

Characterization of the sorption of gaseous and organic solutes onto polydimethyl siloxane solid-phase microextraction surfaces using the Abraham model

Laura Sprunger^a, Amy Proctor^a, William E. Acree Jr.^{a,*}, Michael H. Abraham^b

^a Department of Chemistry, P.O. Box 305070, University of North Texas, Denton, TX 76203-5070, USA

^b Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

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Abstract

Water-to-polydimethylsiloxane (PDMS) and gas-to-PDMS sorption coefficients have been compiled for 170 gaseous and organic solutes. Both sets of sorption coefficients were analyzed using the Abraham solvation parameter model. Correlations were obtained for both “dry” headspace solid-phase microextraction and conventional “wet” PDMS coated surfaces. The derived equations correlated the experimental water-to-PDMS and gas-to-PDMS data to better than 0.17 and 0.18 log units, respectively. In the case of the gas-to-PDMS sorption coefficients, the experimental values spanned a range of approximately 11 log units.

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1. Introduction

Solid-phase microextraction (SPME) is a versatile analytical technique developed by Pawliszyn and coworkers [1,2] that combines sampling and sample preparation into a single step. The analytical technique provides a fast, sensitive, and economical method of sample preparation for a wide range of environmental and manufacturing processes prior to gas chromatographic analyses. The type of fiber, sample volume, extraction and desorption times and temperature affect the pre-concentration efficiency of SPME. Published studies have compared the performance of different SPME fibers for extraction of various chemicals from aqueous solutions. For example, Luks-Bettej et al. [3] compared 7- μ l polydimethylsiloxane (PDMS), 100- μ l PDMS, polyacrylate, carboxen-divinylbenzene, and polydimethylsiloxane-carboxen-divinylbenzene for extracting phthalate esters from aqueous samples. The authors found the two fibers containing divinylbenzene gave the best reproducibility for the samples studied. SPME, while initially developed for gas chromatography,

was later interfaced with liquid chromatography. SPME-LC has become a popular analytical method for semi-volatile, nonvolatile or thermally unstable compounds, such as pharmaceutical drug products, polycyclic aromatic hydrocarbons (PAHs), pesticides and herbicides, proteins and peptides.

Liquid-to-fiber and gas-to-fiber sorption coefficients play an important role in determining the time needed for the extraction and desorption steps. The solvation parameter model of Abraham [4–11] is one of the most useful approaches for the analysis and prediction of partition and sorption coefficients. The basic model relies on two linear free energy relationships, one for solute transfer between two condensed phases:

$$SP = c + e \cdot E + s \cdot S + a \cdot A + b \cdot B + v \cdot V \quad (1)$$

and one for processes involving gas to condensed phase transfer

$$SP = c + e \cdot E + s \cdot S + a \cdot A + b \cdot B + l \cdot L \quad (2)$$

The dependent variable, SP, is some property of a series of solutes in a fixed phase. For SPME applications, the dependent variable would be the logarithm of the solute's water-to-fiber sorption coefficient, $\log K_{\text{PDMS-water}}$ (for Eq. (1)), and the logarithm of the solute's gas-to-fiber sorption coefficient, $\log K_{\text{PDMS-gas}}$ (for Eq. (2)). The independent variables are solute

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

properties as discussed before [4,5]. **E** is the solute excess molar refractivity in units of $(\text{cm}^3 \text{mol}^{-1})/10$; **S** is the solute's dipolarity/polarity descriptor; **A** and **B** are measures of the solute hydrogen-bond acidity and hydrogen-bond basicity, respectively; **V** is the McGowan volume of the solute in units of $(\text{cm}^3 \text{mol}^{-1})/100$; and **L** is the logarithm of the solute gas phase dimensionless Ostwald partition coefficient into hexadecane at 298 K.

The usefulness of Eqs. (1) and (2) is that the terms encode valuable information concerning solute–solvent interactions. The excess molar refraction, **E**, is derived from the solute refractive index, and hence the e-coefficient provides a measure of the general solvent dispersion interactions. The **S** descriptor is a measure of dipolarity and polarizability. The s-coefficient will reflect the ability of the solvent phase to undergo dipole–dipole and dipole-induced interactions with a solute. The **V** and **L** solute descriptors were set up as measures of the endoergic effect of disrupting solvent–solvent interactions. However, solute volume (or size) is always well correlated with polarizability, and so the v- and l-coefficients will include not only an endoergic cavity effect but also exoergic solute–solvent effects that arise through solute polarizability. The **A** descriptor is a measure of solute hydrogen bond acidity, and hence the a-coefficient will reflect the complementary solvent hydrogen bond basicity. Similarly, the b-coefficient will be a measure of the solvent phase hydrogen bond acidity. All this is straightforward for gas-to-condensed phase partitions because there are no interactions to consider in the gas phase. For partitions between two condensed phases, the coefficients in Eq. (1) then refer to differences between the properties of the two phases.

