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*] and 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)

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.

KEY WORDS: Sorption coefficients, polydimethylsiloxane, linear free energy relationship, solid-phase microextraction

---

*To whom correspondence should be addressed. (E-mail: acree@unt.edu)

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-Betlej et al. [3] compared 7-µl polydimethylsiloxane (PDMS), 100-µl 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

$$SP = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + v \cdot \mathbf{V} \tag{1}$$

and one for processes involving gas to condensed phase transfer

2

$$SP = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + l \cdot \mathbf{L} \tag{2}$$

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 $K_{PDMS\text{-}water}$ (for Eq. 1), and the logarithm of the solute's gas-to-fiber sorption coefficient, log $K_{PDMS\text{-}gas}$ (for Eq. 2). The independent variables are solute properties as discussed before [4,5]. $\mathbf{E}$ is the solute excess molar refractivity in units of $(cm^3 \; mol^{-1})/10$; $\mathbf{S}$ is the solute's dipolarity/polarity descriptor; $\mathbf{A}$ and $\mathbf{B}$ are measures of the solute hydrogen-bond acidity and hydrogen-bond basicity, respectively; $\mathbf{V}$ is the McGowan volume of the solute in units of $(cm^3 \; mol^{-1})/100$; and $\mathbf{L}$ 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, $\mathbf{E}$, is derived from the solute refractive index, and hence the e-coefficient provides a measure of the general solvent dispersion interactions. The $\mathbf{S}$ 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 $\mathbf{V}$ and $\mathbf{L}$ 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 $\mathbf{A}$ 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 $K_{PDMS-water}$ and log $K_{PDMS-gas}$ values with the Abraham solvation parameter model. Xia $et\ al$. [12] recently reports an Abraham model correlation for absorption from aqueous solution onto a PDMS membrane

Log $K_{PDMS-water}$ = 0.09(0.16) + 0.49(0.11) **E** − 1.11(0.12) **S** − 2.36(0.07) **A** − 3.78(0.14) **B** +

　　　3.50(0.17) **V**　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　(3)

　　　(N = 32, R^2 = 0.995 and F = 1056)

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 nonaraomtic solutes.

Hierlemann $et\ al$. [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

Log $K_{PDMS-gas}$ = 0.18(0.13) - 0.05(0.18) **E** + 0.21(0.20) **S** + 0.99(0.23) **A** + 0.10(0.23) **B** +

    0.84(0.03) **L**   (4)

    (N = 32, R^2 = 0.969, SE = 0.127 and F = 155)

had a very small standard error of 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 $K_{PDMS-gas}$ = 1.65 to log $K_{PDMS-gas}$ = 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

Hierlemann *et al*. [13] in that we use a considerably larger database (log $K_{PDMS-water}$ values for

168 compounds and log $K_{PDMS-gas}$ 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. 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 $K_{PDMS-water}$ and log $K_{PDMS-gas}$, respectively.

The water-to-PDMS sorption coefficient, $P_{PDMS-water}$, can be converted into a "calculated" experimental gas-to-PDMS sorption coefficient, $K_{PDMS-gas}$, through Eq. 5

$$\text{Log } K_{PDMS-gas} = \log K_{PDMS-water} - \log K_w \qquad (5)$$

and vice versa. In Eq. 5 K_w is the solute's gas phase partition coefficient into water. Large tabulations of K_w data are available in the published literature [48-50] for doing this conversion. In doing the conversions the values of K_w that we used pertain to 298.15 K. Gas-to-PDMS and water-to-PDMS sorption coefficients obtained using Eq. 5 represent "calculated" experimental values in that the PDMS coating was not in physical contact with water for the log $K_{PDMS-water}$ computation, and in the case of the log $K_{PDMS-gas}$ computation the PDMS coating was "wet" with absorbed water molecules. The presence/absence of water molecules may affect the sorption properties of the condensed PDMS phases. The retrieved log $K_{PDMS-water}$ and log $K_{PDMS-gas}$ experimental values are tabulated in Tables 1 and 2, along with their respective literature

references and the "calculated" experimental values based on Eq. 5. The "wet" versus "dry" entries in the next to last columns of Tables 1 and 2 indicates whether the PDMS surface was equilibrated in an aqueous solution or in dry air. The compounds listed in Tables 1 and 2 include both nonpolar and polar molecules, which cover an extremely wide range of hydrophobicities as reflected in the experimental water-to-octanol partition coefficient (log $K_{OTOH-water}$ = -0.74 for methanol [51] to log $K_{OTOH-water}$ > 7 for several of the polycyclic aromatic hydrocarbons and polychlorinated biphenyls [52]).

Molecular descriptors for all of the compounds considered in the present work are also tabulated in Tables 1 and 2. The numerical values came from our inhouse solute descriptor base, which now contains values for more than 4000 different organic and organic metallic compounds. The descriptors were obtained exactly as described before [4,5, 53-55], using various types of experimental data, including water-to-solvent partitions, gas-to-solvent partitions, solubility, and chromatographic data. Solute descriptors used in the present study are all based on experimental data. There is also commercial software [56] and several published estimation schemes [57-60] for calculating the numerical values of solute descriptors from molecular structural information if one is unable to find the necessary partition, solubility, and/or chromatographic data.

3. RESULTS AND DISCUSSION

The 107 experimental "wet" log $K_{PDMS-water}$ values and 61 "calculated" experimental "dry" log $K_{PDMS-water}$ values given in Table 1 were analyzed separately

$$\text{Log } K_{PDMS-water}(\text{wet}) = 0.246(0.072) + 0.568(0.053)\ \mathbf{E} - 1.305(0.088)\ \mathbf{S} - 2.565(0.106)\ \mathbf{A}$$

$$- 3.928(0.119)\ \mathbf{B} + 3.573(0.059)\ \mathbf{V} \tag{6}$$

$$(N = 107, R^2 = 0.993, R_{adj}^2 = 0.992, SD = 0.164, F = 2758.1)$$

and

$$Log \ K_{PDMS-water}(dry) = 0.130(0.045) + 0.341(0.113) \ \mathbf{E} - 1.321(0.149) \ \mathbf{S} - 2.410(0.208) \ \mathbf{A}$$

$$- 4.586(0.179) \ \mathbf{B} + 4.040(0.070) \ \mathbf{V} \qquad (7)$$

$$(N = 61, R^2 = 0.991, R_{adj}^2 = 0.990, SD = 0.134, F = 1186.7)$$

to determine whether absorbed water molecules affect the sorption properties of the PDMS

coating. All regression analyses were performed using SPSS statistical software. The statistics

of both derived correlations are quite good as evidenced by the near unity values of the

correlation coefficients and by the small standard deviations of $SD = 0.164$ and $SD = 0.134$ log

units. Figure 1 compares the calculated values of log $K_{PDMS-water}$ (wet) based on Eq. 6 against the

observed values which span a range of about 7.8 log units.

The equation coefficients of Eq. 6 are in fairly good agreement with the values reported

by Xia *et al*. [12], see Eq. 3, from sorption measurements of 29 benzene derivatives plus

naphthalene, 1-methylnaphthalene and biphenyl onto a PDMS membrane directly from aqueous

solution. Equation coefficients for the dry PDMS surface do differ from those of wet PDMS,

most noticeably in the numerical values of the b- and v-coefficients. The smaller b-value for the

PDMS phase in direct contact with water indicates that the wet surface has more acidic character

than the dry PDMS. Absorbed water molecules should increase PDMS phase acidity due to the

acidic protons on each absorbed water molecule, and the equation coefficients are in accord with

these expectations. Differences in the solubilizing properties/characteristics of "wet" versus

"dry" solvents have been noted previously for diethyl ether [52], dibutyl ether [52,61] and

alcohols [62]. Wet diethyl ether was found to be slightly less dipolar/polarizable, slightly more

basic, slightly more acidic, and slightly less hydrophobic than dry diethyl ether. The effect of the

8

small amount of water in wet dibutyl ether was much larger than the effect of the large amount of water in wet diethyl ether, suggesting that the water in dibutyl ether acts more as complexing agent forming specific hydrogen-bonding complexes with solutes than as a cosolvent. At the present time it is not known whether the large change in the b-coefficient is due to the solubilized/absorbed water acting as a complexing agent or due to cosolvency.

