298 K. The first four descriptors can be regarded as measures of the tendency of the given solute to undergo various solute–solvent interactions. The latter two descriptors, **V** and **L**, are both measures of solute size, and so will be measures of the solvent cavity term that will accommodate the dissolved solute. General dispersion interactions are also related to solute size, hence, both **V** and **L** will also describe the general solute–solvent interactions.

---

* Corresponding author. Tel.: +1 940 565 3543; fax: +1 940 565 4318.
E-mail address: acree@unt.edu (W.E. Acree Jr.).

0378-3812/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.fluid.2009.04.012

The regression coefficients and constants (c, e, s, a, b, v, and l) are obtained by regression analysis of experimental data for a specific process (*i.e.*, a given partitioning process, a given stationary phase and mobile phase combination, *etc.*). In the case of partition coefficients, where two solvent phases are involved, the c, e, s, a, b, v, and l coefficients represent differences in solvent phase properties. For any fully characterized system/process (those with calculated values for the equation coefficients) further values of SP can be estimated for solutes with known values for the solute descriptors. This is the major advantage in using Eqs. (2) and (3) to correlate solute properties having environmental, pharmaceutical and chemical importance.

At present we are developing/updating correlations for additional/existing systems [3–13], and are developing new computation methodologies for calculating solute descriptors from available experimental data and/or structural information [2,14–18]. To date we have published Abraham model correlations for describing both the water-to-organic solvent partition coefficient (see Eq. (1)) and the gas-to-solvent partition coefficient, K:

$$K = \frac{\text{molar concentration of solute in extraction solvent}}{\text{molar concentration of solute in the gas phase}} \qquad (4)$$

where K is the dimensionless gas-to-water partition coefficient (with concentrations in each phased defined in terms of mol dm^{-3}) for more than 50 different common organic solvents. For several solvents, the published correlations include both the "practical" $\log P$ correlation where the solute is distributed between the equilibrium organic phase saturated with water and the aqueous phase that has been saturated with the organic solvent, as well as the "hypothetical" $\log P$ correlation that is calculated as the molar solubility ratio of the solute in the anhydrous organic solvent divided by the solute's molar solubility in water. Even though hypothetical, these latter $\log P$ correlations are still quite useful in that calculated $\log P$ values can be used to predict the solute's infinite dilution activity coefficient or molar solubility in the anhydrous (dry) solvent for those solutes for which the solute descriptors are known.

The aim of the present work is to collect experimental data from the published literature on the partition coefficients from water and from air into chloroform, carbon tetrachloride, dichloromethane and 1-chlorobutane, and to derive $\log P$ and $\log K$ correlations. Abraham model correlations have been previously reported for several of the solvents based on much smaller databases. Abraham et al. [19] published correlations for water-to-chloroform:

$$\log P_{\text{chl}} = 0.327 + 0.157\mathbf{E} - 0.391\mathbf{S} - 3.191\mathbf{A} - 3.437\mathbf{B} + 4.191\mathbf{V}$$
$$(N = 335,\ \text{SD} = 0.25,\ R^2 = 0.971,\ F = 2223) \qquad (5)$$

and for gas-to-chloroform partition coefficients:

$$\log K_{\text{chl}} = 0.168 - 0.595\mathbf{E} + 1.256\mathbf{S} + 0.280\mathbf{A} + 1.370\mathbf{B} + 0.981\mathbf{L}$$
$$(N = 150,\ \text{SD} = 0.23,\ R^2 = 0.985,\ F = 1919) \qquad (6)$$

where N is the number of data points, SD denotes the standard deviation, R^2 gives the squared correlation coefficient and F corresponds to the Fisher's F statistic. The present study differs from that of Abraham et al. in that we are using much larger databases (394 $\log P$ values and 384 $\log K$ values), and are using revised, updated values for the solute descriptors for several compounds. At the time that Eqs. (5) and (6) were developed solute descriptors were calculated by regressing experimental water-to-organic solvent and gas-to-organic solvent partition coefficient data. We are now using our gas-to-water $\log K_{\text{w}}$ correlations to increase the number of equations used in the solute descriptor computations, and have updated numerical values of the solute descriptors of those compounds that have not been used by us since the earlier study was published. We have also reported the water-to-dichloromethane partition coefficient based on only 34 experimental $\log P$ values [20]:

$$\log P_{\text{dcm}} = 0.314 + 0.001\mathbf{E} + 0.022\mathbf{S} - 3.238\mathbf{A} - 4.137\mathbf{B} + 4.259\mathbf{V}$$
$$(N = 38,\ \text{SD} = 0.141,\ R^2 = 0.991,\ F = 680) \qquad (7)$$

the gas-to-carbon tetrachloride partition coefficient correlation based on 89 experimental $\log K$ values [21]:

$$\log K_{\text{ct}} = 0.23 - 0.20\mathbf{E} + 0.35\mathbf{S} + 0.07\mathbf{A} + 0.27\mathbf{B} + 1.041\mathbf{L}$$
$$(N = 89,\ \text{SD} = 0.069,\ R^2 = 0.999,\ F = 11,877) \qquad (8)$$

and have tabulated revised equation coefficients for $\log P$ and $\log K$ correlations for chloroform, carbon tetrachloride and dichloromethane in several of our published solubility studies [22–24]. The solubility studies did not provide any statistical information concerning the partition coefficient correlations, nor have we published the experimental $\log P$ and $\log K$ databases used in deriving our most recent chloroform, carbon tetrachloride and dichloromethane partition coefficient correlations. The present study updates the Abraham model $\log P$ and $\log K$ correlations that we have obtained for chlorinated alkanes. The updated $\log P$ and $\log K$ correlations for 1,2-dichloroethane were recently reported elsewhere [11].

2. Data sets and computation methodology

Most of the experimental data that we were able to retrieve from the published literature [17,25–123] pertained either to the $\log P$ values for "practical" partition between chloroalkane-saturated water and water-saturated chloroalkanes, or to the Raoult's law infinite dilution activity coefficient, $\gamma^{\infty}_{\text{solute}}$, or Henry's law constants, K_{Henry}, for solutes dissolved in the four chloroalkane solvents. In order to apply the Abraham model the infinite dilution activity coefficients and Henry's law constants needed to be converted to $\log K$ values through Eqs. (9) and (10):

$$\log K = \log\left(\frac{RT}{\gamma^{\infty}_{\text{solute}} P^{0}_{\text{solute}} V_{\text{solvent}}}\right) \qquad (9)$$

$$\log K = \log\left(\frac{RT}{K_{\text{Henry}} V_{\text{solvent}}}\right) \qquad (10)$$

or $\log P$ values for partition from water to the anhydrous chloroalkane through Eq. (11):

$$\log P = \log K - \log K_{\text{w}} \qquad (11)$$

In Eqs. (9)–(11) R is the universal gas constant, T is the system temperature, P^{0}_{solute} is the vapor pressure of the solute at T, and V_{solvent} is the molar volume of the solvent. The calculation of $\log P$ requires knowledge of the solute's gas phase partition coefficient into water, K_{w}, which is available for most of the solutes being studied. Eq. (11) was also used to convert the practical $\log P$ to $\log K$(wet) values for solute transfer into each of the four chloroalkane solvent saturated with water. The experimental $\log K$ and $\log P$ values at 298.15 for chloroform, carbon tetrachloride, dichloromethane and 1-chlorobutane are listed in Tables 1–4. We have separated the "wet" and "dry" partition coefficient data for chloroform and carbon tetrachloride as we need to be sure that the solubilizing properties of the anhydrous chloroalkane solvent and water-saturated chloroalkane solvent are the same before combining values into a single data set. For chloroform and carbon tetrachloride there were sufficient experimental $\log P$ and $\log K$ values to treat the "wet" and "dry" experimental values separately.

Our experimental databases also contain measured solubility data for several crystalline solutes dissolved in both the anhydrous chloroalkanes and in water. The solubility data were taken largely from our previously published solubility studies. At the time that