In the present study we have gathered from the published literature water-to-polydimethylsiloxane (PDMS) and gas-to-PDMS sorption coefficients for 169 gaseous and organic solutes. We correlate the measured $\log K_{\text{PDMS-water}}$ and $\log K_{\text{PDMS-gas}}$ values with the Abraham solvation parameter model. Xia et al. [12] recently reported an Abraham model correlation for absorption from aqueous solution onto a PDMS membrane:

$$\begin{aligned} \log K_{\text{PDMS-water}} = & 0.09(0.16) + 0.49(0.11)\mathbf{E} - 1.11(0.12)\mathbf{S} \\ & - 2.36(0.07)\mathbf{A} - 3.78(0.14)\mathbf{B} \\ & + 3.50(0.17)\mathbf{V} \quad (N = 32, \\ & R^2 = 0.995 \text{ and } F = 1056) \end{aligned} \quad (3)$$

based on measured absorption data for 32 compounds. Here and elsewhere N denotes the number of experimental data points, R refers to the correlation coefficient, and F corresponds to the Fisher F -statistic. The authors did not give the standard deviation as part of their reported statistical information. The 32 compounds used in developing Eq. (3) included 29 benzene derivatives plus naphthalene, 1-methylnaphthalene and biphenyl. Given the limited chemical diversity of the compounds studied, combined with the lack of a training set and test set validation analyses, it is difficult to assess the predictive ability of Eq. (3) for nonaromatic solutes.

Hierleman et al. [13] examined the performance of the Abraham linear free energy relationship to describe the sorption

coefficients of organic vapors on thickness-shear-mode resonators coated with different polymers. The derived correlation for the polydimethylsiloxane coated resonators:

$$\begin{aligned} \log K_{\text{PDMS-gas}} = & 0.18(0.13) - 0.05(0.18)\mathbf{E} + 0.21(0.20)\mathbf{S} \\ & + 0.99(0.23)\mathbf{A} + 0.10(0.23)\mathbf{B} \\ & + 0.84(0.03)\mathbf{L} \quad (N = 32 \quad R^2 = 0.969, \\ & \text{SE} = 0.127 \text{ and } F = 155) \end{aligned} \quad (4)$$

had a very small standard error of $\text{SE} = 0.127$ log units. The data set used in deriving the correlation contained only 32 organic compounds that covered a range of sorption coefficients from $\log K_{\text{PDMS-gas}} = 1.65$ to $\log K_{\text{PDMS-gas}} = 4.03$. Poole and coworkers have used the Abraham model to describe the break through volumes and sorption behavior of organic compounds on octadecylsiloxane-bonded silica particle-embedded glass fiber discs and membranes [14–16] and spacer-bonded propanediol sorbents [17] used for solid-phase extractions.

Our investigation differs from the published studies of both Xia et al. [12] and Hierleman et al. [13] in that we use a considerably larger database ($\log K_{\text{PDMS-water}}$ values for 168 compounds and $\log K_{\text{PDMS-gas}}$ values for 142 compounds) that span a much wider range of experimental sorption coefficients. Moreover, we have divided our databases into “wet” and “dry” experimental values, depending on whether the polydimethylsiloxane coating was in direct contact with water (“wet”) or in contact with air (“dry”), as would be the case for sorption of vapors onto dry PDMS. Separate Abraham correlations were obtained for sets of experimental conditions, and for the pooled set of “wet” plus “dry” sorption coefficients. The predictive ability of each derived correlation was assessed by dividing the databases into a separate training and test set. None of the prior studies performed a training set and test set analysis.

2. 2. Data sets and computational methodology

A search of the published literature [12,13,18–47] yielded experimental data for 107 organic solutes sorbed directly onto polydimethylsiloxane from aqueous solution, and experimental values for 64 gaseous solutes absorbed onto a dry PDMS coated fiber at our near 298.15 K. A few of the compounds have been studied by more than one research group. In deciding which of the independent values to include in the database for regression analysis we tried to minimize inter-laboratory differences in experimental methodologies and PDMS samples by selecting data from as small of a number of research groups as possible. Experimental data that were part of a large, multi-compound study were selected in preference to reported values that were part of only a two or three compound study. Independent replicate measurements often differed by less than 0.2 log units. The experimental values are denoted as $\log K_{\text{PDMS-water}}$ and $\log K_{\text{PDMS-gas}}$, respectively.

The water-to-PDMS sorption coefficient, $P_{\text{PDMS-water}}$, can be converted into a “calculated” experimental gas-to-PDMS sorp-

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