The equation coefficients are sufficiently close so that one can obtain a reasonably good Abraham model correlation

Log $K_{PDMS\text{-}water}$(wet+dry) = 0.268(0.038) + 0.601(0.043) **E** – 1.416(0.073) **S** – 2.523(0.092) **A** – 4.107(0.084) **B** + 3.637(0.044) **V**   (8)

(N = 170, R^2 = 0.993, R_{adj}^2 = 0.993, SD = 0.171, F = 4475.2)

by combining all 170 experimental data points into a single regression analysis. The increased number of total points is due to the fact that we had both a "wet" and "dry" log $K_{PDMS\text{-}water}$ value for trichloromethane (log $K_{PDMS\text{-}water}$(wet) = 1.71 [37] and log $K_{PDMS\text{-}water}$(dry) = 1.62 [35]) and trichloroethylene (log $K_{PDMS\text{-}water}$(wet) = 2.41 [38] and log $K_{PDMS\text{-}water}$(dry) = 2.24 [21]). Figure 2 compares the calculated values of log $K_{PDMS\text{-}water}$ based on Eq. 8 against the observed values which span a range of about 8.9 log units. For predictive applications we recommend that one use Eqs. 6 and 7 to estimate log $K_{PDMS\text{-}water}$ values for additional solutes whose solute descriptors fall within the range of values used in deriving the separate log $K_{PDMS\text{-}water}$(wet) and log $K_{PDMS\text{-}water}$(dry) correlations. There were no gaseous solutes in the "wet" $K_{PDMS\text{-}water}$ database, and no large polycyclic aromatic hydrocarbons (PAHs) nor polychlorinated biphenyls (PCBs) in the "dry" $K_{PDMS\text{-}water}$ database. The database used in deriving Eq. 8 contained solutes spanning the wider range of solute descriptors. We provide Eq. 8 as a predictive expression for estimating

what the sorption coefficient would be for the transfer of PAHs and PCBs from water-to-dry PDMS surface.

In order to assess the predictive abilities of Eq. 6 and 7 we divided the "wet" and "dry" databases into training sets and test sets by allowing the SPSS software to randomly select half of the experimental values in the respective log $K_{PDMS-water}$ databases. The two sets of selected data points became the training sets and the compounds that were left served as the test sets. Analysis of the experimental data in the training sets gave

$$\text{Log } K_{PDMS-water}(\text{wet}) = 0.270(0.106) + 0.522(0.085) \textbf{ E} - 1.226(0.140) \textbf{ S} - 2.584(0.158) \textbf{ A}$$

$$- 4.057(0.209) \textbf{ B} + 3.561(0.084) \textbf{ V} \tag{9}$$

$$(N = 54, R^2 = 0.991, R_{adj}^2 = 0.991, SD = 0.172, F = 1115.0)$$

and

$$\text{Log } K_{PDMS-water}(\text{dry}) = 0.076(0.066) + 0.206(0.126) \textbf{ E} - 1.077(0.205) \textbf{ S} - 2.396(0.267) \textbf{ A}$$

$$- 4.713(0.248) \textbf{ B} + 4.126(0.103) \textbf{ V} \tag{10}$$

$$(N = 31, R^2 = 0.995, R_{adj}^2 = 0.994, SD = 0.110, F = 937.9)$$

The training set correlations were then used to predict log $K_{PDMS-water}$(wet) values of the 53 compounds in the "wet" test set and log $K_{PDMS-water}$(dry) values of the 30 compounds in the "dry" test set. For the predicted and experimental we found SD = 0.162 and SD = 0.167, AAE (average absolute error) = 0.125 and AAE = 0.139, and AE (average error) = 0.001 and AE = -0.054, for Eqs. 9 and 10, respectively. There is therefore very little bias in the predictions using Eqs. 9 and 10 with AE equal to 0.001 (Eq. 9) and -0.054 (Eq. 10).

Table 2 contains 64 experimental "dry" gas-to-PDMS sorption coefficients, and 76 "calculated" experimental "wet" log $K_{PDMS-gas}$ values. The next to last column in Table 2

indicates whether the PDMS surface was equilibrated in air or exposed to an aqueous solution. In the latter case the measured water-to-PDMS sorption coefficient was converted to log $K_{PDMS\text{-}gas}$(wet) using Eq. 5 and available log K_w data. The two sets of log $K_{PDMS\text{-}gas}$ values were analyzed separately

$$\text{Log } K_{PDMS\text{-}gas}(\text{wet}) = -0.405(0.095) + 0.053(0.108) \, \mathbf{E} + 0.639(0.146) \, \mathbf{S} + 1.096 \, (0.154) \, \mathbf{A}$$

$$+ \, 0.650(0.183) \, \mathbf{B} + 0.763(0.028) \, \mathbf{L} \tag{11}$$

$$(N = 76, \, R^2 = 0.989, \, R_{adj}^2 = 0.989, \, SD = 0.198, \, F = 1309.9)$$

and

$$\text{Log } K_{PDMS\text{-}gas}(\text{dry}) = -0.045(0.025) - 0.197(0.109) \, \mathbf{E} + 0.493(0.128) \, \mathbf{S} + 1.271(0.170) \, \mathbf{A}$$

$$+ \, 0.347(0.147) \, \mathbf{B} + 0.856(0.016) \, \mathbf{L} \tag{12}$$

$$(N = 64, \, R^2 = 0.993, \, R_{adj}^2 = 0.993, \, SD = 0.122, \, F = 1721.6)$$

to ascertain how much of an effect the absorbed water molecules had on the sorption properties of the PDMS surface. The statistics of both derived correlations are quite good. See Figure 3 for a plot of log $K_{PDMS\text{-}gas}$(wet) data versus calculated values based on Eq. 11. We note that the standard error in the e-coefficient of Eq. 12 is larger than the coefficient itself. There is no chemical reason for eliminating the e$\mathbf{E}$ term from the derived correlation. The E solute descriptor can easily be estimated from molecular structure considerations and there is no practical reason, at least from a predictive standpoint, for eliminating the e$\mathbf{E}$ term. The eE is needed if one wishes to use principal component analysis, PCA, to compare Eq. 12 to Abraham model correlations for other solvents. The analysis would require that all compared correlations have the same mathematical form.

The equation coefficients of Eq. 12 are in fairly agreement with the values reported by Hierlemann *et al*. [13], see Eq. 4, from sorption measurements of 32 compounds on a dry PDMS fiber. The calculated b-coefficient for Eq. 12 is quite small as would be expected from molecular structure considerations. Polydimethylsiloxane consists primarily of a $-Si(CH_3)_2$-O-$Si(CH_3)_2$-O backbone, and except for the terminal ends there should be no acidic hydrogens. Absorbed water molecules would lead to an increased b-coefficient for the "wet" PDMS surface. For predictive applications, Eq. 12 is preferred over Eq. 4 for estimating the sorption of gaseous solutes on dry PDMS fibers. The database used in deriving Eq. 12 contained twice as many experimental values, and the solutes possessed more chemical diversity, and spanned a wider range of solute descriptors.

The equation coefficients are sufficiently close to enable the experimental data to be combined into a single regression analysis. The derived correlation

$$\text{Log } K_{PDMS\text{-}gas}(\text{wet+dry}) = -0.041(0.033) + 0.012(0.066) \, \mathbf{E} + 0.543(0.096) \, \mathbf{S}$$

$$+ 1.143(0.111) \, \mathbf{A} + 0.578(0.105) \, \mathbf{B} + 0.792(0.014) \, \mathbf{L} \tag{13}$$

$$(N = 142, R^2 = 0.995, R_{adj}^2 = 0.994, SD = 0.180, F = 4919.0)$$

provides a reasonably accurate mathematical representation of the gas-to-PDMS sorption coefficients for both "wet" and "dry" PDMS surfaces (see Figure 4). The experimental log $K_{PDMS\text{-}gas}$ values span a range of about 11.0 log units. We recommend Eqs. 11 and 12 be used for predicting log $K_{PDMS\text{-}gas}$ values of additional solutes on "wet" and "dry" PDMS surfaces, provided that the solute's descriptors do not fall too far outside of the range of values used in deriving the respective correlations. We offer Eq. 13 has an additional predictive equation for making predictions outside of the solute descriptor ranges covered by Eqs. 11 and 12.

The predictive abilities of Eqs. 11 and 12 were assessed through a training set and test set analyses as before. Analysis of the experimental data in the training sets gave

$$\text{Log } K_{PDMS\text{-}gas}(\text{wet}) = -0.043(0.145) - 0.045(0.178) \, \mathbf{E} + 0.846(0.218) \, \mathbf{S} + 1.133(0.253) \, \mathbf{A}$$

$$+ 0.574(0.292) \, \mathbf{B} + 0.754(0.039) \, \mathbf{L} \tag{14}$$

$$(N = 38, R^2 = 0.988, R_{adj}^2 = 0.986, SD = 0.202, F = 540.7)$$

and

$$\text{Log } K_{PDMS\text{-}gas}(\text{dry}) = -0.070(0.046) - 0.261(0.159) \, \mathbf{E} + 0.667(0.260) \, \mathbf{S} + 1.496(0.332) \, \mathbf{A}$$

$$+ 0.167(0.305) \, \mathbf{B} + 0.867(0.026) \, \mathbf{L} \tag{15}$$

$$(N = 32, R^2 = 0.991, R_{adj}^2 = 0.989, SD = 0.136, F = 556.4)$$

The training set correlations were then used to predict log $K_{PDMS\text{-}gas}$(wet) values of the 38 compounds in the "wet" test set and log $K_{PDMS\text{-}gas}$(dry) values of the 32 compounds in the "dry" test set. For the predicted and experimental we found SD = 0.203 and SD = 0.119, AAE (average absolute error) = 0.162 and AAE = 0.084, and AE (average error) = -0.033 and AE = -0.024, for Eqs. 14 and 15, respectively. There is therefore very little bias in the predictions using Eqs. 14 and 15 with AE equal to -0.033 (Eq. 14) and -0.024 (Eq. 15).

As mentioned in the introduction, the coefficients in Eq. 2 are easier to interpret than those in Eq. 1, because the former reflect only solute-solvent interactions, whereas the latter refer to differences between solute-water interactions and solute-solvent interactions. We collect in Table 3 coefficients in Eq. 2 for the partition of solutes between the gas phase and various common solvents. Just by inspection, it is difficult to relate the coefficients to each other. However, PCA, allows a simple visual inspection of the overall similarity or difference of phases. In PCA, the five columns of the coefficients e, s, a, b, and l, are rearranged into five columns of principal

components, PCs, that are all mutually orthogonal. This has the effect of collecting most of the information of the original coefficients into the first two PCs; in the present case, 75% of the total information is contained in PC1 and PC2. A plot of the scores of PC2 against PC1 will then show how close the coefficients are in terms of solute-solvent interactions, and hence how close are the phases in chemical terms.

A plot of the scores of PC2 against PC1 is shown in Figure 5. From the composition of PC1 positive s, a, and b, and negative l), it appears that phases with large negative values of PC1 are 'non-polar' and phases with large positive values of PC1 are 'polar' in type. Both wet and dry PDMS (Nos 1 and 2) are near the middle of the non-polar to polar axis. The composition of PC2 (positive e and b, and negative s) cannot be interpreted in such a simple way. However, from Figure 5 it can be seen that wet PDMS and dry PDMS are not very different in terms of solute-solvent interactions from typical organic solvents, being part of a cluster of solvents near the middle of the PC1 vs PC2 plot.

4. ACKNOWLEDGEMENTS

54. REFERENCES

[1]   R. G. Berland, J. Pawliszyn, Water Pollut. Res. J. Can. 24 (1989) 179.

[2]   J. Pawliszyn, Solid Phase Microextraction: Theory and Practice, Wiley, New York, 1997.

[3]   K. Luks-Bettej, P. Popp, B. Janoszka, H. Paschite, J. Chromatogr. A 93 (2001) 938.

[4]   M. H. Abraham, Chem. Soc. Rev. 22 (1993) 73.

[5]   M. H. Abraham, A. Ibrahim, A. M. Zissimos, J. Chromatogr. A 1037 (2004) 29.

[6]   M. H. Abraham, J. Andonian-Haftvan, J. P. Osei-Owusu, P. Sakellariou, J. S. Urieta, M. C. Lopez, R. Fuchs, J. Chem. Soc., Perkin Trans. 2 (1993) 299.

[7]   M. H. Abraham, G. S. Whiting, P. W. Carr, H. Ouyang, J. Chem. Soc., Perkin Trans. 2 (1998) 1385.

[8]   M. H. Abraham, F. Martins, R. C. Mitchell, C. J. Salter, J. Pharm. Sci. 88 (1999) 241.

[9]   M. H. Abraham, J. A. Platts, A. Hersey, A. J. Leo, R. W. Taft, J. Pharm. Sci. 88 (1999) 670.

[10]   M. H. Abraham, J. Le, W. E. Acree, Jr., Coll. Czech. Chem. Comm. 64 (1999) 1748.

[11]   M. H. Abraham, J. Le, W. E. Acree, Jr., P. W. Carr, J. Phys. Org. Chem. 12 (1999) 675.

[12]   X. R. Xia, R. E. Baynes, N. A. Monteiro-Riviere, J. E. Riviere, SAR & QSAR Environ. Res. 18 (2007) 579.

[13]   A. Hierleman, E. T. Zellers, A. J. Ricco, Anal. Chem. 73 (2001) 3458.

[14]   M. L. Mayer, S. K. Poole, C. F. Poole, J. Chromatogr. A 697 (1995) 89.

[15]   M. L. Mayer, C. F. Poole, M. P. Henry, J. Chromatogr. A 695 (1995) 267.

[16]   M. L. Larrivee and C. F. Poole, Anal. Chem. 66 (1994) 139.

[17]   D. S. Selbert, C. F. Poole, M. H. Abraham, Analyst 121 (1996) 511.

[18]   T. L. ter Laak, A. Barendregt, J. L. M. Hermens, Environ. Sci. Technol. 40 (2006) 2184.

[19]   Y. Wang, Y. Wang, Anal. Lett. 40 (2007) 307.

[20]   B. Vrana, P. Popp, A. Paschke, G. Schuurmann, Anal. Chem. 73 (2001) 5191.

[21]   I. De Bo, H. Van Langenhove, J. De Keijser, J. Membrane Sci. 209 (2002) 39.

[22]   V. A. Isidorov, V T. Vinogorova, J. Chromatogr. A 1077 (2005) 195.

[123]   Y. Kamiya, Y. Naito, K. Terada, K. Mizoguchi, A. Tsuboi, Macromolecules 33 (2000)
        3111.

[24]   J.-H. Kwon, T. Wuethrich, P. Mayer and B. I. Escher, Anal. Chem., 2007, in press

[25]   J. Poerschmann, T. Gorecki, F.-D. Kopinke, Environ. Sci. Technol. 34 (2000) 3824.

[26]   E. Y. Zeng, D. Tsukada, J. A. Noblet, J. Peng, J. Chromatogr. A 1066 (2005) 165.

[27]   P. Mayer, W. H. J. Vaes, J. L. M. Hermens, Anal. Chem. 72 (2000) 459.

[28]   P. Mayer, W. H. J. Vaes, F. Wijnker, Femke; K. C. H. M. Legierse, R. Kraaij, J. Tolls, J.
        L. M. Hermens, Environ. Sci. Technol. 34 (2000) 5177.

[29]   A. Kloskowski, W. Chrzanowski, M. Pilarczyk, J. Namiesnik, J. Chem. Thermodyn. 37
        (2005) 21.

[30]   N. De Coensel, K. Desmet, T. Gorecki, P. Sandra, J. Chromatogr. A 1150 (2007) 183.

[31]   Z.-Y. Yang, D. Greenstein, E. Y. Zeng, K. A. Maruya, J. Chromatogr. A 1148 (2007)
        23.

[32]   Z. A. Makrodimitri, R. Dohrn, I. G. Economou, Macromolecules 40 (2007) 1720.

[33]   T. C. Merkel, V. I. Bondar, K. Nagai, B. D. Freeman, I. Pinnau, J. Polym. Sci., Part B:
        Polym. Phys. 38 (2000) 415.

[34]   X.-R. Xia, R. E. Baynes, N. A. Monteiro-Riviere, J. E. Riviere, Toxicol. Mech. Methods, 15 (2005) 307.

[35]   P. Kurzawski, C. Hagleitner, A. Hierlemann, Anal. Chem. 78 (2006) 6910.

[36]   R. D. Raharjo, B. D. Freeman, E. S. Sanders, J. Mem. Sci. 292 (2007) 45.

[37]   J. L. Langenfeld, S. B. Hawthorne, D. J. Miller, Anal. Chem. 68 (1996) 144.

[38]   B. Zimmerman, J. Burck, H.-J. Ache, Sens. Actuators B 41 (1997) 45.

[39]   R. S. Brown, P. Akhtar, J. Kerman, L. Hampel, I. S. Kozin, L. A. Villerius, H. J. C. Klamer, Environ. Sci. Technol. 35 (2001) 4097.

[40]   J. Poerschmann, J. Microcolumn Sep. 12 (2000) 603.

[41]   T. Nilsson, F. Pelusio, L. Montanarella, B. Larsen, S. Facchetti, J. O. Madsen, J. High Resolut. Chromatogr. 18 (1995) 617.

[42]   T. Nilsson, T. O. Larsen, L. Montanarella, J. O. Madsen, J. Microbiol. Methods 25 (1996) 243.

[43]   T. C. Merkel, L. G. Toy, Macromolecules 39 (2006) 7591.

[44]   L. Nardi, J. Chromatogr. A 985 (2003) 39.

[45]   H. A. Leslie, T. L. Ter Laak, F. J. M. Busser, M. H. S. Kraak. J. L. M. Hermens, Environ. Sci.Technol. 36 (2002) 5399.

[46]   T. E. M. Ten Hulscher, H. Van den Heuvel, P. C. M. Van Noort, H. A. J. Govers, J. Chem. Eng. Data 51 (2006) 347.

[47]   J. T. Coates, A. W. Elzerman, J. Contam. Hydrol. 1 (1986) 191.

[48]   M. H. Abraham, J. Andonian-Haftvan, G. S. Whiting, A. Leo and R. S. Taft, J. Chem. Soc., Perkin Trans. 2 (1994) 1777.

[49]   M. H. Abraham, W. E. Acree, Jr., New J. Chem. 28 (2004) 1538.

[50]   M. H. Abraham, A. M. Zissimos, W. E. Acree, Jr., New J. Chem. 27 (2003) 1041.

[51]   M. H. Abraham, H. S. Chadha, G. S. Whiting, R. C. Mitchell, J. Pharm. Sci. 83 (1994)

       1085.

[52]   P. H. Howard, W. M. Meylan, Handbook of Physical Properties of Organic Compounds,

       CRC Press, Inc., Baco Raton, FL (1997)

[53]   M. H. Abraham, C. E. Green, W. E. Acree, Jr., C. E. Hernandez, L. E. Roy, J. Chem.

       Soc., Perkin Trans. 2 (1998) 2677.

[54]   A. M. Zissimos, M. H. Abraham, M. C. Barker, K. J. Box, K. Y. Tam, J. Chem. Soc.,

       Perkin Trans. 2 (2002) 470.

[55]   A. M. Zissimos, M. H. Abraham, C. M. Du, K. Valko, C. Bevan, D. Reynolds, J. Wood,

       K. Y. Tam, J. Chem. Soc., Perkin Trans. 2 (2002) 2001.

[56]   Pharma Algorithms ADME Boxes, Version 3.0; Pharma Algorithms, Toronto, Ontario,

       2006.

[57]   J. A. Platts, D. Butina, M. H. Abraham, A. Hersey, J. Chem. Inf. Comput. Sci. 39 (1999)

       835.

[58]   J. Jover, R. Bosque, J. Sales, J. Chem. Inf. Comput. Sci. 44 (2004) 1098.

[59]   J. S. Arey, W. H. Green, Jr., P. M. Gschwend, J. Phys. Chem. B 109 (2005) 7564.

[60]   F. Mutelet, M. Rogalski, J. Chromatogr. A 923 (2001) 153.

[61]   M. H. Abraham, A. M. Zissimos, W. E. Acree, Jr., Phys. Chem. Chem. Phys. 3 (2001)

       3732.

[62]   M. H. Abraham, J. Le, W. E. Acree, Jr., Collect. Czech. Chem. Commun. 76 (1998) 703.

FIGURE CAPTIONS

Figure 1. Comparison of experimental log $K_{PDMS-water}$(wet) data points versus calculated values based on Eq. 6.

Figure 2. Comparison of experimental log $K_{PDMS-water}$(wet) and log $K_{PDMS-water}$(dry) data points versus calculated values based on Eq. 8.

Figure 3. Comparison of experimental log $K_{PDMS-gas}$(wet) data versus calculated values based on Eq. 11.

Figure 4. Comparison of experimental log $K_{PDMS-gas}$(wet) and log $K_{PDMS-gas}$(dry) data versus calculated values based on Eq. 13.

Figure 5. A plot of the scores of PC2 against the scores of PC1 for the systems in Table 3. Points numbered as in Table 3.

TABLES AND FIGURES FOR

CHARACTERIZATION OF THE SORPTION OF GASEOUS AND ORGANIC SOLUTES

ONTO POLYDIMETHYLSILOXANE SOLID-PHASE MICROEXTRACTION SURFACES

USING THE ABRAHAM MODEL

Laura Sprunger[a], Amy Proctor[a], William E. Acree, Jr.[a*] and Michael H. Abraham[b]

[a] Department of Chemistry, P. O. Box 305070, University of North Texas,

  Denton, TX   76203-5070 (U.S.A.)

[c] Department of Chemistry, University College London, 20 Gordon Street,

  London, WC1H 0AJ (U.K.)

TABLE 1. Experimental Water-to-Polydimethylsiloxane Partition Coefficient Data, log

$K_{PDMS-water}$, Measured Near 25 ^{o}C.

Solute	E	S	A	B	V	log K	Phase	Ref
Methane	0.000	0.000	0.000	0.000	0.2495	1.160	Dry	36
Ethane	0.000	0.000	0.000	0.000	0.3904	1.710	Dry	32
Propane	0.000	0.000	0.000	0.000	0.5313	2.320	Dry	32
Butane	0.000	0.000	0.000	0.000	0.6722	2.930	Dry	36
2-Methylpropane	0.000	0.000	0.000	0.000	0.6722	2.880	Dry	23
Pentane	0.000	0.000	0.000	0.000	0.8131	3.470	Dry	29
2,2-Dimethylpropane	0.000	0.000	0.000	0.000	0.8131	3.230	Dry	23
Hexane	0.000	0.000	0.000	0.000	0.9540	4.040	Dry	29
Heptane	0.000	0.000	0.000	0.000	1.0949	4.610	Dry	29
Octane	0.000	0.000	0.000	0.000	1.2358	4.700	Wet	25
Nonane	0.000	0.000	0.000	0.000	1.3767	5.400	Wet	25
Decane	0.000	0.000	0.000	0.000	1.5176	5.820	Wet	25
Undecane	0.000	0.000	0.000	0.000	1.6585	6.270	Wet	25
Dodecane	0.000	0.000	0.000	0.000	1.7994	6.820	Wet	25
Tridecane	0.000	0.000	0.000	0.000	1.9402	7.270	Wet	25
Tetradecane	0.000	0.000	0.000	0.000	2.0810	7.480	Wet	25
Cyclopropane	0.408	0.230	0.000	0.000	0.4227	1.430	Dry	23
Cyclohexane	0.305	0.100	0.000	0.000	0.8454	3.520	Dry	13
Ethene	0.107	0.100	0.000	0.070	0.3474	1.343	Dry	21
Propene	0.103	0.080	0.000	0.070	0.4883	1.800	Dry	23
1-Butene	0.100	0.080	0.000	0.070	0.6292	2.310	Dry	23
2-Methyl-1-propene	0.120	0.080	0.000	0.080	0.6292	2.160	Dry	23
1,3-Butadiene	0.320	0.230	0.000	0.100	0.5862	1.780	Dry	23
Trichloromethane	0.430	0.490	0.150	0.020	0.6167	1.620	Dry	35
Trichloromethane	0.430	0.490	0.150	0.020	0.6167	1.710	Wet	37
Tetrachloromethane	0.460	0.380	0.000	0.000	0.7391	2.840	Dry	35
1,1,1-Trichloroethane	0.370	0.410	0.000	0.090	0.7576	2.750	Wet	41
1,1,1,2-Tetrachloroethane	0.540	0.630	0.100	0.080	0.8800	2.660	Wet	41
1,1,2,2-Tetrachloroethane	0.600	0.760	0.160	0.120	0.8800	2.170	Wet	41
1,2-Dichloropropane	0.370	0.630	0.000	0.170	0.7761	2.100	Wet	41
Trichloroethylene	0.524	0.370	0.080	0.030	0.7146	2.240	Dry	21
Trichloroethylene	0.524	0.370	0.080	0.030	0.7146	2.410	Wet	38

Tetrachloroethylene	0.639	0.440	0.000	0.000	0.8370	3.270	Dry	35
Dibromochloromethane	0.775	0.680	0.120	0.100	0.7219	2.160	Wet	41
Trifluoromethane	-0.430	0.180	0.110	0.030	0.3026	0.600	Dry	23
Propanone	0.179	0.700	0.040	0.490	0.5470	-0.670	Dry	22
Butanone	0.166	0.700	0.000	0.510	0.6879	-0.320	Dry	22
Pentan-2-one	0.143	0.680	0.000	0.510	0.8288	0.410	Dry	22
Hexan-2-one	0.136	0.680	0.000	0.510	0.9697	0.860	Dry	22
Hexan-3-one	0.136	0.660	0.000	0.510	0.9697	0.980	Dry	22
Heptan-2-one	0.123	0.680	0.000	0.510	1.1106	1.350	Dry	22
Cyclohexanone	0.403	0.860	0.000	0.560	0.8611	0.070	Dry	13
Acetophenone	0.818	1.010	0.000	0.480	1.0140	1.040	Wet	12
4-Chloroacetophenone	0.955	1.090	0.000	0.440	1.136	1.640	Wet	12
Ethyl acetate	0.106	0.620	0.000	0.450	0.7466	0.271	Dry	13
Isobutyl acetate	0.052	0.570	0.000	0.470	1.0284	1.660	Dry	42
Phenyl acetate	0.661	1.130	0.000	0.540	1.073	0.860	Wet	12
Methyl benzoate	0.733	0.850	0.000	0.460	1.0730	1.650	Wet	12
Ethyl benzoate	0.689	0.850	0.000	0.460	1.2140	2.120	Wet	12
Methyl 2-methylbenzoate	0.772	0.870	0.000	0.430	1.2140	2.150	Wet	12
Ethanol	0.246	0.420	0.370	0.480	0.4491	-1.410	Dry	13
Propan-1-ol	0.236	0.420	0.370	0.480	0.5900	-1.160	Dry	35
Propan-2-ol	0.212	0.360	0.330	0.560	0.5900	-1.210	Dry	13
2-Butanol	0.217	0.360	0.330	0.560	0.7309	-0.630	Dry	22
2-Methylpropan-1-ol	0.217	0.390	0.370	0.480	0.7309	-0.390	Dry	22
3-Methyl-1-butanol	0.192	0.390	0.370	0.480	0.8718	-0.100	Dry	22
Benzene	0.610	0.520	0.000	0.140	0.7176	2.100	Wet	44
Benzene	0.610	0.520	0.000	0.140	0.7176	1.99*	Wet	37
Toluene	0.601	0.520	0.000	0.140	0.8573	2.240	Wet	12
Toluene	0.601	0.520	0.000	0.140	0.8573	2.58*	Wet	37
Ethylbenzene	0.613	0.510	0.000	0.150	0.9982	2.710	Wet	12
1,2-Dimethylbenzene	0.663	0.560	0.000	0.160	0.9982	2.500	Wet	34
1,3-Dimethylbenzene	0.623	0.520	0.000	0.160	0.9982	2.950	Wet	44
1,4-Dimethylbenzene	0.613	0.520	0.000	0.160	0.9982	2.760	Wet	12
Propylbenzene	0.604	0.500	0.000	0.150	1.1391	3.140	Wet	12
Isopropylbenzene	0.602	0.490	0.000	0.160	1.1391	3.250	Wet	41
1,2,4-Trimethylbenzene	0.677	0.560	0.000	0.190	1.1391	2.940	Wet	34
1,3,5-Trimethylbenzene	0.649	0.520	0.000	0.190	1.1391	3.250	Wet	41
Styrene	0.849	0.650	0.000	0.160	0.9552	2.860	Wet	41
Chlorobenzene	0.718	0.650	0.000	0.070	0.8388	2.400	Wet	12
1,2-Dichlorobenzene	0.872	0.780	0.000	0.040	0.9612	2.870	Wet	24

1,3-Dichlorobenzene	0.847	0.730	0.000	0.020	0.9612	3.290	Dry	29
1,4-Dichlorobenzene	0.825	0.750	0.000	0.020	0.9612	2.930	Wet	24
1,2,3-Trichlorobenzene	1.030	0.860	0.000	0.000	1.0836	3.450	Wet	24
1,2,4-Trichlorobenzene	0.980	0.810	0.000	0.000	1.0836	3.480	Wet	24
1,3,5-Trichlorobenzene	0.980	0.730	0.000	0.000	1.0836	3.640	Wet	24
1,2,3,4-Tetrachlorobenzene	1.180	0.920	0.000	0.000	1.2060	3.900	Wet	45
1,2,3,5-Tetrachlorobenzene	1.160	0.850	0.000	0.000	1.2060	4.180	Wet	24
1,2,4,5-Tetrachlorobenzene	1.160	0.860	0.000	0.000	1.2060	4.090	Wet	24
Pentachlorobenzene	1.330	0.960	0.000	0.000	1.3280	4.620	Wet	24
Pentachlorobenzene	1.330	0.960	0.000	0.000	1.3280	4.42*	Wet	45
Hexachlorobenzene	1.490	0.990	0.000	0.000	1.4510	5.010	Wet	24
2-Chlorotoluene	0.762	0.650	0.000	0.070	0.9797	3.070	Wet	41
4-Chlorotoluene	0.705	0.740	0.000	0.050	0.9797	2.870	Wet	12
2,4,5-Trichlorotoluene	1.060	0.850	0.000	0.000	1.2250	4.170	Wet	24
Bromobenzene	0.882	0.730	0.000	0.090	0.8914	2.510	Wet	12
Iodobenzene	1.188	0.820	0.000	0.120	0.9750	2.730	Wet	12
Phenyl methyl ether	0.708	0.750	0.000	0.290	0.9160	1.705	Dry	13
4-Chloroanisole	0.838	0.860	0.000	0.240	1.0380	2.370	Wet	12
Aniline	0.955	0.960	0.260	0.410	0.8162	0.010	Wet	24
3,4-Dimethylaniline	0.960	0.970	0.200	0.490	1.0980	1.070	Wet	24
2-Chloroaniline	1.033	0.920	0.250	0.310	0.9390	1.040	Wet	24
4-Chloroaniline	1.060	1.130	0.300	0.310	0.9390	0.840	Wet	12
2,4-Dichloroaniline	1.140	1.150	0.300	0.220	1.0610	1.690	Wet	24
3,4-Dichloroaniline	1.160	1.240	0.350	0.240	1.0610	1.390	Wet	24
Nitrobenzene	0.871	1.110	0.000	0.280	0.8906	1.210	Wet	12
Phenol	0.805	0.890	0.600	0.300	0.7751	-0.530	Wet	24
3-Methylphenol	0.822	0.880	0.570	0.340	0.9160	-0.030	Wet	12
3,5-Dimethylphenol	0.820	0.840	0.570	0.360	1.0569	0.420	Wet	12
4-Ethylphenol	0.800	0.900	0.550	0.360	1.0569	0.600	Wet	12
3-Bromophenol	1.060	1.150	0.700	0.160	0.9500	0.460	Wet	12
2-Chlorophenol	0.853	0.880	0.320	0.310	0.8975	0.560	Wet	24
3-Chlorophenol	0.909	1.060	0.690	0.150	0.8975	0.310	Wet	12
Pentachlorophenol	1.217	0.860	0.610	0.090	1.3870	2.650	Wet	24
4-Fluorophenol	0.670	0.970	0.630	0.230	0.7930	-0.280	Wet	12
Biphenyl	1.360	0.990	0.000	0.260	1.3240	3.370	Wet	12
Naphthalene	1.340	0.920	0.000	0.200	1.0854	2.830	Wet	12
1-Methylnaphthalene	1.337	0.940	0.000	0.220	1.2260	3.260	Wet	12
2-Methylnaphthalene	1.304	0.810	0.000	0.250	1.2260	3.170	Wet	34
1,2-Dimethylnaphthalene	1.431	0.970	0.000	0.250	1.3672	3.470	Wet	34

2,6-Dimethylnaphthalene	1.347	0.820	0.000	0.250	1.3672	3.590	Wet	19
Acenaphthene	1.604	1.050	0.000	0.220	1.2586	3.630	Wet	20
Fluorene	1.588	1.060	0.000	0.250	1.3570	3.720	Wet	18
Phenanthrene	2.055	1.290	0.000	0.260	1.4540	4.000	Wet	27
Anthracene	2.290	1.340	0.000	0.280	1.4540	3.840	Wet	18
Fluoranthene	2.377	1.550	0.000	0.240	1.5850	4.260	Wet	18
Benz[a]anthracene	2.992	1.700	0.000	0.330	1.8230	4.770	Wet	18
Pyrene	2.808	1.710	0.000	0.280	1.5850	4.320	Wet	18
Chrysene	3.027	1.730	0.000	0.330	1.8230	4.690	Wet	18
Benzo[b]fluoranthene	3.194	1.820	0.000	0.400	1.9536	5.160	Wet	20
Benzo[k]fluoranthene	3.190	1.910	0.000	0.330	1.9536	5.330	Wet	20
Benz[a]pyrene	3.625	1.980	0.000	0.440	1.9540	5.240	Wet	18
Benzo[ghi]perylene	4.073	1.900	0.000	0.480	2.0840	5.500	Wet	18
Dibenz[a,h]anthracene	4.000	2.040	0.000	0.440	2.1924	6.200	Wet	18
1-Methylphenanthrene	2.055	1.250	0.000	0.260	1.5950	4.500	Wet	19
Perylene	3.256	1.760	0.000	0.400	1.9540	4.980	Wet	24
Benzonitrile	0.742	1.110	0.000	0.330	0.8710	1.040	Wet	12
Dimethyl sulfide	0.404	0.430	0.000	0.270	0.5539	0.820	Dry	21
Helium	0.000	0.000	0.000	0.000	0.0680	0.470	Dry	32
Neon	0.000	0.000	0.000	0.000	0.0850	0.580	Dry	32
Argon	0.000	0.000	0.000	0.000	0.1900	0.820	Dry	32
Krypton	0.000	0.000	0.000	0.000	0.2460	0.980	Dry	32
Xenon	0.000	0.000	0.000	0.000	0.3290	1.253	Dry	23
Hydrogen	0.000	0.000	0.000	0.000	0.1086	0.420	Dry	33
Oxygen	0.000	0.000	0.000	0.000	0.1830	1.150	Dry	21
Nitrogen	0.000	0.000	0.000	0.000	0.2222	0.850	Dry	32
Nitrous Oxide	0.068	0.350	0.000	0.100	0.2810	0.510	Dry	23
Carbon Dioxide	0.000	0.280	0.050	0.100	0.2809	0.240	Dry	21
Tetrafluoromethane	-0.580	-0.260	0.000	0.000	0.3203	1.570	Dry	32
Sulfur hexafluoride	-0.600	-0.200	0.000	0.000	0.4643	2.100	Dry	23
Benzyl alcohol	0.803	0.870	0.330	0.560	0.9160	-0.350	Wet	12
Phenethyl alcohol	0.784	0.830	0.300	0.660	1.0570	0.120	Wet	12
3-Methylbenzyl alcohol	0.815	0.900	0.330	0.590	1.0570	0.170	Wet	12
2-Chlorobiphenyl	1.480	1.070	0.000	0.200	1.4466	3.970	Wet	40
4,4'-Dichlorobiphenyl	1.640	1.180	0.000	0.160	1.5690	4.590	Wet	40
2,4,4'-Trichlorobiphenyl	1.760	1.330	0.000	0.150	1.6914	4.70*	Wet	20
2,4,4'-Trichlorobiphenyl	1.760	1.330	0.000	0.150	1.6914	5.030	Wet	40
2,4',6'-Trichlorobiphenyl	1.740	1.350	0.000	0.170	1.6914	5.000	Wet	20

2,2',4,5,5'-Pentachlorobiphenyl	2.040	1.610	0.000	0.130	1.9362	5.710	Wet	26
2,2',5,5'-Tetrachlorobiphenyl	1.900	1.480	0.000	0.150	1.8138	5.300	Wet	31
Limonene	0.488	0.280	0.000	0.210	1.3230	4.140	Dry	22
Hexafluoroethane	-0.690	-0.410	0.000	0.000	0.4966	2.400	Dry	32
Hydrogen sulfide	0.350	0.310	0.100	0.070	0.2721	0.300	Dry	43
Camphor	0.500	0.690	0.000	0.710	1.3161	1.480	Dry	30
Acridine	2.536	1.320	0.000	0.580	1.4130	3.170	Wet	39
2,3,3',4,4'-Pentachlorobiphenyl	2.040	1.590	0.000	0.110	1.9362	5.890	Wet	26
2,2',3,4,4',5'-Hexachlorobiphenyl	2.180	1.740	0.000	0.110	2.0586	6.200	Wet	26
2,3,3',4,4',5-Hexachlorobiphenyl	2.210	1.720	0.000	0.090	2.0586	6.280	Wet	26
2,2',3,4,4',5,5'-Heptachlorobiphenyl	2.290	1.870	0.000	0.090	2.1810	6.400	Wet	26
2,3',4,4',5-Pentachlorobiphenyl	2.060	1.590	0.000	0.110	1.9362	5.870	Wet	26
Bromoform	0.974	0.680	0.150	0.060	0.7750	1.870	Wet	40
2,4,5-Trichloroaniline	1.240	1.150	0.300	0.140	1.1830	2.080	Wet	45
2,3,3',5,6-Pentachlorobiphenyl	2.050	1.610	0.000	0.130	1.9362	5.710	Wet	27
2,2',4,4',5,5'-Hexachlorobiphenyl	2.180	1.740	0.000	0.110	2.0586	6.160	Wet	27
2,2',4,4',5,6'-Hexachlorobiphenyl	2.150	1.740	0.000	0.110	2.0586	6.170	Wet	27
2,2',4,4',6,6'-Hexachlorobiphenyl	2.120	1.740	0.000	0.110	2.0586	6.030	Wet	27
Propionaldehyde	0.196	0.650	0.000	0.450	0.5470	-0.867	Dry	13
Butyraldehyde	0.187	0.650	0.000	0.450	0.6879	-0.289	Dry	13
Pyridine	0.631	0.840	0.000	0.520	0.6753	-0.454	Dry	13
Thiophene	0.687	0.570	0.000	0.150	0.6411	1.748	Dry	13
1,2-Dichloroethane	0.420	0.640	0.100	0.110	0.6352	1.161	Dry	13
Benzonitrile	0.742	1.110	0.000	0.330	0.8711	0.859	Dry	13
Diethyl ether	0.041	0.250	0.000	0.450	0.7309	0.664	Dry	13
Ethanethiol	0.392	0.420	0.000	0.200	0.5539	1.115	Dry	13
2,3,5,6-Tetrachlorobiphenyl	1.890	1.480	0.000	0.150	1.8138	5.340	Wet	28

TABLE 2. Experimental Gas-to-Polydimethylsiloxane Partition Coefficient Data,

log $K_{PDMS-gas}$, Measured Near 25 °C.

Solute	E	S	A	B	L	log K	Phase	Ref.
Methane	0.000	0.000	0.000	0.000	-0.323	-0.300	Dry	36
Ethane	0.000	0.000	0.000	0.000	0.492	0.370	Dry	32
Propane	0.000	0.000	0.000	0.000	1.050	0.880	Dry	32
Butane	0.000	0.000	0.000	0.000	1.615	1.410	Dry	36
2-Methylpropane	0.000	0.000	0.000	0.000	1.409	1.180	Dry	23
Pentane	0.000	0.000	0.000	0.000	2.162	1.770	Dry	29
2,2-Dimethylpropane	0.000	0.000	0.000	0.000	1.820	1.390	Dry	23
Hexane	0.000	0.000	0.000	0.000	2.668	2.220	Dry	29
Heptane	0.000	0.000	0.000	0.000	3.173	2.650	Dry	29
Octane	0.000	0.000	0.000	0.000	3.677	2.590	Wet	25
Nonane	0.000	0.000	0.000	0.000	4.182	3.250	Wet	25
Decane	0.000	0.000	0.000	0.000	4.686	3.500	Wet	25
Undecane	0.000	0.000	0.000	0.000	5.191	3.890	Wet	25
Dodecane	0.000	0.000	0.000	0.000	5.696	4.290	Wet	25
Cyclopropane	0.408	0.230	0.000	0.000	1.314	0.880	Dry	23
Cyclohexane	0.305	0.100	0.000	0.000	2.964	2.620	Dry	13
Ethene	0.107	0.100	0.000	0.070	0.289	0.403	Dry	21
Propene	0.103	0.080	0.000	0.070	0.946	0.830	Dry	23
1-Butene	0.100	0.080	0.000	0.070	1.529	1.300	Dry	23
2-Methyl-1-propene	0.120	0.080	0.000	0.080	1.579	1.300	Dry	23
1,3-Butadiene	0.320	0.230	0.000	0.100	1.543	1.330	Dry	23
cis 2-Butene	0.140	0.080	0.000	0.050	1.737	1.460	Dry	23
trans 2-Butene	0.126	0.080	0.000	0.050	1.664	1.400	Dry	23
Trichloromethane	0.430	0.490	0.150	0.020	2.480	2.410	Dry	35
Trichloromethane	0.430	0.490	0.150	0.020	2.480	2.50*	Wet	37
Tetrachloromethane	0.460	0.380	0.000	0.000	2.823	2.650	Dry	35
1,1,1-Trichloroethane	0.370	0.410	0.000	0.090	2.733	2.870	Wet	41
1,1,1,2-Tetrachloroethane	0.540	0.630	0.100	0.080	3.641	3.600	Wet	41
1,1,2,2-Tetrachloroethane	0.600	0.760	0.160	0.120	3.803	3.980	Wet	41
1,2-Dichloropropane	0.370	0.630	0.000	0.170	2.836	3.070	Wet	41
Trichloroethylene	0.524	0.370	0.080	0.030	2.997	2.560	Dry	21
Trichloroethylene	0.524	0.370	0.080	0.030	2.997	2.73*	Wet	38
Tetrachloroethylene	0.639	0.440	0.000	0.000	3.584	3.200	Dry	35
Dibromochloromethane	0.775	0.680	0.120	0.100	3.304	3.440	Wet	41

26

Trifluoromethane	-0.430	0.180	0.110	0.030	-0.274	0.000	Dry	23
Propanone	0.179	0.700	0.040	0.490	1.696	2.160	Dry	22
Butanone	0.166	0.700	0.000	0.510	2.287	2.400	Dry	22
Pentan-2-one	0.143	0.680	0.000	0.510	2.755	2.990	Dry	22
Hexan-2-one	0.136	0.680	0.000	0.510	3.286	3.270	Dry	22
Hexan-3-one	0.136	0.660	0.000	0.510	3.271	3.250	Dry	22
Heptan-2-one	0.123	0.680	0.000	0.510	3.760	3.600	Dry	22
Cyclohexanone	0.403	0.860	0.000	0.560	3.792	3.670	Dry	13
Acetophenone	0.818	1.010	0.000	0.480	4.501	4.400	Wet	12
4-Chloroacetophenone	0.955	1.090	0.000	0.440	5.404	4.860	Wet	12
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	2.431	Dry	13
Isobutyl acetate	0.052	0.570	0.000	0.470	3.161	3.390	Dry	42
Phenyl acetate	0.661	1.130	0.000	0.540	4.414	4.120	Wet	12
Methyl benzoate	0.733	0.850	0.000	0.460	4.704	4.530	Wet	12
Ethyl benzoate	0.689	0.850	0.000	0.460	5.075	4.790	Wet	12
Ethanol	0.246	0.420	0.370	0.480	1.485	2.260	Dry	13
Propan-1-ol	0.236	0.420	0.370	0.480	2.031	2.400	Dry	35
Propan-2-ol	0.212	0.360	0.330	0.560	1.764	2.270	Dry	13
2-Butanol	0.217	0.360	0.330	0.560	2.338	2.760	Dry	22
2-Methylpropan-1-ol	0.217	0.390	0.370	0.480	2.413	2.910	Dry	22
Pentan-1-ol	0.219	0.420	0.370	0.480	3.106	3.347	Dry	13
3-Methyl-1-butanol	0.192	0.390	0.370	0.480	3.011	3.140	Dry	22
Benzene	0.610	0.520	0.000	0.140	2.786	2.730	Wet	44
Toluene	0.601	0.520	0.000	0.140	3.325	2.890	Wet	12
Ethylbenzene	0.613	0.510	0.000	0.150	3.778	2.710	Wet	12
1,2-Dimethylbenzene	0.663	0.560	0.000	0.160	3.939	3.240	Wet	34
1,3-Dimethylbenzene	0.623	0.520	0.000	0.160	3.839	3.560	Wet	44
1,4-Dimethylbenzene	0.613	0.520	0.000	0.160	3.839	3.350	Wet	12
Propylbenzene	0.604	0.500	0.000	0.150	4.230	3.530	Wet	12
Isopropylbenzene	0.602	0.490	0.000	0.160	4.084	3.690	Wet	41
1,2,4-Trimethylbenzene	0.677	0.560	0.000	0.190	4.441	3.570	Wet	34
1,3,5-Trimethylbenzene	0.649	0.520	0.000	0.190	4.344	3.910	Wet	41
Styrene	0.849	0.650	0.000	0.160	3.856	3.770	Wet	41
Chlorobenzene	0.718	0.650	0.000	0.070	3.657	3.220	Wet	12
1,2-Dichlorobenzene	0.872	0.780	0.000	0.040	4.518	3.770	Wet	24
1,3-Dichlorobenzene	0.847	0.730	0.000	0.020	4.410	4.010	Dry	29
1,4-Dichlorobenzene	0.825	0.750	0.000	0.020	4.435	3.670	Wet	24
1,2,3-Trichlorobenzene	1.030	0.860	0.000	0.000	5.419	4.360	Wet	24

1,2,4-Trichlorobenzene	0.980	0.810	0.000	0.000	5.248	4.300	Wet	24
1,3,5-Trichlorobenzene	0.980	0.730	0.000	0.000	5.045	4.210	Wet	24
1,2,3,5-Tetrachlorobenzene	1.160	0.850	0.000	0.000	5.922	5.370	Wet	24
1,2,4,5-Tetrachlorobenzene	1.160	0.860	0.000	0.000	5.926	5.070	Wet	24
Hexachlorobenzene	1.490	0.990	0.000	0.000	7.390	6.510	Wet	24
2-Chlorotoluene	0.762	0.650	0.000	0.070	4.173	3.680	Wet	41
4-Chlorotoluene	0.705	0.740	0.000	0.050	4.205	3.550	Wet	12
Bromobenzene	0.882	0.730	0.000	0.090	4.041	3.580	Wet	12
Iodobenzene	1.188	0.820	0.000	0.120	4.502	4.010	Wet	12
Phenyl methyl ether	0.708	0.750	0.000	0.290	3.890	3.505	Wet	13
Aniline	0.955	0.960	0.260	0.410	3.934	4.300	Wet	24
2-Chloroaniline	1.033	0.920	0.250	0.310	4.674	4.640	Wet	24
4-Chloroaniline	1.060	1.130	0.300	0.310	4.889	5.170	Wet	12
Nitrobenzene	0.871	1.110	0.000	0.280	4.557	4.230	Wet	12
Phenol	0.805	0.890	0.600	0.300	3.766	4.320	Wet	24
3-Methylphenol	0.822	0.880	0.570	0.340	4.310	4.570	Wet	12
3,5-Dimethylphenol	0.820	0.840	0.570	0.360	4.856	5.020	Wet	12
4-Ethylphenol	0.800	0.900	0.550	0.360	4.737	5.100	Wet	12
2-Chlorophenol	0.853	0.880	0.320	0.310	4.178	3.900	Wet	24
3-Chlorophenol	0.909	1.060	0.690	0.150	4.773	5.160	Wet	12
4-Fluorophenol	0.670	0.970	0.630	0.230	3.844	4.260	Wet	12
Biphenyl	1.360	0.990	0.000	0.260	6.014	5.320	Wet	12
Naphthalene	1.340	0.920	0.000	0.200	5.161	4.560	Wet	12
1-Methylnaphthalene	1.337	0.940	0.000	0.220	5.802	5.050	Wet	12
2-Methylnaphthalene	1.304	0.810	0.000	0.250	5.617	5.000	Wet	34
2,6-Dimethylnaphthalene	1.347	0.820	0.000	0.250	6.146	5.520	Wet	19
Acenaphthene	1.604	1.050	0.000	0.220	6.469	5.990	Wet	21
Fluorene	1.588	1.060	0.000	0.250	6.922	6.180	Wet	18
Phenanthrene	2.055	1.290	0.000	0.260	7.632	6.800	Wet	27
Anthracene	2.290	1.340	0.000	0.280	7.568	6.870	Wet	18
Fluoranthene	2.377	1.550	0.000	0.240	8.827	7.700	Wet	18
Pyrene	2.808	1.710	0.000	0.280	8.833	7.820	Wet	18
Chrysene	3.027	1.730	0.000	0.330	10.334	9.480	Wet	18
Benz[a]pyrene	3.625	1.980	0.000	0.440	11.736	10.780	Wet	18
Perylene	3.256	1.760	0.000	0.400	12.053	10.720	Wet	24
Benzonitrile	0.742	1.110	0.000	0.330	4.039	4.130	Wet	12
Dimethylsulfide	0.404	0.430	0.000	0.270	2.037	1.960	Dry	21
Helium	0.000	0.000	0.000	0.000	-1.741	-1.550	Dry	32
Neon	0.000	0.000	0.000	0.000	-1.575	-1.380	Dry	32

Argon	0.000	0.000	0.000	0.000	-0.688	-0.650	Dry	32
Krypton	0.000	0.000	0.000	0.000	-0.211	-0.230	Dry	32
Xenon	0.000	0.000	0.000	0.000	0.378	0.283	Dry	23
Hydrogen	0.000	0.000	0.000	0.000	-1.200	-1.300	Dry	33
Oxygen	0.000	0.000	0.000	0.000	-0.723	-0.360	Dry	21
Nitrogen	0.000	0.000	0.000	0.000	-0.978	-0.950	Dry	32
Nitrous Oxide	0.068	0.350	0.000	0.100	0.164	0.280	Dry	23
Carbon Dioxide	0.000	0.280	0.050	0.100	0.058	0.160	Dry	21
Tetrafluoromethane	-0.580	-0.260	0.000	0.000	-0.817	-0.720	Dry	32
Sulfur hexafluoride	-0.600	-0.200	0.000	0.000	-0.120	-0.120	Dry	23
Benzyl alcohol	0.803	0.870	0.330	0.560	4.221	4.510	Wet	12
Phenethyl alcohol	0.784	0.830	0.300	0.660	4.628	5.100	Wet	12
2,4,4'-Trichlorobiphenyl	1.760	1.330	0.000	0.150	7.904	6.800	Wet	20
2,2',4,5,5'-Pentachlorobiphenyl	2.040	1.610	0.000	0.130	8.868	8.140	Wet	26
2,2',5,5'-Tetrachlorobiphenyl	1.900	1.480	0.000	0.150	8.144	7.500	Wet	31,46
Limonene	0.488	0.280	0.000	0.210	4.725	4.040	Dry	22
Hydrogen sulfide	0.350	0.310	0.100	0.070	0.723	0.700	Dry	43
Camphor	0.500	0.690	0.000	0.710	5.084	4.630	Dry	30
2,2',3,4,4',5'-Hexachlorobiphenyl	2.180	1.740	0.000	0.110	9.772	8.630	Wet	26,46
2,3,3',4,4',5-Hexachlorobiphenyl	2.210	1.720	0.000	0.090	10.200	9.180	Wet	26,46
2,2',3,4,4',5,5'-Heptachlorobiphenyl	2.290	1.870	0.000	0.090	10.415	9.440	Wet	26,46
2,3',4,4',5-Pentachlorobiphenyl	2.060	1.590	0.000	0.110	9.396	8.360	Wet	26,46
Bromoform	0.974	0.680	0.150	0.060	3.784	3.430	Wet	40
2,2',4,4',5,5'-Hexachlorobiphenyl	2.180	1.740	0.000	0.110	9.587	8.378	Wet	27,46
2,2',4,4',6,6'-Hexachlorobiphenyl	2.120	1.740	0.000	0.110	8.715	8.360	Wet	27,47
Propionaldehyde	0.196	0.650	0.000	0.450	1.815	1.653	Dry	13
Butyraldehyde	0.187	0.650	0.000	0.450	2.270	2.041	Dry	13
Pyridine	0.631	0.840	0.000	0.520	3.022	2.986	Dry	13
Thiophene	0.687	0.570	0.000	0.150	2.819	2.778	Dry	13
1,2-Dichloroethane	0.420	0.640	0.100	0.110	2.573	2.431	Dry	13
Benzonitrile	0.742	1.110	0.000	0.330	4.039	3.949	Dry	13
Diethyl ether	0.041	0.250	0.000	0.450	2.015	1.954	Dry	13
Ethanethiol	0.392	0.420	0.000	0.200	2.079	1.955	Dry	13

*Duplicate entry, not used in correlation

TABLE 3. Coefficients in Eqn. 1 for Gas to Solvent Phase Partitions

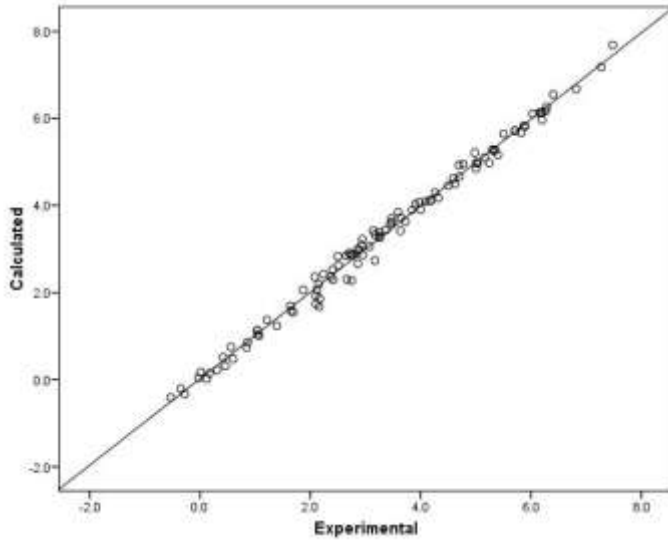| Solvent phase	N	c	e	s	a	b	l
PDMS/dry	1	-0.045	-0.197	0.493	1.271	0.347	0.856
PDMS/wet	2	-0.405	0.053	0.639	1.096	0.650	0.763
methanol	3	-0.004	-0.215	1.173	3.701	1.432	0.769
ethanol	4	0.012	-0.206	0.789	3.635	1.311	0.853
1-butanol	5	-0.039	-0.276	0.539	3.781	0.995	0.934
1-octanol	6	-0.120	-0.203	0.560	2.560	0.702	0.939
ethylene glycol	7	-0.898	0.217	1.427	4.474	2.687	0.568
1-octanol/wet	8	-0.198	0.002	0.709	3.519	1.429	0.858
N-methylformamide	9	-0.599	-0.259	2.003	4.559	0.430	0.706
ethyl acetate	10	0.203	-0.335	1.251	2.949	0.000	0.917
acetone	11	0.154	-0.277	1.522	3.258	0.000	0.863
ether	12	0.206	-0.169	0.873	3.402	0.000	0.882
acetonitrile	13	-0.007	-0.595	2.461	2.085	0.418	0.738
chloroform	14	0.116	-0.467	1.203	0.138	1.432	0.994
chlorobenzene	15	0.053	-0.053	1.254	0.364	0.000	1.041
nitrobenzene	16	-0.295	0.121	1.682	1.247	0.370	0.915
toluene	17	0.121	-0.222	0.938	0.467	0.099	1.012
hexadecane	18	0.000	0.000	0.000	0.000	0.000	1.000
cyclohexane	19	0.163	-0.110	0.000	0.000	0.000	1.013
olive oil	20	-0.156	-0.254	0.859	1.656	0.000	0.873

Figure 1. Comparison of experimental log $K_{PDMS\text{-}water}$(wet) data points versus calculated values based on Eq. 6.
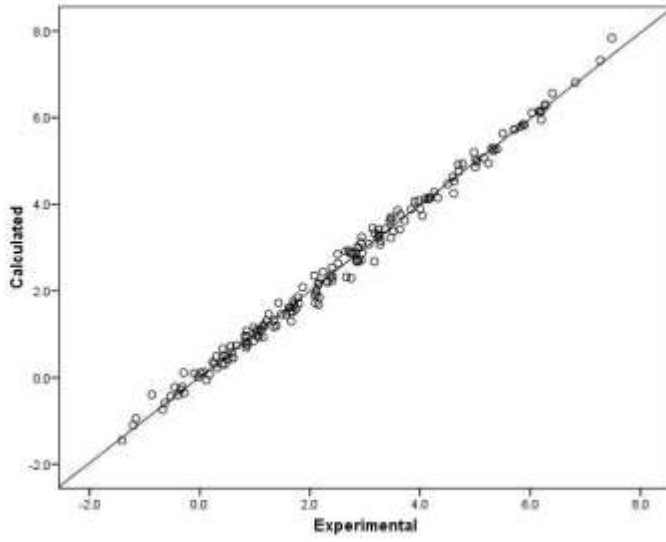
Figure 2. Comparison of experimental log $K_{PDMS-water}$(wet) and log $K_{PDMS-water}$(dry) data points versus calculated values based on Eq. 8.
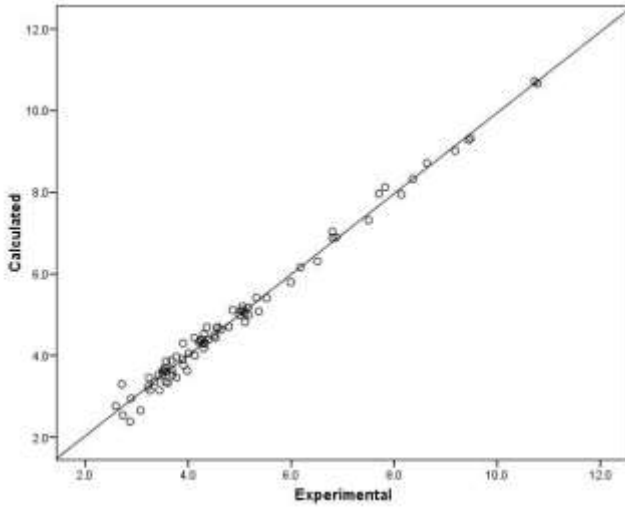
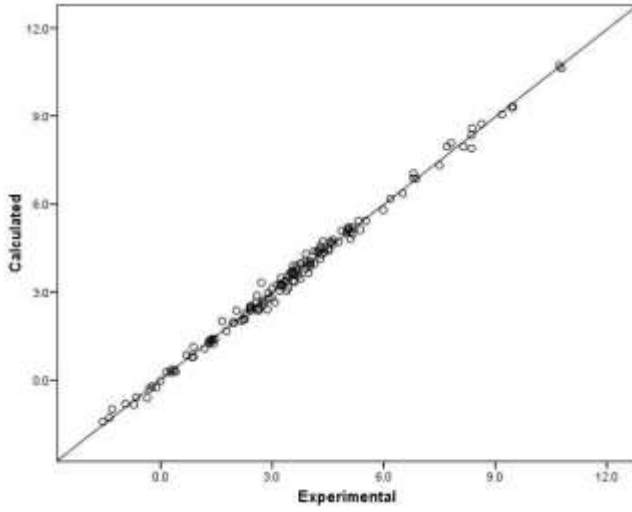Figure 3. Comparison of experimental log $K_{PDMS\text{-}gas}$(wet) data versus calculated values based on Eq. 11.

Figure 4. Comparison of experimental log $K_{PDMS-gas}$(wet) and log $K_{PDMS-gas}$(dry) data versus calculated values based on Eq. 13.
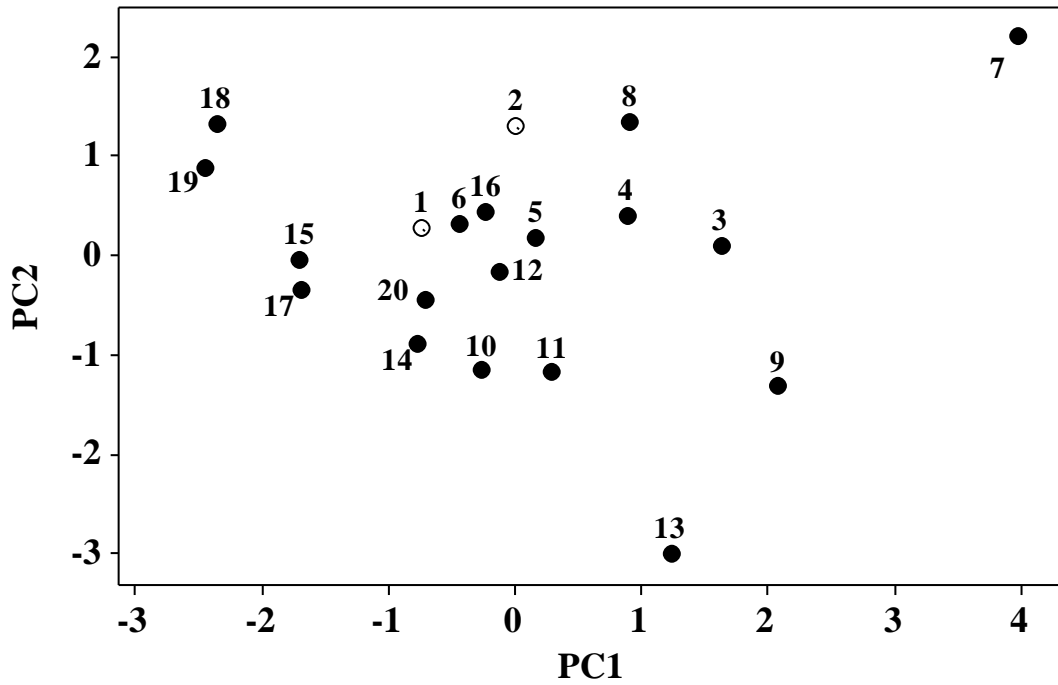
Figure 5. A plot of the scores of PC2 against the scores of PC1 for the systems in Table 3. Points numbered as in Table 3.